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THEORETICAL FOUNDATIONS OF NATURAL AND
MAGNETICALLY-INDUCED OPTICAL ACTIVITY

David Ernest Downie
(Ph.D. Thesis)

March 1970

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THEORETICAL FOUNDATIONS OF NATURAL AND MAGNETICALLY-INDUCED
OPTICAL ACTIVITY

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ABSTRACT

The most fundamental basis of optical activity is the differential response of a molecular system to the probes of left- and right-circularly polarized light. Necessary to such a differential response is the presence of an asymmetry in the system. For natural optical activity this asymmetry is inherent in the molecule, for magnetically-induced optical activity it must be supplied by an external magnetic field.

In the first part of this dissertation the general theory of natural and magnetically-induced optical activity is developed from fundamental assumptions. All pertinent mathematics are included, yet there is an attempt, throughout the derivations, to retain contact with the physics of the phenomena. Also, a consistent notation and formalism is maintained, and, in the second part of the dissertation, this provides a sound foundation for developing extensions of the general theory. Here, for vibrating and substituted chromophores, are determined the vibrational and substitutional symmetry

patterns that enhance and allow the various electronic transitions of natural and magnetically-induced optical activity.

The value of this investigation lies in the deeper understanding obtained for optical activity, in particular the magnetically-induced type. Specific results of interest are the various symmetry patterns and rules developed for substituted and vibrating chromophores. The most important result is the conclusion that magnetically-induced optical activity is quite different from natural optical activity in the type of information it provides. Specifically, magnetically-induced optical activity measures quantities pertinent to the electronic structure of molecules while natural optical activity reveals subtleties regarding molecular stereochemistry. This dichotomy of natural and magnetically-induced optical activity is emphasized throughout the dissertation.

In conclusion, the attempt has been to provide a theoretical textbook of optical activity, one that would prove valuable to neophyte and expert alike. It is hoped that it will be helpful in stimulating investigation into new application of natural and magnetically-induced optical activity.

INTRODUCTION

Theoretical derivations for optical activity, especially the magnetically-induced type, tend to be at best a complex exercise in quantum mechanics and at worst a confusing morass of mathematical notation. It is the object of this dissertation to present a clear physical picture of optical activity, to expand and extend the present theories, and to map out a framework into which future theories can fit. As necessary preliminary steps, in this introduction we briefly describe the physical nature of polarized light and of optically active media, the various measures and uses of optical activity, and the status of current theories. This hopefully will set the stage for the quantum mechanical derivations to follow.

A. Polarization and Doubly-Refracting Media

Electromagnetic radiation, of which light is an example, can be described completely in terms of its measurable quantities -- i.e. wavelength, intensity, phase, and polarization. These characteristics can be used as probes to help determine the nature of atomic and molecular systems. In this dissertation we deal with the measurement of optical activity by the probe of polarization. In order to understand this use of polarized light, it is first necessary to describe briefly the various types of polarization.

A plane electromagnetic wave in free space is a transverse wave, the directions of vibration of its electric and magnetic fields being mutually perpendicular and perpendicular to the direction of propagation. The electric field is designated by the electric field intensity vector $\vec{E}$, the magnetic field by the magnetic field intensity vector $\vec{H}$, and

the flux density of field energy by the Poynting vector $\vec{S}$. In free space the direction of $\vec{S}$ is in the direction of propagation and $|\vec{S}|$ is proportional to the vector cross-product $\vec{E} \times \vec{H}$. These vectors and their relation to $\hat{k}$, the unit propagation vector, are shown in Figure 1. The polarization of an electromagnetic wave is characterized by the motion of the end point of the electric vector. The general polarization case is that in which the motion describes an ellipse with unequal principal axes, and there is a direction of rotation -- i.e. a handedness of polarization. There are two limiting cases which are important. Linear polarization is one of these and is characterized by a preferred axis but no handedness; the other is circular polarization, characterized by a handedness but no preferred axis. These two cases are the polarization types used as probes to measure optical activity.

In free space, a plane wave of specified polarization type will propagate with no variation of this polarization (Footnote 1), with no diminution of amplitude, and at a speed $c = 3 \times 10^8$ meters/sec. Upon entering and traversing various media, this wave can undergo changes in any or all of the above characteristics. We shall consider here only homogeneous, (somewhat) transparent media. The complexities of non-homogeneous media are beyond the scope of this thesis.

All homogeneous transparent media can be divided into two classes; singly-refracting and doubly-refracting. Singly-refracting media are isotropic and optically inactive. These media have a refractive index, and thus a velocity of propagation, which is independent of the direction of propagation and the type of polarization of the incident wave. All experiments with doubly-refracting media are interpretable on the assumption that the propagation of plane monochromatic waves can be sustained in any direction, but for each wave, specified by a wavelength

FIGURE 1. Propagation of electromagnetic wave in free space.

and a direction of propagation, there are two special polarizations, with which there are associated specific refractive indices. These polarizations are analogous to eigenfunctions, the refractive indices to eigenvalues, and both result from the solution of Maxwell's equations for the doubly-refracting medium. Thus we term them the eigen-polarizations and the eigen-indices. We note that singly-refracting media can be considered as doubly-refracting media where the eigen-indices are identical and independent of direction of propagation.

We may further classify homogeneous transparent media as optically inactive and optically active media. An optically inactive medium is one in which, for any given direction of propagation, the eigen-polarizations are linear, are mutually perpendicular, and are perpendicular to the direction of propagation. If the optically inactive medium is doubly-refracting, it is of necessity anisotropic, and the two eigen-indices differ from one another and depend upon the direction of propagation. An optically active medium is by definition doubly-refracting, and is one in which the two eigen-polarizations are not linear for all directions of propagation. These media can be either isotropic or anisotropic. We shall be concerned with the isotropic, optically active medium, in which the difference of eigen-indices is independent of direction and the two eigen-polarizations are always circular and of opposite handedness. This is the situation encountered when dealing with the natural and magnetically-induced optical activity of chemical and biochemical solutions.

B. Types of Optical Activity: Origins and Uses

Optical activity can be measured with either the probe of linear polarized light or with the probes of left- and right- circularly polarized light. When an optically active medium is traversed by a linear polarized light wave in the spectral region in which an optically active chromophore

absorbs, two things occur. The plane of polarization is rotated (optical rotation) and the resultant light becomes elliptically polarized (optical ellipticity). The rotation is defined as the angle of rotation of the plane of polarization while the ellipticity is defined as the angle whose tangent is the ratio of the minor axis of the ellipse to the major axis of the ellipse. When the same optically active medium is traversed by left- and right-circularly polarized light in the same spectral region, one observes both a difference in speed (circular birefringence) and a difference in absorption (circular dichroism) for the left and right components. Both circular birefringence and optical rotation are defined by the difference in the indices of refraction for left- and right- circularly polarized light while both circular dichroism and optical ellipticity are defined by the difference in the absorption coefficients for the left and right components. All four of these measurements -- optical rotatory dispersion, optical ellipticity, circular birefringence, and circular dichroism -- give identical information, the differences being in their probe of polarization and their definition. In Table I, we present the four measures according to these criteria. Rationale for choosing one particular method of measurement of optical activity over any of the others is determined by convenience of measurement and/or of data interpretation. The rationale is discussed in the following paragraphs.

In the case of natural optical activity, one conventionally measures either circular dichroism (CD) or optical rotatory dispersion (ORD), where ORD is the variation with wavelength of the optical rotation. These are to be preferred over the corresponding circular birefringence and optical ellipticity because of ease of experimental measurement. In the case of magnetically-induced optical activity, the same reason dictates that the conventional measurements are magnetic circular dichroism (MCD) and magnetic optical rotatory dispersion (MORD), commonly known as the Faraday Effect.

TABLE IMeasures of Optical Activity

Probe Definition	Linearly Polarized Light	Right- and Left- Circularly Polarized Light
Difference in indices of refraction for left- and right- circularly polarized light $n_L - n_R$	Optical Rotation	Circular Birefringence
Difference in absorption coefficient for left- and right- circularly polarized light $\chi_L - \chi_R$	Optical Ellipticity	Circular Dichroism

In choosing between CD and ORD, MCD and MORD, the ease of data interpretation favors CD and MCD. Inspection of Figure 2 readily confirms this. Here I have sketched possible curves for CD and ORD of a chromophoric transition in an asymmetric environment at a wavelength λ_0 . Note that there is only one peak for CD compared to two for ORD. Also, the CD curve rapidly falls to zero while the ORD curve exhibits "tails" which fall off slowly. While these tails can sometimes be useful for investigation of transitions in wavelength regions not directly available for instrumental measurement, in general, they do no more than add an annoying background to other transitions. Thus, a less cluttered spectrum and lack of background make CD (and also MCD, for which identical arguments can be advanced) the preferable measurement from an interpretive point of view.

Before leaving Figure 2, we should note the similarity of shapes of the ORD curve to the dispersion of the index of refraction and of the CD curve to that of the absorption coefficient. This similarity is, of course, not surprising when one considers that circular birefringence (and thus ORD) depends on an index of refraction difference and circular dichroism (CD) on an absorption coefficient difference.

As will become increasingly evident throughout the remainder of this thesis, optical activity requires the presence of an asymmetry. This can exist as an inherent characteristic of the molecular system being investigated, as in asymmetric molecules which have natural optical activity, or it can be externally introduced, as by a magnetic field in the measurement of magnetically-induced optical activity. The detailed role of these asymmetries and the descriptions of the physical origins of natural and magnetically-induced optical activity will be examined in detail in the more complete derivations which follow this introduction. For the moment, we note that optical activity arises from the generation, by the optically active system, of small electric field components perpendicular to the applied electric field of the incident

FIGURE 2. Circular Dichroism (CD) and Optical Rotatory Dispersion (ORD) of a chromophoric transition at λ_0 .

light, and small magnetic field components perpendicular to the applied magnetic field of the incident light. For example, optical rotation is an obvious illustration of this effect as the introduction of these small (perpendicular) components result in a small net rotation of the fields of linearly polarized light as this light traverses an optically active medium.

Natural optical activity is characterized by the introduction of special components into the electronic and magnetic polarization and thus into the electric and magnetic induced fields. These new, small components of the electronic polarization are proportional to, and parallel to, the incident magnetic field and thus are perpendicular to the incident electric field. Conversely, the new, small components of the magnetic polarization are proportional to, and parallel to, the electric field and thus are perpendicular to the magnetic field. The constants of proportionality can be termed cross-field polarizabilities. As is shown in Chapter 2, these constants and the associated optical activity result from the variation of the amplitudes of the incident fields over the dimensions of the molecule. This phenomenon is justifiably ignored when considering simple absorption, a measure dependent on the more familiar electronic polarization. It is, therefore, reasonable that variations in the geometrical structuring of the molecule would have a greater effect on natural optical activity than on absorption. This is borne out by the primary uses of natural optical activity, which have been to determine stereochemical relations of asymmetric molecules (2).

Magnetically-induced optical activity results from the perturbation of the electronic polarizability by an external magnetic field. In the absence of this perturbation, this polarizability is simply a constant giving components of the electronic polarization proportional and parallel to the electric field of the incident light. When the external magnetic field is introduced, terms appear in this polarizability which result in small components of the electric polarization still proportional to, but now

perpendicular to, the incident electric field. In the derivation of magnetically-induced optical activity, the amplitudes of the incident fields are considered constant over the molecular dimensions. Thus there is not the intimate relation with variations in geometrical structuring that one finds with natural optical activity. In fact, it will be seen that it is not molecular asymmetry that is important for magnetically-induced optical activity, but rather molecular symmetry. In order to understand this, we must anticipate the results of the theoretical derivations and present the quantum-mechanical equations for magnetically-induced optical activity.

Optical activity is of necessity associated with a chromophoric transition. For a transition from a ground state a to an excited state b the natural and magnetically-induced partial molecular rotation (ORD and MORD) are given by $[\phi_{ab}(\omega)]$ and $[\phi_{ab}(\omega)]_M$, the natural and magnetically-induced partial molecular ellipticity (and therefore the CD and MCD) by $[\theta_{ab}(\omega)]$ and $[\theta_{ab}(\omega)]_M$. $[\phi_{ab}(\omega)]$ and $[\phi_{ab}(\omega)]_M$ are expressed in degrees of rotation per unit path length per molar concentration of optically active substance. $[\theta_{ab}(\omega)]$ and $[\theta_{ab}(\omega)]_M$ are expressed in degrees ellipticity per unit path length per molar concentration of optically active substance. The quantum mechanical equations for optical activity are listed below. (Footnotes 2, 3).

$$[\phi_{ab}(\omega)] = -\frac{4\pi N}{hc} f_2(\omega, \omega_{ba}) R_{ab}$$

$$[\theta_{ab}(\omega)] = -\frac{4\pi N}{hc} f_4(\omega, \omega_{ba}) R_{ab}$$

$$[\phi_{ab}(\omega)]_M = -\frac{24\pi NH'}{hc} \left[f_1(\omega, \omega_{ba}) A_{ab} + f_2(\omega, \omega_{ba}) B_{ab} + \frac{1}{kT} f_2(\omega, \omega_{ba}) C_{ab} \right]$$

$$[\theta_{ab}(\omega)]_M = -\frac{24\pi NH'}{hc} \left[f_3(\omega, \omega_{ba}) A_{ab} + f_4(\omega, \omega_{ba}) B_{ab} + \frac{1}{kT} f_4(\omega, \omega_{ba}) C_{ab} \right]$$

The expression for the absorption coefficient is:

$$[k_{ab}(\omega)] = -\frac{4\pi N}{hc} f_4(\omega, \omega_{ba}) D_{ab}$$

H' is the magnetic field strength, h is Planck's constant, c the speed of light, N is Avogadro's number. The transition frequency ω_{ba} is related to the transition energy by the formula $E_{ba} = \frac{h}{2\pi} \omega_{ba} = \hbar \omega_{ba}$.

The line shape functions $f_1(\omega, \omega_{ba})$, $f_2(\omega, \omega_{ba})$, $f_3(\omega, \omega_{ba})$ and $f_4(\omega, \omega_{ba})$ are shown in Figure 3 and are given by the expressions:

$$f_1(\omega, \omega_{ba}) = \frac{2\omega_{ba}\omega^2[(\omega_{ba}^2 - \omega^2)^2 - \omega^2\Gamma_{ba}^2]}{\hbar[(\omega_{ba}^2 - \omega^2)^2 + \omega^2\Gamma_{ba}^2]^2}$$

$$f_2(\omega, \omega_{ba}) = \frac{\omega^2(\omega_{ba}^2 - \omega^2)}{(\omega_{ba}^2 - \omega^2)^2 + \omega^2\Gamma_{ba}^2}$$

$$f_3(\omega, \omega_{ba}) = \frac{4\omega_{ba}\omega^3(\omega_{ba}^2 - \omega^2)\Gamma_{ba}}{\hbar[(\omega_{ba}^2 - \omega^2)^2 + \omega^2\Gamma_{ba}^2]^2}$$

$$f_4(\omega, \omega_{ba}) = \frac{\omega^3\Gamma_{ba}}{(\omega_{ba}^2 - \omega^2)^2 + \omega^2\Gamma_{ba}^2}$$

ω is the frequency and Γ_{ba} is the bandwidth of the transition.

R_{ab} is the natural rotational strength; A_{ab} , B_{ab} , C_{ab} the magnetic rotational strengths; and D_{ab} the oscillator strength.

They are given by the expressions:

$$R_{ab} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Im}\{\vec{\mu}_{ba} \cdot \vec{m}_{ab}\}$$

$$A_{ab} = \frac{1}{2d_a} \sum_{a,b}^{\text{mem}} [\vec{m}_{bb} - \vec{m}_{aa}] \cdot \text{Im}\{\vec{\mu}_{ab} \times \vec{\mu}_{ba}\}$$

$$B_{ab} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Im}\left\{ \sum_{d \neq a} \frac{\vec{m}_{da}}{\hbar\omega_{da}} \cdot \vec{\mu}_{ab} \times \vec{\mu}_{bd} + \sum_{d \neq b} \frac{\vec{m}_{bd}}{\hbar\omega_{db}} \cdot \vec{\mu}_{ab} \times \vec{\mu}_{da} \right\}$$

$$C_{ab} = \frac{1}{2d_a} \sum_{a,b}^{\text{mem}} \vec{m}_{aa} \cdot \text{Im}\{\vec{\mu}_{ab} \times \vec{\mu}_{ba}\}$$

$$D_{ab} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Re}\{\vec{\mu}_{ba} \cdot \vec{\mu}_{ab}\}$$

where d_a is the degeneracy of the ground state a , $\vec{\mu}_{ab}$ is a transition electric dipole moment between states a and b , $\vec{m}_{ab}$ a transition magnetic dipole moment between states a and b , $\vec{m}_{aa}$ a permanent magnetic dipole moment of state a , and the summation is over all transitions degenerate with $a \rightarrow b$.

Similar definitions hold for the moments $\vec{\mu}_{ba}$, $\vec{\mu}_{bd}$, $\vec{\mu}_{da}$, $\vec{m}_{da}$, $\vec{m}_{bd}$, $\vec{m}_{bb}$. The notations $\text{Im}\{\}$ and $\text{Re}\{\}$ denote the imaginary and real parts of the expression in the brackets.

The existence or non-existence of natural and magnetically-induced optical

FIGURE 3. Line Shape Functions for Absorption, Natural and Magnetically-Induced Optical Activity.

activity and of absorption is determined by whether or not the above rotational strengths and the oscillator strengths are zero or non-zero. It will be seen in the later derivations that symmetry arguments play a predominant role in these determinations.

Inspection of the quantum mechanical equations for the magnetically-induced optical activity will make clear the role played by molecular symmetry. There are three types of terms for magnetically-induced optical activity. In a shorthand notation, they are: the "A" terms, the "B" terms, and the "C" terms. These correspond to the expressions involving the magnetic rotational strengths A_{ab} , B_{ab} , and C_{ab} . Of the three, the "A" and "C" terms involve permanent magnetic moments. For a molecular state to have a permanent magnetic moment, it must be degenerate. Possession of degenerate states, in turn, requires the molecule to have a 3-fold or higher axis of symmetry. Thus unless the molecule of interest exhibits at least a minimum degree of symmetry, there will be no "A" or "C" terms. This requirement does not apply to the "B" term which can occur for all molecules. The "B" terms result from the final state of the transition being "Mixed" with other molecular states by the perturbation of the external magnetic field. There are no permanent magnetic moments involved, and therefore, no degeneracy is required.

The "A" terms result from Zeeman splitting of the degenerate ground and/or excited states. The "C" terms result from the Boltzman population distribution over the sublevels of the Zeeman-split degenerate ground state and hence are temperature dependent. The "B" terms, as mentioned above, arise from mixing of states by the external magnetic field. All magnetically-induced optical activity terms are linear functions of the external magnetic field.

In Table II are listed the uses to which CD (and/or ORD) and MCD

TABLE 11Applications of CD and ORD

1. Study of relative and absolute configurations of asymmetric molecules (2).
2. Study of magnetically allowed transitions (such as $n-\pi^*$) and estimation of magnetic moments (3).
3. Determination of relative orientations of interacting transition dipoles and dimer configurations (4).
4. Determination of polarization directions of transitions responsible for strong absorption bands (5).

Applications of MCD and MORD (Footnote 4)

1. Determination of degeneracy in either ground or excited states (8, 9).
2. Resolution of overlapping absorption bands (10).
3. Assignment of symmetries of excited states of allowed transitions (8, 11).
4. Assignment of symmetries of vibrational part of excited vibronic state of electronically forbidden transition (13).
5. Determinations of relative polarizations of transitions (4, 14).
6. Determination of magnetic moments - permanent moments for ground and excited states and transition moments (15, 16, 17, 18).
7. Determination of influence of substitutions on chromophores (7, 19).

(and/or MORD) have been put. This table does not pretend to be exhaustive - especially for CD - but most of the major applications are listed. The CD applications have been extensively discussed elsewhere (see Table II for references), and no further elaboration is necessary here. However, a few words about the MCD applications would be useful. Determination of degeneracy and resolution of overlapping absorption bands can be made. The former depends on the recognition of the presence of "A" and/or "C" terms. The "A" terms can be recognized by their line shape function which differs from those of the "B" and "C" terms. (See Figure 3). The "C" terms can be identified via their temperature dependence. Band resolution depends on the possibility that the MCD of adjacent bands will be of opposite sign. This is in contrast to the absorption which is the same sign (positive) for all bands. Assignment of symmetries and determination of relative polarization rely on the determination of relative magnitudes and signs of the "A", "B", and "C" terms. Simple group theory arguments play a prominent role in both of these applications. Determination of magnetic moments and of the influence of substituents can be obtained from calculation of the ratios A_{ab}/D_{ab} , B_{ab}/D_{ab} and C_{ab}/D_{ab} . Finally, the influence of substituents on chromophores can be examined via the variation of A_{ab} , B_{ab} , and C_{ab} with said substitution. Detailed discussion of these applications, their theoretical and experimental basis, and their limitations can be found in Schatz and McCaffery (6a) and in the references listed in Table II.

C. Quantum Mechanical Theories of Optical Activity

Many attempts have been made by various researchers (see Table III for references) to develop satisfactory quantum mechanical theories of natural and magnetically-induced optical activity, with work on the former being the most common. However, much is left to be desired in both areas. A satisfactory theory of optical activity should explain not only natural and magnetically-induced optical activity for a single, simple non-vibrating, unsubstituted chromophore, but also form a basis for evaluation of vibronic interactions,

substitutional effects, and chromophore-chromophore interactions. Some of these areas have been investigated to a greater or lesser degree. It is the purpose of this dissertation to expand some of the partially investigated topics, to examine some previously untreated areas, and in general, to present a more unified theory of natural and magnetically-induced optical activity than has been done previously.

It is not the intent here to present a history of the theories of optical activity. This has been done in several places. In particular, Lowry (20) and the reviews of Mason (21a, 21b) deal with natural optical activity while Groenewege (22), Stephens (23) and the reviews of Schatz and McCaffery (6a) and of Buckingham and Stephens (6b) deal with magnetically-induced optical activity. Rather we shall briefly discuss at what stage the theories of each type of optical activity have evolved and where this dissertation will add to their completeness and/or improve their precision.

In order to understand the connection between the various theoretical treatments of optical activity, one must understand the philosophy underlying perturbation theory (Footnote 5). Most problems that one encounters in physics and chemistry do not lend themselves to solutions in closed form. Because of this, a common practice is to approximate the complex problem with a simpler problem plus some small perturbations (deviations from the simpler problem). If the simpler case is not capable of being solved in closed form, then the procedure is repeated until a problem that is solvable is obtained. Thus one has a complex problem approximated by a solvable problem plus a series of small perturbations. This will lead to the expectation values of the observables of the complex system being expressed in terms of the expectation values of the observables of the simple system (which are assumed to be known). Almost all of the quantum mechanical theories of optical activity rely on a

perturbation approach (Footnote 6).

The mechanics of the perturbation theory approach are straightforward. Let the following notation hold:

$\mathcal{H}$ - Hamiltonian of complex system

ψ_n - Eigenfunctions of $\mathcal{H}$ (wave functions of complex system)

E_n - Eigenvalues of $\mathcal{H}$ (energies of Hamiltonian of complex system)

$\mathcal{H}^0$ - Hamiltonian of simple (solvable) system

ψ_n^0 - Eigenfunctions of $\mathcal{H}^0$ (known wavefunctions of solvable system)

E_n^0 - Eigenvalues of $\mathcal{H}^0$ (known energies of Hamiltonian of solvable system)

$$\mathcal{H} = \mathcal{H}^0 + \sum_k \mathcal{H}_k^1$$

$\mathcal{H}_k^1$ - Perturbation Hamiltonian

$$\mathcal{H} \psi_n = E_n \psi_n$$

$$\mathcal{H}^0 \psi_n^0 = E_n^0 \psi_n^0$$

It can be shown (27) that the eigenfunction of the complex system, ψ_n , can be expanded in the eigenfunctions of the simple system, ψ_n^0 , with coefficients dependent on the perturbation Hamiltonians.

$$\psi_n = \psi_n^0 + \sum_k \sum_l \frac{(\psi_l^0 | \mathcal{H}_k^1 | \psi_n^0)}{E_l^0 - E_n^0} \psi_l^0$$

We emphasize that the $\mathcal{H}_k^1$ (more accurately the ratio $\frac{(\psi_l^0 | \mathcal{H}_k^1 | \psi_n^0)}{E_l^0 - E_n^0}$) must be small enough so that the series expansion will converge. Otherwise this expansion is not valid. The eigenfunctions of the complex system, ψ_n , are then substituted into the expressions for the expectation values for the observables of the complex system. Let an observable be denoted by $\hat{O}$, where $\hat{O}$ is a scalar, vector, or tensor operator. Its expectation value in the complex system is given by:

$$\hat{O}_{nn} = \int \psi_n^* \hat{O} \psi_n d\tau = (\psi_n | \hat{O} | \psi_n) = (n | \hat{O} | n)$$

where the integration is over all coordinate space. Upon substituting the expansions for ψ_n , one obtains the expectation values of the observables of the complex system, $\hat{O}_{nn}$, in terms of the expectation values and transition probabilities of the observables of the simple system. This is done in detail in the later derivations. It should be noted that the above equations are for non-degenerate perturbation theory. The details of degenerate perturbation theory are also considered in the later derivations.

The calculation of natural optical activity is generally divided into three distinct stages (28, 29). The optical activity is first related to the difference in the complex refractive indices of left- and right-circularly polarized light. These indices are then expressed in terms of the induced electric and magnetic moments by solving Maxwell's equations, with the optically active media specified by the phenomenological equations for the induced fields $\vec{D}$ and $\vec{B}$. These moments are then quantum mechanically calculated, via time dependent perturbation theory, as the expectation values of the molecular electric and magnetic moments averaged over all orientations of the molecule. This three step approach has the advantage that the physical basis of the optical activity is retained to a greater degree than in other methods of derivation, mainly because there is less tendency to get lost in the complex mathematics.

In order to derive the equations for magnetically-induced optical activity, only one modification is involved. When the induced moments are calculated, the expectation values of these observables are evaluated using wave functions which are eigenfunctions of the Hamiltonian for what we shall term the magnetic system. This magnetic system comprises both the molecular system and the external magnetic field. Its Hamiltonian consists of the

molecular Hamiltonian plus a perturbation Hamiltonian due to the interaction of the molecular magnetic moments with the magnetic field. When the eigenfunctions of the Hamiltonian of the magnetic system are expanded, via time-independent perturbation theory, in terms of those of the molecular Hamiltonian, the equations for the expectation values of the induced moments take on a form which lead directly to equations for both natural and magnetically-induced optical activity.

We must now consider how to evaluate the effects of vibronic structure, substitution, and chromophore-chromophore interaction for both types of optical activity. To do this, we must elaborate on the derivation of natural and magnetically-induced optical activity and further subdivide the system Hamiltonian. Let us write (Footnote 8):

$$\mathcal{H} = \mathcal{H}' + \mathcal{H}_M^2 + \mathcal{H}_0^3 + \mathcal{H}_0^4$$

$\mathcal{H}$ - system Hamiltonian

$\mathcal{H}'$ - molecular Hamiltonian for vibrating, substituted, interacting set of chromophores

$\mathcal{H}_0^3$ - time varying perturbation Hamiltonian of light wave leading to refractivity and absorption

$\mathcal{H}_0^4$ - time varying perturbation Hamiltonian of light wave leading to natural optical activity

$\mathcal{H}_M^2$ - magnetic perturbation Hamiltonian leading to magnetically-induced optical activity

where:

$$\mathcal{H}' = \mathcal{H}^0 + \mathcal{H}_I^1 + \mathcal{H}_V^1 + \mathcal{H}_S^1$$

$\mathcal{H}^0$ - molecular Hamiltonian for non-vibrating, unsubstituted, non-interacting set of chromophores

$\mathcal{H}_I^1$ - chromophore-chromophore interaction perturbation Hamiltonian

$\mathcal{H}_V^1$ - vibrational perturbation Hamiltonian

$\mathcal{H}_S^1$ - substitutional perturbation Hamiltonian

$$\therefore \mathcal{H} = \mathcal{H}^0 + \mathcal{H}_I^1 + \mathcal{H}_V^1 + \mathcal{H}_S^1 + \mathcal{H}_M^2 + \mathcal{H}_0^3 + \mathcal{H}_0^4$$

We first apply the time varying perturbations $\mathcal{H}_0^3$ and $\mathcal{H}_0^4$.

Here the wave functions of the molecular system in the presence of light are

expanded in terms of the wave functions of the molecular system in the absence of light, with coefficients being functions of $\mathcal{H}_0^3$ and $\mathcal{H}_0^4$. The next step in the general procedure is to find the smallest remaining perturbation Hamiltonian and separate it out, thus leaving a "remainder" Hamiltonian. We then expand the eigenfunctions of the original Hamiltonian in terms of the eigenfunctions of the "remainder" Hamiltonian, with coefficients as functions of this smallest perturbation Hamiltonian. Of the four perturbation Hamiltonians, $\mathcal{H}_N^2$, $\mathcal{H}_I^1$, $\mathcal{H}_V^1$ and $\mathcal{H}_S^1$, the magnetic perturbation $\mathcal{H}_N^2$ is generally considered to be the smallest. Thus, the eigenfunctions of $\mathcal{H}$ are expanded in terms of the eigenfunctions of $\mathcal{H}'$ with the coefficients being functions of $\mathcal{H}_0^3$, $\mathcal{H}_0^4$, and $\mathcal{H}_N^2$. These steps are the basis of the derivation of natural and magnetically-induced optical activity. The procedure is then to consider the next larger perturbation. Suppose it is $\mathcal{H}_V^1$. The eigenfunctions of $\mathcal{H}'$ are then expanded in terms of the eigenfunctions of $\mathcal{H}'' = \mathcal{H}_0 + \mathcal{H}_I^1 + \mathcal{H}_S^1$ with the expansion coefficients being functions of $\mathcal{H}_V^1$. This process is continued until all the perturbations are accounted for sequentially, and we are at the stage where we are expanding in terms of the eigenfunctions of $\mathcal{H}''$, the solvable problem -- solvable in that we know, or assume we know, the eigenfunctions of $\mathcal{H}''$. The end result is that the eigenfunctions of $\mathcal{H}$ are expressed in terms of those of $\mathcal{H}''$, with expansion coefficients determined by the various perturbations. These expanded eigenfunctions are used to calculate the expectation values of the induced moments, which in turn lead to the desired equations for optical activity upon application of the first two steps of the aforementioned three step approach.

It should be noted that the sequential method of perturbation application is only valid if successive perturbations become larger and larger (in order of mathematical application). If two or more of these perturbations are of the same order of magnitude, a simultaneous approach is necessary for these particular perturbations. This can be the case

when dealing with $\mathcal{H}_I^1$, $\mathcal{H}_V^1$, and $\mathcal{H}_S^1$ and the various possibilities will be considered in detail in the later theoretical sections. It is possible that there can be spectroscopically observable effects from one of the three perturbations $\mathcal{H}_I^1$, $\mathcal{H}_V^1$ or $\mathcal{H}_S^1$ being of the same order of magnitude as $\mathcal{H}_M^2$. However, in the interests of not overcomplicating the problem, we shall ignore this possibility. It is something that bears investigation in the future.

We now consider the current status of the general theories of natural and magnetically-induced optical activity and their various extensions. These extensions include vibronic structuring, substitutional influences, chromophore-chromophore interactions (polymeric systems) and combinations of these. In Table III there is a synopsis of the various theoretical treatments -- general and extended -- including a descriptive name for the method, the important perturbations, and reference to the authors of these works. If there has been little or no treatment, this is indicated by the lack of a reference. Two or more references given generally indicate different methods of attacking that particular theoretical problem. Finally, the degree of investigation is not necessarily proportional to the number of references given or even to the number of papers written on the subject. Later, in this dissertation, we shall attempt to propose future research which will hopefully fill in the theoretical outline presented in Table III.

The theoretical treatment of optical activity begins in Chapter 2 with a general tutorial derivation of natural and magnetically-induced optical activity. The attempt is to present a clear and physically meaningful account of the derivation without omitting any important mathematics. This is accomplished by liberally filling the derivation with discussions about physical meaning and relegating detailed and possibly confusing mathematics to appendices.

TABLE III

Theoretical Treatments of Natural and Magnetically-induced Optical Activity
Pertinent Perturbations and References for various Extensions

Type of Theory	Natural Optical Activity	Magnetically-induced Optical Activity
General Theory	Condon (28) Moscowitz (29) Maaskant and Oosterhoff (30) Downie (this work)	Groenewege (22) Stephens (23) Buckingham and Stephens (6b) Downie (this work)
Substitutional Influences	Schellman (31) Tinoco (32) Downie (this work)	Downie (this work)
Vibronic Structuring	Weigang (33) Downie (this work)	Downie (this work)
Excitonic Interaction	Tinoco (32) Harris (25)	Harris (26) Tinoco and Bush (34)
Weak and Strong Coupling	Tinoco (32) Harris (25)	Harris (26)
Vibrational and Substitutional Perturbations	Downie (this work)	Downie (this work)
Substitution and Interaction	Tinoco (32)	-----
Vibration, Substitution, Interaction	-----	-----

Following this general derivation, in Chapter 3 a general discussion of optical activity of complex systems is presented. The validity of the perturbation theory approach is reviewed and the various approximating simple systems used in analyzing the complexities of vibration, substitution and chromophore-chromophore interaction are detailed. In summary, Chapter 3 sets the stage for the extensions to the general theory.

In Chapter 4 we investigate one such extension, the vibrational and substitutional structuring of natural and magnetically-induced optical activity. Here, the intent is to determine, using symmetry considerations, the specific vibrational and substitutional symmetry patterns that alter, enhance, and allow the various electronic transitions in molecular optical activity. Thus, for natural optical activity, the substitutional symmetry rules of Schellman (31) and the vibronic structuring results of Weigang (33) are confirmed and extended. For magnetically-induced optical activity, neither of these problems have been treated before (Footnote 9). The key tools in this analysis are a third order perturbation expansion and a group theoretical symmetry treatment by computer.

We conclude this introduction with an emphasis on the theoretical framework set forth in Table III. In this skeletal structure, one can include most of the past and present work on natural and magnetically-induced optical activity, and it offers a guide to future theoretical developments. The importance of having such a framework should not be minimized as, by keeping it in mind while proceeding through the various theoretical derivations, the reader will always have before himself an overall view of optical activity and what it can tell him. In Chapter 5, we shall refer to

this table to see what we have contributed to the theory of natural and magnetically-induced optical activity and what remains to be done.

We now begin the theory of natural and magnetically-induced optical activity.

FOOTNOTES

1. Except for a perfectly monochromatic wave (a physically non-realizable phenomenon), any sample of electromagnetic radiation will be of mixed polarization. In experimental work calling for measurement with a specific type of polarization, it is a measure of the efficiency of the apparatus as to how pure one can obtain a specified state of polarization.
2. These equations for molecular rotation and ellipticity are derived in Chapter 2. Consideration of these equations is not a prerequisite to the understanding of the remainder of Chapter 1. They are included here only for readers who are happier when they have mathematics to which to refer.
3. For readers not familiar with quantum mechanical notation, see Appendix I.
4. For a more complete list of applications of MCD and MORD, see References (6), (7), (8).
5. The use of perturbation theory is only valid under certain limiting conditions. If these conditions are not satisfied, a more general procedure must be used. Unfortunately, this general procedure, diagonalization of the representation of the Hamiltonian, is itself limited by its difficulty of application. Therefore, in this thesis we will restrict our specific extensions of the theory of optical activity to cases where perturbation theory is applicable. However, in Chapter III we do develop the necessary formalism for the more general procedure

and specify under what conditions perturbation theory ceases to be valid.

6. Karplus and Kölker (24) have given a variation approach for natural optical activity while Harris has used the Hartree-Fock method for both natural (25) and magnetically-induced optical activity (26).
7. In these relations, it is assumed that the wave functions are normalized so that $\int \psi_n^* \psi_n d\tau = 1$.
8. In general, the superscripts on the perturbation Hamiltonians indicate the relative sizes of these perturbations, a larger superscript indicating a higher order (smaller) perturbation. For a discussion of the relative magnitude of the various types of perturbations, see Appendix II.
9. Stephens (12) wrote a short note giving some preliminary equations for vibrational structuring in magnetically-induced optical activity, but these were far from complete and were applied to one particular rare-earth system.

Chapter 2

General Theory for Optical ActivityA. Synopsis of General Theory

A quantum mechanical theory of natural and magnetically-induced optical activity is presented. The treatment is for a general chromophore; the analysis of the influence of vibrations, substitutions and chromophore-chromophore interactions being delayed until Chapters 3, 4, and 5. Since the purpose is to present a tutorial derivation, every attempt is made to make the analysis physically meaningful. This has resulted in much of the complex mathematics being relegated to appendices so as not to disturb the continuity of the derivation. Also this derivation may be read at either of two levels. For the reader who is interested in understanding the physical basis of optical activity (Footnote 1) but does not feel it profitable to explore the more detailed mathematics of the quantum theory, this synopsis extracts from the detailed derivation the pertinent equations, explores their origin, and through discussion of their physical meaning, analyzes their implications. The second of the two levels includes following through the details of the derivation. In part B of this chapter, an extensive mathematical treatment of optical activity is presented. A study of this detailed derivation along with the synopsis of the theory will prepare the reader to fashion extensions of the theory of optical activity and will lead to a better understanding of the interrelation of the physics and mathematics.

Before we begin this detailed treatment of optical activity, an examination of the demand for this new derivation is in order. Considering that there have been three recent quantitative quantum mechanical

derivations of magnetically-induced optical activity (6, 22, 26) and many more of natural optical activity, it is natural that we consider this question. The new treatment can best be justified by examining the current theories, their strengths, and their weaknesses. Harris' theories of natural (25) and magnetically-induced (26) optical activity are unique in that CD and MCD are derived by determining the net power absorbed by a system illuminated by left- and right- circularly polarized light. The other two theories base their derivation on the measure of rotation and/or ellipticity of linearly polarized light. The derivation of Harris is done primarily for the purpose of providing a background for the theory of optical activity of polymers and, due to its brevity and complexity, is not appropriate for study by one who is about to be introduced to the quantum theory of optical activity. The derivation of Groenewege (22) is more detailed and attempts to treat both natural and magnetically-induced optical activity. However, the organization of the paper is poor, there are some questionable assumptions regarding the order of application of perturbations, and still worse, the results for magnetically-induced optical activity are incorrect. The last is due to a failure to treat the complex notation for the electromagnetic fields consistently throughout the paper. The last, and best, major derivation of magnetically-induced optical activity is presented in two places: the paper of Buckingham and Stephens (6) and the doctoral thesis of Stephens (23). This is a rather detailed derivation and determines the quantum mechanical equations for CD and MCD as well as those for ORD and MORD. The treatment of CD and MCD involves the solution for optical activity within regions of absorption and requires a more complex mathematical notation. Stephens used a tensor notation which, unfortunately, tended to obscure the physical basis of optical activity. Because of this complexity and

loss of physical meaning, the derivation is difficult to read and to understand. In the theory presented in this dissertation, we attempt to combine the good points of all previous approaches and, if possible, to eliminate the bad. Thus we adhere closely to the theoretical format used by Stephens and most workers in the field of natural optical activity, but deviate in places where clarity can be improved. We derive directly only the ORD and MORD and thus are able to use a vector notation for the electromagnetic fields. This type of notation is more familiar to most chemists and lends itself more readily to physical understanding than the more complex tensor notation. The CD and MCD can be obtained from the ORD and MORD as will be discussed later. As a final justification, we contend that the derivation presented here offers an excellent platform on which to build extensions of the theory of optical activity. This was the object of the writer and therefore effort was expended to provide a flexible and consistent notation, to search out key words and thoughts which yield a more comprehensive physical understanding, and to present in this and other sections a unified approach, via perturbation techniques, to the theories of optical activity.

The basic procedure followed in deriving the general equations for natural and magnetically-induced optical activity is the three step approach described in both Chapter 1 and in part B of this chapter. At the risk of repeating some of this work, we outline below the major steps of the derivation, at all times attempting to maintain a clear physical picture of what the various steps of the derivation signify.

Consider a sample that has different complex indices of refraction for left- and right circularly polarized light. It will be shown that this condition is requisite for the existence of optical activity. For this

sample there will be different indices of refraction (the real part of the complex index) and different extinction coefficients (the imaginary part of the complex index) for the left and right components. On the one hand the difference in indices of refraction results in different velocities of propagation in the medium for left- and right-circularly polarized light -- i.e. the phenomenon of circular birefringence. As linearly polarized light is equivalent to the sum of equal parts of left- and right- circularly polarized light, this differential velocity leads to a rotation of the plane of polarization of linearly polarized light -- i.e. ORD and/or MORD. On the other hand, the difference in extinction coefficients results in the differential absorption of the left and right components -- i.e. CD and/or MCD. In fact, the reader will recognize that not only are these the definitions for optical rotation and circular dichroism, but inherent in these descriptions is the basis for measurement of these phenomena.

Thus we find that the ORD and/or MORD is given by the formula (most of the equation numbers relate to equations derived in part B of this chapter):

$$(2-36) \quad \varphi(z, \omega) = \frac{\omega z}{2c} (n_L - n_R)$$

CD and/or MCD is given by:

$$(2-37) \quad \theta(z, \omega) = \frac{\omega z}{2c} (\kappa_L - \kappa_R)$$

where ω is the radian frequency of the light, c is the speed of light, z is the pathlength, $(n_L - n_R)$ is the difference in the indices of refraction, and $(\kappa_L - \kappa_R)$ is the difference in extinction coefficients. As is to be expected, these measures of optical activity are directly proportional to the pathlength. They are also directly proportional to

the concentration of the solute molecules. This, however, is not immediately evident as the concentration dependence is hidden in $(n_L - n_R)$ and $(\chi_L - \chi_R)$. Likewise one should not be deceived by the apparently simple frequency dependence as both $(n_L - n_R)$ and $(\chi_L - \chi_R)$ will turn out to be complex functions of ω . The object of the rest of the derivation will be to determine the exact forms and sources of the differences $(n_L - n_R)$ and $(\chi_L - \chi_R)$.

There are two procedures that can be followed to determine these differences. The first involves determining $(n_L - n_R)$ and $(\chi_L - \chi_R)$ simultaneously. This was the method of derivation used by Stephens and necessitated the complexities of a tensor notation. The second procedure is the one we shall use here. It entails the primary calculation of one of the differences and then a secondary calculation of the other difference from the first, via the general set of expressions known as the Kronig-Kramers transforms (29, 35), (Footnote 2). As the primary calculation of $(\chi_L - \chi_R)$ involves the more complex question of optical activity through regions of absorption, we shall calculate primarily $(n_L - n_R)$ and then calculate secondarily $(\chi_L - \chi_R)$.

The solution of Maxwell's equations under the restrictions imposed by an optically active medium (in the form of constitutive equations for the induced electric and magnetic fields) yield two solutions for forward propagating waves. These correspond to the field equations for left- and right- circularly polarized light and yield two values for the index of refraction, n_L and n_R . Maxwell's equations are (in a medium without free charges or conductivity):

$$\begin{aligned}
 \nabla \times \vec{E}_{L0} &= -\frac{1}{c} \dot{\vec{B}}_{L0} & \nabla \cdot \vec{B}_{L0} &= 0 \\
 \nabla \times \vec{H}_{L0} &= \frac{1}{c} \dot{\vec{D}}_{L0} & \nabla \cdot \vec{D}_{L0} &= 0
 \end{aligned}
 \tag{2-43}$$

where $\vec{E}_{L0}$ and $\vec{H}_{L0}$ are the macroscopic incident electric and magnetic

fields at the molecule, $\vec{D}_{L_0}$ and $\vec{B}_{L_0}$ are the macroscopic induced electric and magnetic fields at the molecule. These field vectors are real quantities but for reasons which will become clear as we progress, it is convenient to write each of them as the sum of two complex conjugates. As an example, we write the incident electric field intensity as:

$$(2-38a) \quad \vec{E}_{L_0} = \frac{1}{2} [\vec{\tilde{E}}_{L_0} + \vec{\tilde{E}}_{L_0}^*]$$

where $\vec{\tilde{E}}_{L_0}$ is the complex field intensity, $\vec{\tilde{E}}_{L_0}^*$ its complex conjugate, at a position defined by the vector $\vec{L} = z\hat{k} + \vec{R}$. $\vec{\tilde{E}}_{L_0}$ is given by:

$$(2-38b) \quad \vec{\tilde{E}}_{L_0} = \vec{\tilde{E}}_0 e^{i\omega[t - \frac{n}{c}(z + \hat{k} \cdot \vec{R})]}$$

where $\hat{k}$ is a unit vector in the propagation direction, n is the index of refraction, and $\hat{k} \cdot \vec{L} = z + \hat{k} \cdot \vec{R}$ is the z coordinate of the location where the field intensity is measured. The coordinate system used here is illustrated in Figure 7 of part B of this chapter.

The constitutive equations specifying the optically active medium are given by:

$$(2-41) \quad \begin{aligned} \vec{D}_{L_0} &= \epsilon \vec{E}_{L_0} - g \dot{\vec{H}}_{L_0} - f_1 (\vec{E}_{L_0} \times \vec{H}') \\ \vec{B}_{L_0} &= \mu \vec{H}_{L_0} + g \dot{\vec{E}}_{L_0} - f_2 (\vec{H}_{L_0} \times \vec{H}') \end{aligned}$$

The parameters $\mu, \epsilon, g, f_1, f_2$ are functions of molecular electric and magnetic moments, and of ω , and are quantum mechanically derived in part B of this chapter. The vector H' represents the static external magnetic field and is assumed parallel to the direction of propagation (Footnote 3). The terms involving g give rise to natural optical activity, those involving f_1 and f_2 to magnetically-induced optical activity. If g is zero and $\vec{H}'$ is zero, there is no optical activity and

equations (2-41) reduce to the more familiar

$$\vec{D}_{L_0} = \epsilon \vec{E}_{L_0}$$

$$\vec{B}_{L_0} = \mu \vec{H}_{L_0}$$

It is shown in Chapter 4 that g is zero for a non-asymmetric molecule but f_1 and f_2 can be non-zero for all molecules. Thus while only asymmetric molecules possess natural optical activity, with a non-zero, properly oriented magnetic field all molecules will exhibit magnetically-induced optical activity.

Upon substitution of the constitutive equations (2-41) and the expressions for the induced and incident fields (2-38) into Maxwell's equations, the $\vec{D}_{L_0}$, $\vec{B}_{L_0}$, and $\vec{H}_{L_0}$ fields are eliminated. This results in two vector equations in the $\vec{E}_{L_0}$ field. The first is

$$(2-53) \quad (n^2 - \mu\epsilon) \vec{E}_{L_0} + \frac{i\omega g}{n} (n^2 + \mu\epsilon) (\hat{k} \times \vec{E}_{L_0}) + i\omega(\mu f_1 + \epsilon f_2) (\vec{E}_{L_0} \times \vec{H}') = 0$$

and the second is the complex conjugate of the first. Decomposing either of these equations into its components gives three linearly independent equations in the components of the electric field intensity.

Written in matrix form we have:

$$(2-54) \quad \begin{bmatrix} n^2 - \mu\epsilon & -i\omega \left[\frac{g}{n} (n^2 + \mu\epsilon) + (\mu f_1 + \epsilon f_2) H'_z \right] & -i\omega(\mu f_1 + \epsilon f_2) H'_y \\ i\omega \left[\frac{g}{n} (n^2 + \mu\epsilon) + (\mu f_1 + \epsilon f_2) H'_z \right] & n^2 - \mu\epsilon & i\omega(\mu f_1 + \epsilon f_2) H'_x \\ i\omega(\mu f_1 + \epsilon f_2) H'_y & -i\omega(\mu f_1 + \epsilon f_2) H'_x & n^2 - \mu\epsilon \end{bmatrix} \begin{bmatrix} \tilde{E}_{L_0x} \\ \tilde{E}_{L_0y} \\ \tilde{E}_{L_0z} \end{bmatrix} = 0$$

As stated previously, the external magnetic field is colinear with the direction of propagation, in this case the z axis. We thus set

$H'_x = H'_y = 0$ and $H'_z = H'$. The above matrix equation then reduces to the condition of transversality ($\tilde{E}_{L_0z} = 0$) and to the secondary matrix equation:

$$(2-56) \quad \begin{bmatrix} n^2 - \mu\epsilon & -i\omega \left[\frac{g}{n} (n^2 + \mu\epsilon) + (\mu f_1 + \epsilon f_2) H' \right] \\ i\omega \left[\frac{g}{n} (n^2 + \mu\epsilon) + (\mu f_1 + \epsilon f_2) H' \right] & n^2 - \mu\epsilon \end{bmatrix} \begin{bmatrix} \tilde{E}_{Lox} \\ \tilde{E}_{Loy} \end{bmatrix} = 0$$

As $\tilde{E}_{Lox}$ and $\tilde{E}_{Loy}$ are linearly independent variables, this matrix equation will only be true when the determinant of the index of refraction matrix is zero.

$$\begin{vmatrix} n^2 - \mu\epsilon & -i\omega \left[\frac{g}{n} (n^2 + \mu\epsilon) + (\mu f_1 + \epsilon f_2) H' \right] \\ i\omega \left[\frac{g}{n} (n^2 + \mu\epsilon) + (\mu f_1 + \epsilon f_2) H' \right] & n^2 - \mu\epsilon \end{vmatrix} = 0$$

This characteristic equation yields four solutions for n . Two of these correspond to propagation in the $-\hat{k}$ direction and can be ignored. The other two correspond to the indices of refraction for forward propagating left- and right-circularly polarized light. When we make the approximations $\mu \cong 1$, $\epsilon f_2 \ll \mu f_1$, $\frac{1}{\sqrt{\epsilon}} \cong 1$ (these approximations are justified in part B of this chapter) we find:

$$(2-59) \quad n_L \cong \sqrt{\epsilon\mu} + \omega \left(g + \frac{f_1}{2} H' \right)$$

$$n_R \cong \sqrt{\epsilon\mu} - \omega \left(g + \frac{f_1}{2} H' \right)$$

Thus we have for the difference in indices of refraction

$$(2-60) \quad n_L - n_R \cong 2\omega \left[g + \frac{f_1}{2} H' \right]$$

Substituting into equation (2-36) we have the optical rotation expressed in terms of the parameters g and f_1 , and in terms of the component of the magnetic field:

$$\phi(z, \omega) = \frac{\omega^2 z}{2c} [2g + f_1 H']$$

The first term is the natural optical rotation (ORD) and the second term the magnetically-induced optical rotation (MORD). Two things should be noted in the above equations. First of all the two

types of optical activity are independent and additive. Secondly, the magnetically-induced optical activity is a linear function of the magnitude of the external magnetic field.

The next step in the derivation is the quantum mechanical determination of the expressions for the parameters g and f_1 . However, before we begin this, we may profitably digress to discuss the physical implications in the constitutive equations and to present simple models for natural and magnetically-induced optical activity. By comparing the constitutive equations for an optically active medium

$$\vec{D}_{Lo} = \epsilon \vec{E}_{Lo} - g \dot{\vec{H}}_{Lo} - f_1 (\dot{\vec{E}}_{Lo} \times \vec{H}') \quad (2-41)$$

$$\vec{B}_{Lo} = \mu \vec{H}_{Lo} + g \dot{\vec{E}}_{Lo} - f_2 (\dot{\vec{H}}_{Lo} \times \vec{H}')$$

with those for an optically inactive medium,

$$\vec{D}_{Lo} = \epsilon \vec{E}_{Lo}$$

$$\vec{B}_{Lo} = \mu \vec{H}_{Lo}$$

we see that in the constitutive equation for $\vec{D}_{Lo}$ it is the introduction of small components perpendicular to $\vec{E}_{Lo}$ that is responsible for optical activity while for $\vec{B}_{Lo}$ it is components perpendicular to $\vec{H}_{Lo}$. These additional components produce a rotation of the induced field $\vec{D}_{Lo}$ with respect to $\vec{E}_{Lo}$ and of $\vec{B}_{Lo}$ with respect to $\vec{H}_{Lo}$, and thus a net rotation of the plane of polarization. We may best illustrate the molecular origin of this rotation by reference to Figure 4a for natural optical activity and to Figures 4b and 4c for magnetically-induced optical activity. As with both types of optical activity, we are dealing with absorption and refraction in the visible and ultraviolet

a. Diagram for Natural Optical Rotation

b. Diagram for Magnetically-induced Optical Rotation

c. Force Diagram for Magnetically-induced Optical Rotation

FIGURE 4. Models for Optical Activity

regions of the spectrum, we are concerned with electronic movement only. Thus we may represent a molecule by its molecular orbitals, i.e. those volumes where the electrons may be found.

In Figure 4a we show a linearly polarized electromagnetic field incident upon the most basic asymmetric molecular system, a helical molecular orbital fixed in space (Footnote 4). A little thought will convince one that any asymmetric molecular orbital can be constructed from a set of helical molecular orbitals of various radii, pitch, and handedness. Thus if we can demonstrate that the presence of a helical molecular orbital will result in rotation of the incident fields, then we will have shown it for any asymmetric molecular orbital (and therefore any asymmetric molecule absorbing in the visible or ultraviolet). To demonstrate this rotation, consider the action of the electric field intensity $\vec{E}_0$ on the helical molecular orbital. The electric field will produce electronic flow in the helix. This helical flow in turn produces a small magnetic field component proportional to $\vec{E}_0$ and perpendicular to $\vec{H}_0$, thus resulting in a net rotation of the magnetic field. A comparable argument holds for the production of a small electric field component by the incident magnetic field $\vec{H}_0$, and the net result is a rotation of the plane of polarization. As without the helicity, there would be no such rotation, we may conclude that an asymmetry is necessary for natural optical activity.

We now turn to magnetically-induced optical activity. Unlike natural optical activity, an asymmetry is not required, and we choose a simple symmetric model; a circular molecular orbital. We again fix our model in space; this time with its axis colinear with the direction of propagation and thus with the direction of the magnetic field. The geometry is shown in Figure 4b. Viewing the system in the negative $\hat{k}$ direction (looking directly into the light), we see that a magnetic field

in the $\hat{k}$ direction will cause a clockwise flow of electrons in the circular molecular orbital. The forces on the electrons due to static magnetic fields of conventional strength will be quite small compared to the forces on the electrons due to the electromagnetic fields. However, in Figure 4c we minimize this difference for purposes of illustration. Here we show the net tangential forces acting on an electron in the molecular orbital loop for positive and negative swings of the electric field strength. (In this diagram we do not include forces in the radial direction as they are not important to the argument). For positive swings of $\vec{E}_{L_0}$ the tangential forces are greater on the right side of the loop. This tends to remove the electrons from the right side of the loop with respect to the left side, resulting in a small component of the electric field perpendicular to $\vec{E}_{L_0}$ and pointing from left to right. A parallel argument holds for negative swings and, as can be seen from the diagrams, leads to a net rotation of the light.

Having described simple models for the origin of optical activity, we now return to the problem of deriving the constitutive equations and their associated parameters g and f , from the microscopic molecular properties. The connection between the microscopic and macroscopic quantities originates in the microscopic origins of the electric polarization per unit volume $\vec{P}_{L_0}$ and the magnetic polarization per unit volume $\vec{M}_{L_0}$. The contributions of $\vec{P}_{L_0}$ and $\vec{M}_{L_0}$ to the macroscopic induced fields $\vec{D}_{L_0}$ and $\vec{B}_{L_0}$ are given by the familiar relations:

$$\begin{aligned} \vec{D}_{L_0} &= \vec{E}_{L_0} + 4\pi \vec{P}_{L_0} \\ (2-40) \quad \vec{B}_{L_0} &= \vec{H}_{L_0} + 4\pi \vec{M}_{L_0} \end{aligned}$$

Microscopically $\vec{P}_{L_0}$ can be expressed as the volume average of all the electronic oscillators in the limit of zero volume. $\vec{M}_{L_0}$ can be

expressed in a similar manner as a function of the magnetic oscillators (Footnote 5). These electronic and magnetic oscillators are averages over all molecular orientations of the corresponding molecular oscillators. Finally these molecular electronic and magnetic oscillators are themselves averages. Each individual molecule has an electronic oscillator and a magnetic oscillator for each of its electronic states and the molecular oscillators are averages over all electronic states in the molecule. Of these three sets of averages - volume, orientation, and state - the orientation average plays the most important role in the physics of optical activity. Before averaging, the oscillators can have components in any direction. After averaging, all contributions to the molecular oscillators reduce to components either parallel to or perpendicular to the incident fields. As stated before, it is the small, perpendicular components that are responsible for optical activity.

The averages discussed here are explicitly expressed by the following set of equations, where we will ultimately relate $\vec{P}_{Lo}$ and $\vec{M}_{Lo}$ to the expectation values of $\vec{\mu}$ and $\vec{m}$ in the third-order radiative states Ψ_{Ra}^3 , the states of the magnetic system in the presence of the incident electromagnetic radiation. We have:

$$\vec{P}_{Lo} = N_o \underline{\underline{\vec{\mu}}}$$

(2-39)

$$\vec{M}_{Lo} = N_o \underline{\underline{\vec{m}}}$$

where multiplication of $\underline{\underline{\vec{\mu}}}$ and $\underline{\underline{\vec{m}}}$ by N_o , the number of molecules per unit volume, defines the volume average. The doubly averaged moments $\underline{\underline{\vec{\mu}}}$ and $\underline{\underline{\vec{m}}}$ may be written in the equivalent form:

$$\underline{\underline{\vec{\mu}}} \equiv \overline{\vec{\mu}}$$

$$\underline{\underline{\vec{m}}} \equiv \overline{\vec{m}}$$

where the upper bars indicate the average over all orientations. The underlying bars indicate the state average, and for $\underline{\vec{\mu}}$ and $\underline{\vec{m}}$ we may write:

$$\underline{\vec{\mu}} = \sum_a \rho_a^2 \overline{\vec{\mu}_{Raa}}$$

$$\underline{\vec{m}} = \sum_a \rho_a^2 \overline{\vec{m}_{Raa}}$$

The sum is over all the states Ψ_{Ra}^3 , and ρ_a^2 is the fraction of the molecules in the state Ψ_a^2 , a second-order wave function of the magnetic system. Here $\rho_a^3 = \rho_a^2$ as there is no population change in the states upon irradiation of the magnetic system by the electromagnetic field. The individual electronic and magnetic oscillators, $\vec{\mu}_{Raa}$ and $\vec{m}_{Raa}$ are the expectation values of the electric moment $\vec{\mu}$ and the magnetic moment $\vec{m}$ in the state Ψ_{Ra}^3 . Thus:

$$\vec{\mu}_{Raa} = \langle \Psi_{Ra}^3 | \vec{\mu} | \Psi_{Ra}^3 \rangle$$

$$\vec{m}_{Raa} = \langle \Psi_{Ra}^3 | \vec{m} | \Psi_{Ra}^3 \rangle$$

Introducing these last three sets of relations into equations (2-39), we have:

$$\vec{P}_{Lo} = N_o \sum_a \rho_a^2 \overline{\langle \Psi_{Ra}^3 | \vec{\mu} | \Psi_{Ra}^3 \rangle}$$

$$\vec{M}_{Lo} = N_o \sum_a \rho_a^2 \overline{\langle \Psi_{Ra}^3 | \vec{m} | \Psi_{Ra}^3 \rangle}$$

Substituting these equations for the polarizations into equations (2-40), we have for the induced fields:

$$\vec{D}_{Lo} = \vec{E}_{Lo} + 4\pi N_o \sum_a \rho_a^2 \overline{\langle \Psi_{Ra}^3 | \vec{\mu} | \Psi_{Ra}^3 \rangle} = \vec{E}_{Lo} + 4\pi N_o \underline{\vec{\mu}}$$

$$\vec{B}_{Lo} = \vec{H}_{Lo} + 4\pi N_o \sum_a \rho_a^2 \overline{\langle \Psi_{Ra}^3 | \vec{m} | \Psi_{Ra}^3 \rangle} = \vec{H}_{Lo} + 4\pi N_o \underline{\vec{m}}$$

In order to develop the constitutive equations (2-41), the moments $\underline{\underline{\vec{\mu}}}$ and $\underline{\underline{\vec{m}}}$, which are induced by the local microscopic field, must be determined in terms of the macroscopic fields $\vec{E}_L$, $\vec{H}_L$ and their time derivatives $\dot{\vec{E}}_L$, $\dot{\vec{H}}_L$. Although the local fields, in general, are not equal to the corresponding macroscopic fields (Footnote 6), we shall assume such a relation in this dissertation. Since $\underline{\underline{\vec{\mu}}}$ and $\underline{\underline{\vec{m}}}$ are then directly related to the macroscopic fields, and the fields in turn are dependent on these moments, one can envisage the production of optical activity as light traverses an optically active medium as a type of "snowball" phenomenon. The molecular electronic and magnetic moments are induced by the electromagnetic fields and the fields in turn are slightly changed by the induced moments. The altered fields induce moments in subsequently encountered molecules, these moments then changing the fields some more and so on. This process leads to all the various manifestations of optical activity.

The evaluation of $\underline{\underline{\vec{\mu}}}$ and $\underline{\underline{\vec{m}}}$ is predicated upon the determination of the third-order radiative wave functions ψ_{Ra}^3 and the second-order population coefficient ρ_a^2 . The latter is related to the first-order coefficient ρ_a^1 through equation (2-86):

$$(2-86) \quad \rho_a^2 \cong \frac{\rho_a^1}{d_a} \left[1 + \frac{{}^1\vec{m}_{aa} \cdot \vec{H}'}{kT} \right]$$

where d_a is the degeneracy of the first-order complex system wave functions ψ_a^1 . The complex system, while not including external field perturbations such as the static magnetic and the electromagnetic fields, does include what we shall term the molecular perturbations -- i.e. vibrations, substitutions and chromophore-chromophore interactions (Footnote 7). The moment ${}^1\vec{m}_{aa}$ is the expectation value of $\vec{m}$ in ψ_a^1 and

k is the Boltzman constant. In equation (2-86) we have a splitting of a ground state degeneracy by the magnetic field and the resulting population redistribution in the split state leads to the "C" term in magnetically-induced optical activity. If the ground state is not degenerate ($^1\vec{m}_{aa}$ equal to zero, d_a equal to one) or if the magnetic field is zero, then $\rho_a^2 = \frac{\rho_a^1}{d_a}$, the population of any one member of the degenerate set being equal to the total population of the set divided by the degeneracy, and there is no "C" term. Turning now to the Ψ_{Ra}^3 , they are expanded in terms of the Ψ_a^1 in a two step procedure. First, via time dependent perturbation theory in the light wave (radiative electromagnetic field), the third-order radiative wave functions are expanded in terms of the second-order magnetic wave functions Ψ_a^2 , those wave functions of the complex system plus external static magnetic field. Secondly, via time independent perturbation theory in the static magnetic field, the Ψ_a^2 are expanded in terms of the Ψ_a^1 . For a clearer picture of the various systems described above, examples of such systems, and specification of the Hamiltonians and perturbations to be discussed below, see Table IV of part B of this chapter.

These results for ρ_a^2 and the Ψ_{Ra}^3 are used in conjunction with the previously mentioned averaging procedures to obtain the moments $\underline{\underline{\vec{\mu}}}$ and $\underline{\underline{\vec{m}}}$, and thus, using equations (2-39) and (2-40), the constitutive equations. Before presenting the results (repeating details of the derivation of part B of this chapter would add little to the physical picture presented here), we again digress to discuss the various perturbation Hamiltonians involved in the expansions and to determine what they can tell us about the sources of natural and magnetically-induced optical activity. The total Hamiltonian of the system can be

written (Footnote 8):

$$(2-16) \quad \mathcal{H} = \mathcal{H}' + \mathcal{H}_M^2 + \mathcal{H}_O^3 + \mathcal{H}_O^4$$

$\mathcal{H}'$ - first-order complex system molecular Hamiltonian

$\mathcal{H}_M^2$ - second-order external static magnetic field perturbation Hamiltonian

$\mathcal{H}_O^3$ - third-order electromagnetic field perturbation Hamiltonian

$\mathcal{H}_O^4$ - fourth-order electromagnetic field perturbation Hamiltonian

It is shown in part B that $\mathcal{H}_M^2$ and $\mathcal{H}_O^4$ have a similar form:

$$(2-20) \quad \begin{aligned} \mathcal{H}_M^2 &= -\vec{m} \cdot \vec{H}' \\ \mathcal{H}_O^4 &= -\vec{m} \cdot (\nabla \times \vec{A}_{Li})_0 \end{aligned}$$

where $\vec{A}_{Li}$ is the vector potential of the light wave, $(\nabla \times \vec{A}_{Li})_0$ is a magnetic field component of the light wave at the molecule of interest, $\vec{H}'$ is the static magnetic field, and $\vec{m}$ is the molecular magnetic moment.

The natural optical activity arises from a combination of the two perturbations $\mathcal{H}_O^3 + \mathcal{H}_O^4$, the magnetically-induced optical activity from the two perturbations $\mathcal{H}_O^3 + \mathcal{H}_M^2$. Although $\mathcal{H}_O^3$, which by itself leads to refractivity and absorption, is common to both types of optical activity, it does not mix them. Therefore, natural and magnetically-induced optical activity are separate and independent. Thus when we talk about their sources, we may confine ourselves to separate discussions of $\mathcal{H}_O^4$ and $\mathcal{H}_M^2$.

Referring back to Figure 4, we examine more closely $\mathcal{H}_O^4$ and $\mathcal{H}_M^2$. In discussing magnetically-induced optical activity, we were concerned with the flow of current in a circular loop and its interaction with the static magnetic field. The model we chose was a current loop

fixed in space in such a way that its axis, and therefore its magnetic moment, was parallel to the static magnetic field. If we were to describe such an interaction of magnetic moment and field, we would do it via the projection of the magnetic moment on the field. But this is exactly the form of the external magnetic field Hamiltonian $\mathcal{H}_M^2 = -\vec{m} \cdot \vec{H}'$. Considering natural optical activity, we first note that $\mathcal{H}_0^4$ results from expansion of the vector potential over the dimensions of the molecule (see Part B of this chapter). Thus this type of optical activity depends on the variation of the amplitudes of the incident fields over the dimensions of the molecule and is closely related to its geometrical structuring. This is in contrast to magnetically-induced optical activity. However, like magnetically-induced optical activity, natural optical activity depends on the interaction of a magnetic moment with a magnetic field. Here the magnetic field is that of the electromagnetic wave and the magnetic moment is that moment induced in an asymmetric molecule by the electric field of the electromagnetic wave.

Having discussed the physical implications of the various Hamiltonians, we present below the results derived in part B of this chapter for $\vec{\underline{\underline{\mu}}}$ and $\vec{\underline{\underline{m}}}$.

$$(2-103) \quad \begin{aligned} \vec{\underline{\underline{\mu}}} &= \alpha \vec{E}_{L_0} - \beta \vec{H}_{L_0} - \eta (\vec{E}_{L_0} \times \vec{H}') \\ \vec{\underline{\underline{m}}} &= \chi \vec{H}_{L_0} + \beta \vec{E}_{L_0} - \xi (\vec{H}_{L_0} \times \vec{H}') \end{aligned}$$

where

$$(2-102) \quad \begin{aligned} \alpha &= \frac{2}{3\hbar\omega^2} \sum_a \rho_a \sum_b \omega_{ba} f_2(\omega, \omega_{ba}) D_{ab} \\ \beta &= -\frac{2}{3\hbar\omega^2} \sum_a \rho_a \sum_b f_2(\omega, \omega_{ba}) R_{ab} \\ \eta &= -\frac{2}{3\hbar\omega^2} \sum_a \rho_a \left\{ \sum_b \left[f_1(\omega, \omega_{ba}) A_{ab} + f_2(\omega, \omega_{ba}) B_{ab} \right. \right. \\ &\quad \left. \left. + \frac{1}{kT} f_2(\omega, \omega_{ba}) C_{ab} \right] \right\} \end{aligned}$$

$$f_1(\omega, \omega_{ba}) = \frac{2\omega_{ba}\omega^2[(\omega_{ba}^2 - \omega^2)^2 - \omega^2\Gamma_{ba}^2]}{\hbar[(\omega_{ba}^2 - \omega^2)^2 + \omega^2\Gamma_{ba}^2]^2} \quad (2-101)$$

$$f_2(\omega, \omega_{ba}) = \frac{\omega^2(\omega_{ba}^2 - \omega^2)}{(\omega_{ba}^2 - \omega^2)^2 + \omega^2\Gamma_{ba}^2}$$

$$D_{ab} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Re}\{\vec{\mu}_{ba} \cdot \vec{\mu}_{ab}\} \quad (2-100)$$

$$R_{ab} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Im}\{\vec{\mu}_{ba} \cdot \vec{m}_{ab}\}$$

$$A_{ab} = \frac{1}{2d_a} \sum_{a,b}^{\text{mem}} [\vec{m}_{bb} - \vec{m}_{aa}] \cdot \text{Im}\{\vec{\mu}_{ab} \times \vec{\mu}_{ba}\}$$

$$B_{ab} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Im}\left\{ \sum_{d \neq a} \frac{\vec{m}_{da}}{\hbar\omega_{da}} \cdot \vec{\mu}_{ab} \times \vec{\mu}_{bd} + \sum_{d \neq b} \frac{\vec{m}_{bd}}{\hbar\omega_{db}} \cdot \vec{\mu}_{ab} \times \vec{\mu}_{da} \right\}$$

$$C_{ab} = \frac{1}{2d_a} \sum_{a,b}^{\text{mem}} \vec{m}_{aa} \cdot \text{Im}\{\vec{\mu}_{ab} \times \vec{\mu}_{ba}\}$$

In the above equations, we have suppressed superscripts, ρ_a' being now replaced by ρ_a , $\vec{m}_{aa}$ by $\vec{m}_{aa}$, $\vec{\mu}_{ab}$ by $\vec{\mu}_{ab}$, etc.

Important quantities in these equation are defined as follows:

$\omega_{ba} = \omega_b - \omega_a$, d_a is the degeneracy of the state a , the $\vec{m}_{aa}$, $\vec{\mu}_{ab}$ etc. are expectation values and transition probabilities of the magnetic and electric moments in the first order states, Γ_{ba} is an artificially introduced line width. The frequency functions $f_1(\omega, \omega_{ba})$ and $f_2(\omega, \omega_{ba})$ are line shape functions. D_{ab} is the oscillator strength, R_{ab} the natural rotational strength, A_{ab} , B_{ab} , C_{ab} the magnetic rotational strengths, and the sums are over members of states a and b .

The quantities χ and ξ are never calculated as they result in negligible contribution to the optical activity. However, we retain

them here to maintain a symmetrical appearance in the moments $\underline{\underline{\vec{\mu}}}$ and $\underline{\underline{\vec{m}}}$.

Substituting the above equations for $\underline{\underline{\vec{\mu}}}$ and $\underline{\underline{\vec{m}}}$ into the equations

$$\vec{D}_{L0} = \vec{E}_{L0} + 4\pi N_0 \underline{\underline{\vec{\mu}}}$$

$$\vec{B}_{L0} = \vec{H}_{L0} + 4\pi N_0 \underline{\underline{\vec{m}}}$$

we obtain:

$$(2-41) \quad \begin{aligned} \vec{D}_{L0} &= \epsilon \vec{E}_{L0} - g \dot{\vec{H}}_{L0} - f_1 (\vec{E}_{L0} \times \vec{H}') \\ \vec{B}_{L0} &= \mu \vec{H}_{L0} + g \dot{\vec{E}}_{L0} - f_2 (\dot{\vec{H}}_{L0} \times \vec{H}') \end{aligned}$$

These are the desired constitutive equations. The parameters $\epsilon, \mu, g, f_1, f_2$ can be expressed in terms of the parameters $\alpha, \chi, \beta, \eta, \xi$.

$$(2-42) \quad \begin{aligned} \epsilon &= 1 + 4\pi N_0 \alpha \\ \mu &= 1 + 4\pi N_0 \chi \\ g &= 4\pi N_0 \beta \\ f_1 &= 4\pi N_0 \eta \\ f_2 &= 4\pi N_0 \xi \end{aligned}$$

Under the conditions where χ and ξ are negligibly small we may make the previous approximation $\mu \cong 1$, $\epsilon f_2 \ll \mu f_1$. With these approximations, we have shown that

$$(2-60) \quad n_L - n_R = 2\omega \left[g + \frac{f_1}{2} H' \right]$$

when Maxwell's equations are solved under the restriction imposed by the constitutive equations. Or, substituting in equations (2-42),

$$(2-61) \quad n_L - n_R = 8\pi N_0 \omega \left[\beta + \frac{\eta}{2} H' \right]$$

Substituting $(n_L - n_R)$ into the equation for the optical rotation

(equation (2-36)) we have:

$$(2-62) \quad \varphi(z, \omega) = \frac{4\pi N_0 z}{c} \omega^2 \left[\beta + \frac{\eta}{2} H' \right]$$

Substituting β and η from equation (2-102) into (2-62), we have

$$\varphi(z, \omega) = \phi(z, \omega) + \phi_M(z, \omega)$$

where:

$$(2-104) \quad \begin{aligned} \phi(z, \omega) &= -\frac{8\pi z}{3\hbar c} \sum_a N_a \sum_b f_2(\omega, \omega_{ba}) R_{ab} \\ \phi_M(z, \omega) &= -\frac{4\pi z H'}{3\hbar c} \sum_a N_a \sum_b \left[f_1(\omega, \omega_{ba}) A_{ab} + f_2(\omega, \omega_{ba}) B_{ab} + \frac{1}{kT} f_2(\omega, \omega_{ba}) C_{ab} \right] \end{aligned}$$

$\phi(z, \omega)$ is the natural optical rotation, $\phi_M(z, \omega)$ is the magnetically-induced optical rotation, $N_a = \rho_a N_0$ is the number of molecules in state a . We now determine the partial rotation for one particular transition $a \rightarrow b$ and convert to partial molecular rotation using the following equations (See References (2a), (2b), and (23)).

$$(2-105) \quad \begin{aligned} [\phi_{ab}(\omega)] &= \frac{18N}{\pi N_a z} \phi_{ab}(z, \omega) \\ [\phi_{ab}(\omega)]_M &= \frac{18N}{\pi N_a z} \phi_{Mab}(z, \omega) \end{aligned}$$

We then have

$$(2-106) \quad \begin{aligned} [\phi_{ab}(\omega)] &= -\frac{48N}{\hbar c} f_2(\omega, \omega_{ba}) R_{ab} \\ [\phi_{ab}(\omega)]_M &= -\frac{24NH'}{\hbar c} \left[f_1(\omega, \omega_{ba}) A_{ab} + f_2(\omega, \omega_{ba}) B_{ab} + \frac{1}{kT} f_2(\omega, \omega_{ba}) C_{ab} \right] \end{aligned}$$

These are the equations for the natural and magnetically-induced partial molecular rotation that were presented without proof in Chapter 1. To obtain the corresponding equations for partial molecular ellipticity, one takes the Kronig Kramers transform of the partial molecular rotation. This is done in Appendix VI and the equations for natural and magnetically-induced partial molecular optical ellipticity are:

$$\begin{aligned}
 & [\Theta_{ab}(\omega)] = -\frac{48N}{\hbar c} f_4(\omega, \omega_{ba}) R_{ab} \\
 (2-107) \quad & [\Theta_{ab}(\omega)]_M = -\frac{24NH'}{\hbar c} \left[f_3(\omega, \omega_{ba}) A_{ab} + f_4(\omega, \omega_{ba}) B_{ab} + \frac{1}{K_T} f_4(\omega, \omega_{ba}) C_{ab} \right]
 \end{aligned}$$

where

$$(2-108) \quad f_3(\omega, \omega_{ba}) = \frac{4\omega_{ba} \omega^3 (\omega_{ba}^2 - \omega^2) \Gamma_{ba}}{\hbar [(\omega_{ba}^2 - \omega^2) + \omega^2 \Gamma_{ba}^2]^2}$$

$$f_4(\omega, \omega_{ba}) = \frac{\omega^3 \Gamma_{ba}}{(\omega_{ba}^2 - \omega^2)^2 + \omega^2 \Gamma_{ba}^2}$$

Equations (2-106) and (2-107) give the partial molecular optical rotation and the partial molecular optical ellipticity in terms of frequency functions and rotational strengths. The frequency functions are given by equations (2-101) and (2-108). The rotational strengths are given by equations (2-100). These equations -- (2-106), (2-107), (2-101), (2-108), (2-100) -- express the results of the general theory of natural and magnetically-induced optical activity and are the equations which were stated without proof in Chapter I.

In summary, we have presented a quantum mechanical derivation of natural and magnetically-induced optical activity. We have endeavored to include all details, yet to stress the physics underlying the mathematics. To this end, we have divided this chapter into two parts; part A presenting a more physical derivation of optical activity and part B detailing the mathematics.

We conclude part A of this chapter with a brief outline of the physical origins and asymmetry requirements for optical activity.

Natural optical activity arises from a time dependent perturbation of the molecular states by a perturbation Hamiltonian that originates in the small variations of the incident electromagnetic fields

over the molecular dimensions. This fact, coupled with the observation that natural optical activity occurs only for asymmetric molecules, leads to the conclusion that it is the asymmetric character of the stereochemical structuring that is responsible for such optical activity. In Chapter 4 we discuss in more detail this asymmetry requirement.

Magnetically-induced optical activity differs from natural optical activity in several ways, two of which are quite revealing. First, the external magnetic field, rather than the molecular structuring, provides the necessary asymmetry. Secondly, the variation of the electromagnetic fields over the molecular dimensions is not important to the derivation. These two differences indicate that we will find no direct relation between magnetically-induced optical activity and molecular stereochemistry such as exists for natural optical activity. However, magnetically-induced optical activity does yield information about the electronic properties of the molecule.

There are three types of magnetically-induced optical activity, denoted as the "A", "B", and "C" terms. As the "A" and "C" terms have similar origins, we shall discuss them first.

A molecular state possessing spin and/or orbital angular momentum is $2J+1$ degenerate, where J is the angular momentum quantum number. The $2J+1$ members of such a degenerate state can be split by an external magnetic field, the new energies given by perturbation relations such as equation (2-20). This is termed the Zeeman splitting. The occurrence of an "A" term usually involves transitions from a non-degenerate ground state to the members of a Zeeman split degenerate excited state while a "C" term involves transitions from the members of a Zeeman split degenerate ground state to a non-degenerate excited state. In either case, the members of the degenerate state are characterized by two quantum numbers, J and M_J , where M_J represents the projection

of the angular momentum on the magnetic field. As units of angular momentum are associated with the photons of circularly polarized light, namely -1 for the left component and $+1$ for the right component, we note that transitions involving a $\Delta M_J = -1$ will be stimulated by left- circularly polarized light while those involving a $\Delta M_J = +1$ will be stimulated by right- circularly polarized light.

In Figures 5a and 6a, we have illustrated the important transitions leading to "A" and "C" terms for three-fold degenerate states ($J=1$). The basis of the "A" and "C" terms are best illustrated by reference to magnetic circular dichroism, the measurement of the differential absorption of left- and right- circularly polarized light. For the system pictured in Figure 5a, a degenerate excited state, the Zeeman shifted, signed absorptions of the left and right components are shown in 5b, and in 5c the resulting MCD - an "A" term - is illustrated. For the system pictured in Figure 6a, a degenerate ground state, the important factor is not the Zeeman splitting per se, but the Boltzman population redistribution resulting from that splitting. Due to this redistribution, there are more possible transitions from the lower member of the split ground state than there are from the upper member. This results in a greater absorption for the component of circularly polarized light associated with transitions from the lower member. The intensity differing, signed absorptions for the left and right components are shown in Figure 6b, and in 6c the resulting MCD - a "C" term - is illustrated.

A final word on the "A" and "C" terms. As both depend upon a degeneracy, so both depend upon the existence in the molecular system of a three-fold or higher axis of symmetry. This molecular symmetry requirement for the "A" and "C" terms can be contrasted to the molecular asymmetry requirement for natural optical activity.

a. Allowed transitions.
Degenerate excited state
split by magnetic field.

b. Signed absorptions for
left- and right-circularly
polarized light.

c. Magnetically-induced
optical activity.

FIGURE 5. Physical Origins of "A" Term

a. Allowed transitions.
Degenerate ground state
split by magnetic field.

b. Signed absorptions for
left- and right-circularly
polarized light.

c. Magnetically-induced
optical activity.

FIGURE 6. Physical Origins of "C" Term

Turning now to the "B" term of magnetically-induced optical activity, we see that there is no such symmetry requirement as exists for the "A" and "C" terms. The source of the "B" term is not a Zeeman type splitting, but rather a mixing of states by the external magnetic field in such a way that the resulting hybrid state is a differential absorber of left- and right- circularly polarized light. There has been little work done on the symmetry or asymmetry conditions for the existence of "B" terms (however, see (6a) and (17)). This aspect will be discussed in more detail in Chapter 4.

This concludes part A of this chapter. Readers who are interested in the details of the quantum mechanical derivation may go on to part B. However, this is not necessary to the understanding of the remainder of the dissertation and may be omitted. In either case, the results of this chapter are the foundation upon which we shall build extensions of the theory of optical activity, beginning in Chapter 3.

B. Detailed Derivation

The detailed derivation of the quantum mechanical equations for natural and magnetically-induced optical activity is most naturally divided into three sections. The first section derives the expression for optical activity as proportional to the difference in the complex indices of refraction for left- and right- circularly polarized light. In the second section, these indices are expressed in terms of a set of molecular parameters. These parameters couple the moments induced in individual molecules to the electromagnetic fields of the light traversing the medium and to the static external magnetic field. Finally, in the third section of the derivation, the induced moments and the explicit form of these coupling parameters are calculated quantum mechanically. However, before we begin the derivation, we must specify a coordinate system and a method for locating individual molecules in this coordinate system. Then in the framework of this coordinate system, we specify the static magnetic field, the electromagnetic fields, and the various terms of the Hamiltonian of the magnetic system.

We assume that light of wavelength λ is incident on the optically active system at $z=0$, and propagates through the system in the positive z direction -- i.e. in the direction of the unit vector $\hat{k}$. At z we specify a macrovolume whose width is Δz and whose cross-section spans the cross-section of the sample. The width Δz must satisfy two conditions; it must be smaller than the wavelength λ , and it must be large enough such that the sample can be considered homogeneous throughout the macrovolume. If these conditions are incompatible the electromagnetic fields are not continuous functions of z and the statistical concentration fluctuations

in the sample cannot be ignored. Within each macrovolume are many microvolumes; their location specified by the vectors $\vec{R}$ from the center of the macrovolume to the centers of the microvolumes. The appropriate microvolume for a solution is a region containing one solute particle (monomer or aggregate) surrounded by that particle's share of the solvent. Finally, the vector from the center of the microvolume to the i^{TH} charged particle that can be acted on by the various fields is given by $\vec{r}_i$. The only charged particles considered in this derivation will be electrons. A macrovolume and microvolume are illustrated in Figure 7. The vector from the origin of the coordinate system to the i^{TH} charged particle under consideration is given by:

$$(2-1) \quad \vec{S}_i = z\hat{k} + \vec{R} + \vec{r}_i$$

We must now specify the static external magnetic field and the electromagnetic fields of the propagating light wave at the position determined by the vector $\vec{S}_i$. This is done most readily via the concept of the vector potential. For the electromagnetic fields, the vector potential at the position specified by $\vec{S}_i$ is given by:

$$(2-2) \quad \vec{A}_{Li} = \frac{1}{2} [\vec{\tilde{A}}_{Li} + \vec{\tilde{A}}_{Li}^*]$$

$$\begin{aligned} \text{where } \vec{\tilde{A}}_{Li} &= \vec{\tilde{A}}_0 e^{i\omega t} = \vec{\tilde{A}}_0 e^{-i\frac{\omega n}{c}(\hat{k} \cdot \vec{r}_i)} = \vec{\tilde{A}}_0 e^{i\omega(t - \frac{n}{c}\hat{k} \cdot \vec{r}_i)} \\ &= \vec{\tilde{A}}_0 e^{-i\frac{\omega n}{c}(\hat{k} \cdot \vec{S}_i)} = \vec{\tilde{A}}_0 e^{i\omega(t - \frac{n}{c}\hat{k} \cdot \vec{S}_i)} \end{aligned}$$

FIGURE 7: Definition and location of macrovolume and microvolume used to describe optical activity.

$\vec{\tilde{A}}_{Li}$ - time dependent complex vector potential at $\vec{S}_i$

$\vec{\tilde{A}}_{Li}^0$ - time independent complex vector potential at $\vec{S}_i$

$\vec{\tilde{A}}_{Lo}$ - time dependent complex vector potential at $\vec{L} = z\hat{k} + \vec{R}$,
the center of the microvolume

$\vec{\tilde{A}}_{Lo}^0$ - time independent complex vector potential at $\vec{L} = z\hat{k} + \vec{R}$,
the center of the microvolume

$\vec{\tilde{A}}_o$ - time dependent complex vector potential at any
point on the vertical plane through the origin

$\vec{\tilde{A}}_o^0$ - time independent complex vector potential at any
point on the vertical plane through the origin

The electromagnetic fields $\vec{E}_{Li}$ and $\vec{H}_{Li}$ are related to $\vec{\tilde{A}}_{Li}$ by:

$$(2-3) \quad \vec{E}_{Li} = -\frac{1}{c} \dot{\vec{\tilde{A}}}_{Li}$$

$$\vec{H}_{Li} = \nabla \times \vec{\tilde{A}}_{Li}$$

where $\nabla \times \vec{\tilde{A}}_{Li}$ is the curl of $\vec{\tilde{A}}_{Li}$ and $\dot{\vec{\tilde{A}}}_{Li}$ is the time derivative of $\vec{\tilde{A}}_{Li}$.

For the external magnetic field, the vector potential $\vec{\tilde{A}}_{Mi}$ must be such that

$$\vec{H}' = \nabla \times \vec{\tilde{A}}_{Mi}$$

The only variations of $\vec{H}'$ that we shall be concerned about is over the microvolume. Therefore, the gradient ∇ is with respect to the variations in $\vec{\mathcal{L}}_i$. Therefore, equation (2-4) gives the necessary expression for $\vec{\tilde{A}}_{Mi}$, as can be seen by substitution into the foregoing equation for $\vec{H}'$.

$$(2-4) \quad \vec{\tilde{A}}_{Mi} = -\frac{1}{2} (\vec{\mathcal{L}}_i \times \vec{H}')$$

The total vector potential then is given by:

$$(2-5) \quad \vec{\tilde{A}}_i = \vec{\tilde{A}}_{Li} + \vec{\tilde{A}}_{Mi}$$

We must now determine the Hamiltonian of a microvolume of the magnetic system. We ignore any solvent contribution (Footnote 5).

The Hamiltonian is composed of the kinetic and potential energy operators of the molecule in the presence of external fields plus the three perturbation Hamiltonians $\mathcal{H}_I^1$, $\mathcal{H}_S^1$, $\mathcal{H}_V^1$, which have been previously defined (see Chapter 1). Thus:

$$(2-6) \quad \mathcal{H} = \mathcal{T} + \mathcal{V} + \mathcal{H}_I^1 + \mathcal{H}_S^1 + \mathcal{H}_V^1$$

$$(2-7) \quad \begin{aligned} \mathcal{T} &= \sum_i \frac{1}{2m} |m\dot{\vec{\pi}}_i|^2 \\ \mathcal{V} &= \sum_i eV_i \end{aligned}$$

where the sums are over all electrons in the microvolume, V_i is the potential of the i^{th} electron, m and e are the mass and charge of the electron, and $m\dot{\vec{\pi}}_i$ is the kinetic momentum of the i^{th} electron.

As we adopt a Coulomb gauge ($\nabla \cdot \vec{A}_i = 0$), there is no contribution of the external fields (static magnetic or electromagnetic) to the potential energy. However, in the presence of external fields characterized by a vector potential $\vec{A}_i$ the kinetic momentum is not equal to the canonical momentum $\vec{p}_i$ but is given by:

$$(2-8) \quad m\dot{\vec{\pi}}_i = \vec{p}_i - \frac{e}{c} \vec{A}_i$$

where $\vec{p}_i$ is defined by Hamilton's equation

$$\frac{\partial (\vec{p}_i)_x}{\partial t} = - \frac{\partial \mathcal{H}}{\partial x}$$

Substituting (2-8) into (2-7) and then into (2-6), we have:

$$(2-9) \quad \mathcal{H} = \sum_i \left[\frac{1}{2m} (\vec{p}_i - \frac{e}{c} \vec{A}_i)^2 + e V_i \right] + \mathcal{H}_I^1 + \mathcal{H}_S^1 + \mathcal{H}_V^1$$

Using equation (2-5), expanding (2-9), and dropping terms in $(\vec{A}_{Li} \cdot \vec{A}_{Li})$ and $(\vec{A}_{Mi} \cdot \vec{A}_{Mi})$ we have:

$$(2-10) \quad \begin{aligned} \mathcal{H} = \sum_i \left[\frac{1}{2m} |\vec{p}_i|^2 + e V_i \right] - \sum_i \frac{e}{mc} (\vec{p}_i \cdot \vec{A}_{Mi}) \\ - \sum_i \frac{e}{mc} (\vec{p}_i - \frac{e}{c} \vec{A}_{Mi}) \cdot \vec{A}_{Li} + \mathcal{H}_I^1 + \mathcal{H}_S^1 + \mathcal{H}_V^1 \end{aligned}$$

We must now expand $\vec{A}_{Li}$ about the center of the microvolume, that is about $\vec{r}_i = 0$. When this is done the third term of equation (2-10) separates into two terms; a third-order time varying electromagnetic field perturbation $\mathcal{H}_0^3$ which, upon application, results in refractivity and absorption, and a fourth-order time varying electromagnetic field perturbation $\mathcal{H}_0^4$ which, upon application, results in natural circular birefringence and natural circular dichroism (ORD and CD) (Footnote 8).

Magnetically-induced circular birefringence and circular dichroism (MORD and MCD) result from the combined perturbation of $\mathcal{H}_M^2$ (the static magnetic field perturbation given by the second term in equation (2-10) and $\mathcal{H}_0^3$.

From Appendix III we have:

$$\vec{A}_{Li} \cong \vec{A}_{Lo} + \frac{1}{2} (\nabla \times \vec{A}_{Li})_0 \times \vec{r}_i$$

Therefore (2-10) becomes:

$$(2-11) \quad \begin{aligned} \mathcal{H} = \mathcal{H}^0 + \mathcal{H}_M^2 - \sum_i \frac{e}{mc} (\vec{p}_i - \frac{e}{c} \vec{A}_{Mi}) \cdot \vec{A}_{Lo} \\ - \sum_i \frac{e}{2mc} (\vec{p}_i - \frac{e}{c} \vec{A}_{Mi}) \cdot (\nabla \times \vec{A}_{Li})_0 \times \vec{r}_i \\ + \mathcal{H}_I^1 + \mathcal{H}_S^1 + \mathcal{H}_V^1 \end{aligned}$$

where

$$(2-12) \quad \mathcal{H}^0 = \sum_i \left[\frac{1}{2m} |\vec{p}_i|^2 + e V_i \right]$$

$$(2-13) \quad \mathcal{H}_M^2 = - \sum_i \frac{e}{mc} (\vec{p}_i \cdot \vec{A}_{Mi}) = - \sum_i \frac{e}{2mc} (\vec{r}_i \times \vec{p}_i) \cdot \vec{H}'$$

Substituting (2-5) into (2-8) and rearranging, we have:

$$(2-14) \quad \vec{p}_i - \frac{e}{c} \vec{A}_{Mi} = m \dot{\vec{r}}_i + \frac{e}{c} \vec{A}_{Li}$$

Substituting into the third term of (2-11), we have:

$$(2-15) \quad \begin{aligned} \mathcal{H} = \mathcal{H}^0 + \mathcal{H}_M^2 - \sum_i \frac{e}{mc} (m \dot{\vec{r}}_i + \frac{e}{c} \vec{A}_{Li}) \cdot \vec{A}_{Lo} \\ - \sum_i \frac{e}{2mc} (\vec{p}_i - \frac{e}{c} \vec{A}_{Mi}) \cdot (\nabla \times \vec{A}_{Li})_0 \times \vec{r}_i + \mathcal{H}_I^1 + \mathcal{H}_S^1 + \mathcal{H}_V^1 \end{aligned}$$

One may ask why substitute (2-14) into the third term of (2-11) but not into the fourth term. Actually we could have substituted into the fourth term and there would have been no great difference, as later on the additional terms which result are ignored due to their small size. The rationale for this method is that it makes the derivation somewhat clearer.

Dropping the terms in $(\vec{A}_{Li} \cdot \vec{A}_{Lo})$ and in $\vec{A}_{Mi} \cdot (\nabla \times \vec{A}_{Li})_0 \times \vec{r}_i$ in (2-15) as they involve squares of the fields, we have:

$$(2-16) \quad \begin{aligned} \mathcal{H} &= \mathcal{H}^0 + \mathcal{H}_I^1 + \mathcal{H}_S^1 + \mathcal{H}_V^1 + \mathcal{H}_M^2 + \mathcal{H}_0^3 + \mathcal{H}_0^4 \\ &= \mathcal{H}' + \mathcal{H}_M^2 + \mathcal{H}_0^3 + \mathcal{H}_0^4 \quad \text{where} \quad \mathcal{H}' = \mathcal{H}^0 + \mathcal{H}_I^1 + \mathcal{H}_S^1 + \mathcal{H}_V^1 \end{aligned}$$

$$(2-17) \quad \mathcal{H}_0^3 = - \sum_i \frac{e}{c} (\dot{\vec{r}}_i \cdot \vec{A}_{Lo})$$

$$(2-18) \quad \mathcal{H}_0^4 = - \sum_i \frac{e}{2mc} \vec{p}_i \cdot (\nabla \times \vec{A}_{Li})_0 \times \vec{r}_i = - \sum_i \frac{e}{2mc} (\vec{r}_i \times \vec{p}_i) \cdot (\nabla \times \vec{A}_{Li})_0$$

We know the magnetic moment $\vec{m}$ is given by:

$$(2-19) \quad \vec{m} = \sum_i \frac{e}{2mc} (\vec{r}_i \times \vec{p}_i)$$

The equations for $\mathcal{H}_M^2$, $\mathcal{H}_0^3$, $\mathcal{H}_0^4$ are therefore:

$$\mathcal{H}_M^2 = -\vec{m} \cdot \vec{H}'$$

$$(2-20) \quad \mathcal{H}_0^3 = -\frac{1}{c} (\sum_i e \dot{\vec{r}}_i) \cdot \vec{A}_0$$

$$\mathcal{H}_0^4 = -\vec{m} \cdot (\nabla \times \vec{A}_{Li})_0$$

Now that the external fields, static magnetic and electromagnetic, have been specified (via their vector potentials) and the various terms in the Hamiltonian of the magnetic system delineated, we turn to the first section of the quantum mechanical derivation of optical activity.

1. Expressions for Natural and Magnetically-induced Optical Activity in terms of the complex indices of refraction for left-and right- circularly polarized light

Having obtained expressions for the electromagnetic fields that are traversing the sample, we may now determine the effect on these fields when the sample has different complex indices of refraction for left- and right- circularly polarized light -- i.e. when it is optically active. Consider the electric field intensity to be given by an expression analogous to equation (2-2)

$$(2-21) \quad \vec{E}_{Li} = \frac{1}{2} [\vec{\tilde{E}}_{Li} + \vec{\tilde{E}}_{Li}^*]$$

where from (2-2) and (2-3)

$$\vec{\tilde{E}}_{Li} = -\frac{i\omega}{c} \vec{\tilde{A}}_{Li}$$

$$\vec{\tilde{E}}_0 = -\frac{i\omega}{c} \vec{\tilde{A}}_0$$

Therefore at any point of the medium (located by the vector $\vec{S}_i$),

we have:

$$(2-22) \quad \vec{E}_{Li} = \vec{E}_0 e^{i\omega(t - \frac{\tilde{n}}{c} \hat{k} \cdot \vec{S}_i)}$$

where $\tilde{n} = n - i\kappa$ is the complex index of refraction. In optically active media, its specific form is dependent only on the type of polarization of the propagating fields.

Let us now determine the field at the macrovolume located at z . As $\vec{E}_{Li}$ is determined completely by $\vec{E}_{Li}$, we may do all our mathematics with the latter in this first part of the derivation.

Substituting equation (2-1) into (2-22) we have:

$$\vec{E}_{Li} = \vec{E}_0 e^{i\omega(t - \frac{\tilde{n}}{c} z)} e^{-i\omega \frac{\tilde{n}}{c} (\hat{k} \cdot \vec{R} + \hat{k} \cdot \vec{r}_i)}$$

As $|\frac{\omega \tilde{n}}{c}| \approx \frac{2\pi}{\lambda}$ we may represent the last exponential as approximately

$$e^{-i2\pi \left(\frac{\hat{k} \cdot \vec{R} + \hat{k} \cdot \vec{r}_i}{\lambda} \right)}$$

As the projections of $\vec{R}$ and $\vec{r}_i$ on the z axis ($\hat{k} \cdot \vec{R}$ and $\hat{k} \cdot \vec{r}_i$) are smaller than Δz (see Figure 7) and therefore much smaller than the wavelength, this exponential has an argument which can be considered zero. Therefore, this exponential can be set equal to unity over the macrovolume. Thus we have:

$$(2-23) \quad \vec{E}_{Li} \cong \vec{E}_0 e^{i\omega(t - \frac{\tilde{n}}{c} z)}$$

For left- circularly polarized light $\vec{E}_0 = (\hat{i} - i\hat{j})E_0$

For right- circularly polarized light $\vec{E}_0 = (\hat{i} + i\hat{j})E_0$

If the electromagnetic wave incident upon the sample is linearly polarized in the x direction, it consists of equal amounts of left- and right- circularly polarized light. In this case, the electric field intensity at z is given by:

$$(2-24) \quad \vec{E}_{Li} = E_0 (\hat{i} - i\hat{j}) e^{i\omega(t - \frac{\tilde{n}_L}{c}z)} + E_0 (\hat{i} + i\hat{j}) e^{i\omega(t - \frac{\tilde{n}_R}{c}z)}$$

here

$$(2-25) \quad \begin{aligned} \tilde{n}_L &= n_L - i\kappa_L \\ \tilde{n}_R &= n_R - i\kappa_R \end{aligned}$$

where n_L and n_R are indices of refraction, κ_L and κ_R are extinction coefficients for left- and right- circularly polarized light. Expanding (2-24) and taking the real part, we have:

$$(2-26) \quad \begin{aligned} \vec{E}_{Li}(z, \omega) &= \text{Re}\{\vec{E}_{Li}\} \\ &= E_0 e^{-\kappa_L \frac{\omega z}{c}} \left[\hat{i} \cos \omega \left(t - \frac{n_L z}{c}\right) + \hat{j} \sin \omega \left(t - \frac{n_L z}{c}\right) \right] \\ &\quad + E_0 e^{-\kappa_R \frac{\omega z}{c}} \left[\hat{i} \cos \omega \left(t - \frac{n_R z}{c}\right) - \hat{j} \sin \omega \left(t - \frac{n_R z}{c}\right) \right] \end{aligned}$$

The expression for complex optical activity is written as (2):

$$(2-27) \quad \vec{\Phi}(z, \omega) = \varphi(z, \omega) - i\Theta(z, \omega)$$

where $\varphi(z, \omega)$ is the optical rotation (circular birefringence)

$\Theta(z, \omega)$ is the optical ellipticity (circular dichroism)

The rotation of the plane of polarization is expressed in terms of the x and y components of $\vec{E}_{Li}(z, \omega)$ (2):

$$(2-28) \quad \varphi(z, \omega) = \left\{ \tan^{-1} \left[\frac{-E_{Ly}(z, \omega)}{E_{Lx}(z, \omega)} \right] \right\} \Big|_{|\vec{E}_{Li}(z, \omega)| = |\vec{E}_{Li}(z, \omega)|_{\max}}$$

The ellipticity of the polarized light is expressed in terms of the minimum and maximum of $\vec{E}_{Li}$ -- i.e. the minor and major axes (2):

$$(2-29) \quad \Theta(z, \omega) = \tan^{-1} \left[\frac{|\vec{E}_{Li}(z, \omega)|_{\min}}{|\vec{E}_{Li}(z, \omega)|_{\max}} \right]$$

now $\vec{E}_{Li}(z, \omega) = \hat{i} E_{Lx}(z, \omega) + \hat{j} E_{Ly}(z, \omega)$

therefore

$$(2-30) \quad E_{Lx}(z, \omega) = E_0 \left\{ e^{-\gamma_L \frac{\omega z}{c}} \cos \omega(t - n_L \frac{z}{c}) + e^{-\gamma_R \frac{\omega z}{c}} \cos \omega(t - n_R \frac{z}{c}) \right\}$$

$$(2-31) \quad E_{Ly}(z, \omega) = E_0 \left\{ e^{-\gamma_L \frac{\omega z}{c}} \sin \omega(t - n_L \frac{z}{c}) - e^{-\gamma_R \frac{\omega z}{c}} \sin \omega(t - n_R \frac{z}{c}) \right\}$$

now $|\vec{E}_{Li}(z, \omega)| = [E_{Lx}^2(z, \omega) + E_{Ly}^2(z, \omega)]^{1/2}$

therefore

$$(2-32) \quad |\vec{E}_{Li}(z, \omega)| = E_0 \left\{ e^{-2\gamma_R \frac{\omega z}{c}} + e^{-2\gamma_L \frac{\omega z}{c}} + 2e^{-\frac{\omega z}{c}(\gamma_L + \gamma_R)} \cos 2\omega[t - (n_L + n_R) \frac{z}{2c}] \right\}^{1/2}$$

The maximum value of $|\vec{E}_{Li}(z, \omega)|$ occurs when $\omega t = (n_L + n_R) \frac{\omega z}{2c} + \pi(k + 1/2)$ where k is an integer. In this case we have:

$$(2-33) \quad |\vec{E}_{Li}(z, \omega)|_{\max} = E_0 \left\{ e^{-\frac{\omega z}{c} \gamma_R} + e^{-\frac{\omega z}{c} \gamma_L} \right\}$$

The minimum value of $|\vec{E}_{Li}(z, \omega)|$ occurs when $\omega t = (n_L + n_R) \frac{\omega z}{2c} + \pi k$ where k is an integer. In this case we have:

$$(2-34) \quad |\vec{E}_{Li}(z, \omega)|_{\min} = E_0 \left\{ e^{-\frac{\omega z}{c} \gamma_R} - e^{-\frac{\omega z}{c} \gamma_L} \right\}$$

We now are prepared to calculate $\varphi(z, \omega)$ and $\vartheta(z, \omega)$.

$$(2-35) \quad \begin{aligned} \varphi(z, \omega) &= \left\{ \tan^{-1} \left[\frac{-E_{Ly}(z, \omega)}{E_{Lx}(z, \omega)} \right] \right\} |\vec{E}_{Li}(z, \omega)| = |\vec{E}_{Li}(z, \omega)|_{\max} \\ &= \left\{ \tan^{-1} \left[\frac{-E_{Ly}(z, \omega)}{E_{Lx}(z, \omega)} \right] \right\} \omega t = (n_L + n_R) \frac{\omega z}{2c} + \pi(k + 1/2) \end{aligned}$$

Substituting this value of $\omega t = (n_L + n_R) \frac{\omega z}{2c} + \pi(k + 1/2)$ into the equations for $E_{Lx}(z, \omega)$ (equation (2-30)) and for $E_{Ly}(z, \omega)$ (equation (2-31)) and then substituting these equations into

(2-35), we have:

$$\varphi(z, \omega) = \tan^{-1} \left\{ \frac{e^{-\frac{\omega z}{c} \chi_R} \sin \frac{\omega z}{2c} (n_L - n_R) - e^{-\frac{\omega z}{c} \chi_L} \sin \frac{\omega z}{2c} (n_R - n_L)}{e^{-\frac{\omega z}{c} \chi_R} \cos \frac{\omega z}{2c} (n_L - n_R) + e^{-\frac{\omega z}{c} \chi_L} \cos \frac{\omega z}{2c} (n_L - n_R)} \right\}$$

This reduces to:

$$(2-36) \quad \varphi(z, \omega) = \frac{\omega z}{2c} (n_L - n_R)$$

Substituting $|\vec{E}_{Li}(z, \omega)|_{\max}$ (equation (2-33)) and $|\vec{E}_{Li}(z, \omega)|_{\min}$ (equation (2-34)) into (2-29), we obtain:

$$Q(z, \omega) = \tan^{-1} \left\{ \frac{e^{-\frac{\omega z}{c} \chi_R} - e^{-\frac{\omega z}{c} \chi_L}}{e^{-\frac{\omega z}{c} \chi_R} + e^{-\frac{\omega z}{c} \chi_L}} \right\} = \tan^{-1} \left\{ \frac{1 - e^{-\frac{\omega z}{c} (\chi_L - \chi_R)}}{1 + e^{-\frac{\omega z}{c} (\chi_L - \chi_R)}} \right\}$$

since $\frac{\omega z}{c} (\chi_L - \chi_R) \ll 1$ we replace the numerator by $\frac{\omega z}{c} (\chi_L - \chi_R)$ and the denominator by 2. Remembering also that for x small, $\tan^{-1} \{x\} \cong x$ we have:

$$(2-37) \quad Q(z, \omega) = \frac{\omega z}{2c} (\chi_L - \chi_R)$$

2. Expression of indices of refraction in terms of parameters relating induced moments to external fields

As mentioned in part A of this chapter, we only deal with the indices of refraction n_L and n_R , knowing that we can calculate the extinction coefficients χ_L and χ_R (and the accompanying circular dichroism) from n_L and n_R via the Kronig-Kramers transform.

The constitutive equations for the medium can be obtained from the induced molecular moments (calculated quantum mechanically in the third section of this derivation). When Maxwell's equations are

solved under the conditions specified by the constitutive equations, one obtains one or more solutions for the field intensities $\vec{E}$ and $\vec{H}$ and for the associated indices of refraction. For an optically active medium, there are two solutions for forward propagating waves, corresponding to left- and to right- circularly polarized light.

In the microvolume located by the vector $\vec{L}$ the average induced electric and magnetic dipole moments for an optically active medium are given by (as shown in section 3):

$$\begin{aligned} \underline{\underline{\vec{\mu}}} &= \alpha \vec{E}_{L_0} - \beta \vec{H}_{L_0} - \eta (\vec{E}_{L_0} \times \vec{H}') \\ \underline{\underline{\vec{m}}} &= \chi \vec{H}_{L_0} + \beta \vec{E}_{L_0} - \xi (\vec{H}_{L_0} \times \vec{H}') \end{aligned} \quad (2-103)$$

Here we recall (by analogy to (2-2)) that

$$\begin{aligned} \vec{E}_{L_0} &= \frac{1}{2} [\vec{\tilde{E}}_{L_0} + \vec{\tilde{E}}_{L_0}^*] \quad ; \quad \vec{\tilde{E}}_{L_0} = \vec{\tilde{E}}_0 e^{i\omega t} e^{-i\omega \frac{n}{c}(z + \hat{k} \cdot \vec{R})} \\ \vec{H}_{L_0} &= \frac{1}{2} [\vec{\tilde{H}}_{L_0} + \vec{\tilde{H}}_{L_0}^*] \quad ; \quad \vec{\tilde{H}}_{L_0} = \vec{\tilde{H}}_0 e^{i\omega t} e^{-i\omega \frac{n}{c}(z + \hat{k} \cdot \vec{R})} \end{aligned} \quad (2-38)$$

$\vec{H}'$ is the external magnetic field and $\alpha, \beta, \eta, \chi, \xi$ are molecular parameters whose explicit form is not important in this section of the derivation. In fact, we never do calculate the exact equations for χ and ξ as their contribution will be shown to be negligible. However, in the interest of obtaining symmetrical equations for $\underline{\underline{\vec{\mu}}}$ and $\underline{\underline{\vec{m}}}$ they are included here. The double bars under the moments indicate two averages; the first over all available molecular states and the second over all molecular orientations.

We must obtain the constitutive equations for the optically active medium. The connections between the macroscopic fields and the microscopic induced moments are given by the relations:

$$(2-39) \quad \begin{aligned} \vec{P}_{L_0} &= N_0 \underline{\underline{\vec{\mu}}} \\ \vec{M}_{L_0} &= N_0 \underline{\underline{\vec{m}}} \end{aligned}$$

where $\vec{P}_{L_0}$ is the electric polarization per unit volume, $\vec{M}_{L_0}$ is the magnetic polarization per unit volume, and N_0 is the number of molecules per unit volume. Both of these field vectors, $\vec{P}_{L_0}$ and $\vec{M}_{L_0}$ and all other field vectors referred to in this part of the derivation are measured at the center of the microvolume located by the vector $\vec{L}$. The induced electric and magnetic fields are given by:

$$(2-40) \quad \begin{aligned} \vec{D}_{L_0} &= \vec{E}_{L_0} + 4\pi \vec{P}_{L_0} = \vec{E}_{L_0} + 4\pi N_0 \underline{\underline{\vec{\mu}}} \\ \vec{B}_{L_0} &= \vec{H}_{L_0} + 4\pi \vec{M}_{L_0} = \vec{H}_{L_0} + 4\pi N_0 \underline{\underline{\vec{m}}} \end{aligned}$$

Substituting the equations for $\underline{\underline{\vec{\mu}}}$ and $\underline{\underline{\vec{m}}}$ (equations (2-103)) into (2-40), we obtain the constitutive equations for an optically active medium

$$(2-41) \quad \begin{aligned} \vec{D}_{L_0} &= \epsilon \vec{E}_{L_0} - g \dot{\vec{H}}_{L_0} - f_1 (\dot{\vec{E}}_{L_0} \times \vec{H}') \\ \vec{B}_{L_0} &= \mu \vec{H}_{L_0} + g \dot{\vec{E}}_{L_0} - f_2 (\dot{\vec{H}}_{L_0} \times \vec{H}') \end{aligned}$$

where

$$(2-42) \quad \begin{aligned} \epsilon &= 1 + 4\pi N_0 \alpha \\ \mu &= 1 + 4\pi N_0 \chi \\ g &= 4\pi N_0 \beta \\ f_1 &= 4\pi N_0 \eta \\ f_2 &= 4\pi N_0 \xi \end{aligned}$$

We now must solve Maxwell's equations for the optically active medium specified by equations (2-41). For a medium with no free charges or conductivity, Maxwell's equations are:

$$(2-43) \quad \begin{aligned} (a) \quad \nabla \times \vec{E}_{L_0} &= -\frac{1}{c} \dot{\vec{B}}_{L_0} & (c) \quad \nabla \cdot \vec{D}_{L_0} &= 0 \\ (b) \quad \nabla \times \vec{H}_{L_0} &= \frac{1}{c} \dot{\vec{D}}_{L_0} & (d) \quad \nabla \cdot \vec{B}_{L_0} &= 0 \end{aligned}$$

Substituting equations (2-38) into (2-43), we get two sets of independent equations. The first set is:

$$(2-44) \quad \begin{aligned} \nabla \times \vec{\tilde{E}}_{L_0} &= -\frac{1}{c} \dot{\vec{\tilde{B}}}_{L_0} & \nabla \cdot \vec{\tilde{D}}_{L_0} &= 0 \\ \nabla \times \vec{\tilde{H}}_{L_0} &= \frac{1}{c} \dot{\vec{\tilde{D}}}_{L_0} & \nabla \cdot \vec{\tilde{B}}_{L_0} &= 0 \end{aligned}$$

The second set is the complex conjugate of the first set. As solution of either set yields the same result, we need to concentrate on only one of these sets. We also revise our constitutive equations

$$(2-45) \quad \begin{aligned} \vec{\tilde{D}}_{L_0} &= \epsilon \vec{\tilde{E}}_{L_0} - g \vec{\tilde{H}}_{L_0} - f_1 (\dot{\vec{\tilde{E}}}_{L_0} \times \vec{H}') \\ \vec{\tilde{B}}_{L_0} &= \mu \vec{\tilde{H}}_{L_0} + g \vec{\tilde{E}}_{L_0} - f_2 (\dot{\vec{\tilde{H}}}_{L_0} \times \vec{H}') \end{aligned}$$

where we have taken advantage of the fact that $\epsilon, \mu, g, f_1, f_2$ are real. This is a result of $\alpha, \chi, \beta, \eta, \xi$ being real (to be shown in section 3 of the derivation).

We now rewrite equations (2-44) in a more solvable form. For any vector $\vec{\tilde{V}}_{L_0} = \vec{\tilde{E}}_{L_0}, \vec{\tilde{H}}_{L_0}, \vec{\tilde{D}}_{L_0}, \vec{\tilde{B}}_{L_0}$ we have:

$$\vec{\tilde{V}}_{L_0} = \vec{\tilde{V}}_0 e^{i\omega t} e^{-i\omega \frac{\eta}{c}(z + \hat{k} \cdot \vec{R})}$$

The time derivative $\dot{\vec{\tilde{V}}}_{L_0}$ is given by:

$$(2-46) \quad \dot{\vec{\tilde{V}}}_{L_0} = i\omega \vec{\tilde{V}}_{L_0}$$

In evaluating the space derivatives, the curl $\nabla \times \vec{\tilde{V}}_{L_0}$ and the divergence $\nabla \cdot \vec{\tilde{V}}_{L_0}$, we recognize that we are evaluating Maxwell's equations in a specific macrovolume -- i.e. at a specified z . Thus our spatial derivatives are, with respect to the components of $\vec{R}$,

$$(2-47) \quad \begin{aligned} \nabla \cdot \vec{\tilde{V}}_{L_0} &= -i\omega \frac{\eta}{c} (\hat{k} \cdot \vec{\tilde{V}}_{L_0}) \\ \nabla \times \vec{\tilde{V}}_{L_0} &= -i\omega \frac{\eta}{c} (\hat{k} \times \vec{\tilde{V}}_{L_0}) \end{aligned}$$

Using the relations (2-46) and (2-47), we can simplify Maxwell's equations (2-44) and the constitutive equations (2-45):

$$(2-48) \quad \begin{aligned} (a) \quad n(\hat{k} \times \vec{E}_{L0}) &= \vec{B}_{L0} & (c) \quad \hat{k} \cdot \vec{D}_{L0} &= 0 \\ (b) \quad n(\hat{k} \times \vec{H}_{L0}) &= -\vec{D}_{L0} & (d) \quad \hat{k} \cdot \vec{B}_{L0} &= 0 \end{aligned}$$

$$(2-49) \quad \begin{aligned} \vec{D}_{L0} &= \epsilon \vec{E}_{L0} - i\omega g \vec{H}_{L0} - i\omega f_1 (\vec{E}_{L0} \times \vec{H}') \\ \vec{B}_{L0} &= \mu \vec{H}_{L0} + i\omega g \vec{E}_{L0} - i\omega f_2 (\vec{H}_{L0} \times \vec{H}') \end{aligned}$$

Substitution of (2-49) into (2-48c) and (2-48d) yields:

$$\begin{aligned} \epsilon(\hat{k} \cdot \vec{E}_{L0}) - i\omega g(\hat{k} \cdot \vec{H}_{L0}) - i\omega f_1(\hat{k} \cdot \vec{E}_{L0} \times \vec{H}') &= 0 \\ \mu(\hat{k} \cdot \vec{H}_{L0}) + i\omega g(\hat{k} \cdot \vec{E}_{L0}) - i\omega f_2(\hat{k} \cdot \vec{H}_{L0} \times \vec{H}') &= 0 \end{aligned}$$

For any general direction of the external magnetic field $\vec{H}'$, these equations have the approximate solution:

$$(2-50) \quad \begin{aligned} \hat{k} \cdot \vec{E}_{L0} &= 0 \\ \hat{k} \cdot \vec{H}_{L0} &= 0 \end{aligned}$$

This solution is valid as $\omega f_2 \ll \omega f_1 \ll 1$ and $\epsilon, \mu \approx 1$. For the special case $\vec{H}' = \hat{k} H'$, i.e. the magnetic field $\vec{H}'$ along the direction of propagation of the light, equations (2-50) offer an exact solution. These equations predict the transverse nature of the electromagnetic fields.

We now combine equations (2-48a) and (2-48b), (2-49), and (2-50) to obtain an equation in $\vec{E}_{L0}$. This equation then can be solved for the eigen-polarizations and eigen-indices of refraction associated with optical activity.

Substituting (2-49) into (2-48)

$$(2-51) \quad \begin{aligned} (a) \quad n(\hat{k} \times \vec{E}_L) &= \mu \vec{H}_L + i\omega g \vec{E}_L - i\omega f_2 (\vec{H}_L \times \vec{H}') \\ (b) \quad -n(\hat{k} \times \vec{H}_L) &= \epsilon \vec{E}_L - i\omega g \vec{H}_L - i\omega f_1 (\vec{E}_L \times \vec{H}') \end{aligned}$$

We must eliminate $\vec{H}_L$ from these two equations. Taking the cross product of (2-51b) with $\hat{k}$ we have (using (2-50)):

$$-n(\hat{k} \times \hat{k} \times \vec{H}_L) = -n[\hat{k}(\hat{k} \cdot \vec{H}_L) - \vec{H}_L(\hat{k} \cdot \hat{k})] = n\vec{H}_L$$

therefore,

$$-n(\hat{k} \times \hat{k} \times \vec{H}_L) = n\vec{H}_L = \epsilon(\hat{k} \times \vec{E}_L) - i\omega g(\hat{k} \times \vec{H}_L) - i\omega f_1(\hat{k} \times \vec{E}_L \times \vec{H}')$$

or
$$i\omega g(\hat{k} \times \vec{H}_L) = \epsilon(\hat{k} \times \vec{E}_L) - n\vec{H}_L - i\omega f_1(\hat{k} \times \vec{E}_L \times \vec{H}')$$

substituting this last equation into (2-51b) we can eliminate $\hat{k} \times \vec{H}_L$

$$\begin{aligned} -n\epsilon(\hat{k} \times \vec{E}_L) + n^2\vec{H}_L + i\omega f_1 n(\hat{k} \times \vec{E}_L \times \vec{H}') \\ = i\omega g\epsilon \vec{E}_L + \omega^2 g^2 \vec{H}_L + \omega^2 f_1 g(\vec{E}_L \times \vec{H}') \end{aligned}$$

dropping terms in g^2 and $f_1 g$ as these are products of two small quantities:

$$(2-52) \quad n^2\vec{H}_L = i\omega g\epsilon \vec{E}_L + n\epsilon(\hat{k} \times \vec{E}_L) - i\omega f_1 n(\hat{k} \times \vec{E}_L \times \vec{H}')$$

Substituting $\vec{H}_L$ (from equation (2-52)) into (2-51a) we obtain:

$$\begin{aligned} n(\hat{k} \times \vec{E}_L) &= i\omega g \frac{\mu\epsilon}{n^2} \vec{E}_L + \frac{\mu\epsilon}{n}(\hat{k} \times \vec{E}_L) - \frac{i\omega f_1 \mu}{n}(\hat{k} \times \vec{E}_L \times \vec{H}') \\ &\quad + i\omega g \vec{E}_L + \frac{\omega^2 f_2 g \epsilon}{n^2}(\vec{E}_L \times \vec{H}') - \frac{i\omega f_2 \epsilon}{n}(\hat{k} \times \vec{E}_L \times \vec{H}') \\ &\quad - \frac{\omega^2 f_1 f_2}{n}(\hat{k} \times \vec{E}_L \times \vec{H}' \times \vec{H}') \end{aligned}$$

The last term is zero and we can drop the term in $(\vec{\tilde{E}}_{Lo} \times \vec{H}') as $f_2 g$ can be ignored (for the same reasons as g^2 and $f_1 g$).$

Taking the cross product with $\hat{k}$ and combining terms (using (2-50)), we have:

$$-\frac{1}{n}(n^2 - \mu\epsilon)\vec{\tilde{E}}_{Lo} = \frac{i\omega g}{n^2}(n^2 + \mu\epsilon)(\hat{k} \times \vec{\tilde{E}}_{Lo}) + \frac{i\omega}{n}(f_1\mu + f_2\epsilon)(\vec{\tilde{E}}_{Lo} \times \vec{H}')$$

rearranging

$$(2-53) \quad (n^2 - \mu\epsilon)\vec{\tilde{E}}_{Lo} + \frac{i\omega g}{n}(n^2 + \mu\epsilon)(\hat{k} \times \vec{\tilde{E}}_{Lo}) + i\omega(f_1\mu + f_2\epsilon)(\vec{\tilde{E}}_{Lo} \times \vec{H}') = 0$$

We may separate this vector equation into components

$$\begin{aligned} & \hat{i} \left[(n^2 - \mu\epsilon)\tilde{E}_{Lox} - \frac{i\omega g}{n}(n^2 + \mu\epsilon)\tilde{E}_{Loy} + i\omega(f_1\mu + f_2\epsilon)(\tilde{E}_{Loz}H'_y - \tilde{E}_{Loy}H'_z) \right] \\ & + \hat{j} \left[(n^2 - \mu\epsilon)\tilde{E}_{Loy} + \frac{i\omega g}{n}(n^2 + \mu\epsilon)\tilde{E}_{Lox} + i\omega(f_1\mu + f_2\epsilon)(\tilde{E}_{Lox}H'_z - \tilde{E}_{Loz}H'_x) \right] \\ & + \hat{k} \left[(n^2 - \mu\epsilon)\tilde{E}_{Loz} + i\omega(f_1\mu + f_2\epsilon)(\tilde{E}_{Loy}H'_x - \tilde{E}_{Lox}H'_y) \right] = 0 \end{aligned}$$

This yields three linearly independent equations in the variables

$\tilde{E}_{Lox}, \tilde{E}_{Loy}, \tilde{E}_{Loz}$. In matrix form

$$(2-54) \quad \begin{bmatrix} n^2 - \mu\epsilon & -i\omega \left[\frac{g}{n}(n^2 + \mu\epsilon) + (f_1\mu + f_2\epsilon)H'_z \right] & i\omega(f_1\mu + f_2\epsilon)H'_y \\ i\omega \left[\frac{g}{n}(n^2 + \mu\epsilon) + (f_1\mu + f_2\epsilon)H'_z \right] & n^2 - \mu\epsilon & -i\omega(f_1\mu + f_2\epsilon)H'_x \\ -i\omega(f_1\mu + f_2\epsilon)H'_y & i\omega(f_1\mu + f_2\epsilon)H'_x & n^2 - \mu\epsilon \end{bmatrix} \begin{bmatrix} \tilde{E}_{Lox} \\ \tilde{E}_{Loy} \\ \tilde{E}_{Loz} \end{bmatrix} = 0$$

For the case we are interested in here, that of magnetically-induced optical activity, the magnetic field is along the direction of propagation of the electromagnetic field and we have:

$$H'_x = H'_y = 0$$

$$H'_z = H'$$

Substituting these into the matrix equation (2-54);

$$(2-55) \quad \begin{bmatrix} n^2 - \mu\epsilon & -i\omega \left[\frac{g}{n} (n^2 + \mu\epsilon) + (\mu f_1 + \epsilon f_2) H' \right] & 0 \\ i\omega \left[\frac{g}{n} (n^2 + \mu\epsilon) + (\mu f_1 + \epsilon f_2) H' \right] & n^2 - \mu\epsilon & 0 \\ 0 & 0 & n^2 - \mu\epsilon \end{bmatrix} \begin{bmatrix} \tilde{E}_{Lox} \\ \tilde{E}_{Loy} \\ \tilde{E}_{Loz} \end{bmatrix} = 0$$

First of all, this yields $(n^2 - \mu\epsilon) \tilde{E}_{Loz} = 0$ or $\tilde{E}_{Loz} = 0$. This again demonstrates the electromagnetic fields are transverse. Secondly, we have the matrix equation for $\tilde{E}_{Lox}$ and $\tilde{E}_{Loy}$

$$(2-56) \quad \begin{bmatrix} n^2 - \mu\epsilon & -i\omega \left[\frac{g}{n} (n^2 + \mu\epsilon) + (\mu f_1 + \epsilon f_2) H' \right] \\ i\omega \left[\frac{g}{n} (n^2 + \mu\epsilon) + (\mu f_1 + \epsilon f_2) H' \right] & n^2 - \mu\epsilon \end{bmatrix} \begin{bmatrix} \tilde{E}_{Lox} \\ \tilde{E}_{Loy} \end{bmatrix} = 0$$

It will be seen that $n^2 \cong \mu\epsilon$. We therefore have

$$\begin{bmatrix} n^2 - \mu\epsilon & -i\omega [2ng + (\mu f_1 + \epsilon f_2) H'] \\ i\omega [2ng + (\mu f_1 + \epsilon f_2) H'] & n^2 - \mu\epsilon \end{bmatrix} \begin{bmatrix} \tilde{E}_{Lox} \\ \tilde{E}_{Loy} \end{bmatrix} = 0$$

For this matrix equation to be satisfied, the determinant of the matrix must be zero.

$$(2-57) \quad (n^2 - \mu\epsilon)^2 - \omega^2(2ng + (\mu f_1 + \epsilon f_2)H')^2 = 0$$

This can be factored

$$[(n^2 - \mu\epsilon) - \omega(2ng + (\mu f_1 + \epsilon f_2)H')][(n^2 - \mu\epsilon) + \omega(2ng + (\mu f_1 + \epsilon f_2)H')] = 0$$

This can be factored further

$$\begin{aligned} & [n - \omega g + \sqrt{\mu\epsilon + \omega H'(\mu f_1 + \epsilon f_2) + \omega^2 g^2}][n - \omega g - \sqrt{\mu\epsilon + \omega H'(\mu f_1 + \epsilon f_2) + \omega^2 g^2}] \\ & \times [n + \omega g + \sqrt{\mu\epsilon - \omega H'(\mu f_1 + \epsilon f_2) + \omega^2 g^2}][n + \omega g - \sqrt{\mu\epsilon - \omega H'(\mu f_1 + \epsilon f_2) + \omega^2 g^2}] = 0 \end{aligned}$$

The first and third roots correspond to waves traveling in the negative $\hat{k}$ direction and we shall not concern ourselves with these.

The second and fourth roots correspond to left- and right-circularly polarized waves traveling in the $+\hat{k}$ direction. They yield the values of n_L and n_R :

$$n_L \cong \omega g + \sqrt{\mu\epsilon} \left[1 + \frac{\omega H'}{\mu\epsilon} (\mu f_1 + \epsilon f_2) \right]^{\frac{1}{2}}$$

$$n_R \cong -\omega g + \sqrt{\mu\epsilon} \left[1 - \frac{\omega H'}{\mu\epsilon} (\mu f_1 + \epsilon f_2) \right]^{\frac{1}{2}}$$

where we have dropped the small term $\omega^2 g^2$. By expanding the square roots in both n_L and n_R we have:

$$(2-58) \quad n_L \cong \sqrt{\mu\epsilon} + \omega g + \frac{\omega H'}{2\sqrt{\mu\epsilon}} (\mu f_1 + \epsilon f_2)$$

$$n_R \cong \sqrt{\mu\epsilon} - \omega g - \frac{\omega H'}{2\sqrt{\mu\epsilon}} (\mu f_1 + \epsilon f_2)$$

The electric field intensity corresponding to the first root

is $\tilde{E}_{Loz}(\hat{i} - i\hat{j})$, or left-circularly polarized light; corresponding to the second root is $\tilde{E}_{Loz}(\hat{i} + i\hat{j})$, or right-circularly polarized light.

In section 3 of this derivation, we show that $\mu \cong 1$, $f_2 \ll f_1$, $\frac{1}{\sqrt{\epsilon}} \cong 1$. Thus we have:

$$\begin{aligned} n_L &\cong \sqrt{\mu\epsilon} + \omega \left[g + \frac{f_1 H'}{2} \right] \\ (2-59) \quad n_R &\cong \sqrt{\mu\epsilon} - \omega \left[g + \frac{f_1 H'}{2} \right] \end{aligned}$$

The difference $n_L - n_R$ is thus given by:

$$(2-60) \quad n_L - n_R \cong 2\omega \left[g + \frac{f_1 H'}{2} \right]$$

Substituting in for g and f_1 from equations (2-42)

$$(2-61) \quad n_L - n_R \cong 8\pi N_0 \omega \left[\beta + \frac{\eta H'}{2} \right]$$

The first term represents the natural optical rotation (ORD), and the second term the magnetically-induced optical rotation (MORD). Substituting (2-61) into (2-36), we have for the optical rotation:

$$(2-62) \quad \varphi(z, \omega) = \frac{4\pi N_0 z}{c} \omega^2 \left[\beta + \frac{\eta H'}{2} \right]$$

We now turn to section 3 of the derivation where we determine β and η in terms of molecular quantities.

3. Quantum Mechanical Determination of Parameters β and η via Calculation of Induced Moments $\underline{\underline{\mu}}$ and $\underline{\underline{m}}$

In order to determine β and η we must determine the quantum mechanical expressions for the average induced moments $\underline{\underline{\mu}}$ and $\underline{\underline{m}}$. Anticipating the results of this section of the derivation, we write below the equations (2-103) for $\underline{\underline{\mu}}$ and $\underline{\underline{m}}$ which illustrate the role of β and η .

$$(2-103) \quad \underline{\underline{\mu}} = \alpha \vec{E}_{L_0} - \beta \vec{H}_{L_0} - \eta (\vec{E}_{L_0} \times \vec{H}') \\ \underline{\underline{m}} = \chi \vec{H}_{L_0} + \beta \vec{E}_{L_0} - \xi (\vec{H}_{L_0} \times \vec{H}')$$

These moments, $\underline{\underline{\mu}}$ and $\underline{\underline{m}}$, are obtained by doubly averaging ${}^3\vec{\mu}_{Raa}$ and ${}^3\vec{m}_{Raa}$, first over all occupied molecular states and then over all possible molecular orientations. The moments ${}^3\vec{\mu}_{Raa}$ and ${}^3\vec{m}_{Raa}$ are the expectation values of $\underline{\underline{\mu}}$ and $\underline{\underline{m}}$ in the third-order radiative molecular states. These are the time dependent states of the molecule in the presence of molecular perturbations (vibration, substitution, and chromophore-chromophore interaction) and in the presence of external field perturbations (static magnetic and radiative electromagnetic). These third-order wave functions are related, via two perturbation expansions, to the wave functions of the first-order states, the molecular states existing in the presence of molecular perturbations but in the absence of external field perturbations. The first expansion is based on time dependent perturbation theory in the radiative electromagnetic fields and yields the third-order radiative wave functions in terms of a set of second-order magnetic wave functions. In the second expansion, these second-order wave functions are expanded in the first-order complex wave functions via time independent

perturbation theory in the static magnetic field. Using the first expansion, the expectation values of $\vec{\mu}$ and $\vec{m}$ in the third-order states are expressed in terms of the expectation values and transition probabilities of $\vec{\mu}$ and $\vec{m}$ in the second-order states. The second expansion is then used to eliminate the second-order wave functions and thus to relate directly the expectation values of $\vec{\mu}$ and $\vec{m}$ in the third-order states to the expectation values and transition probabilities of $\vec{\mu}$ and $\vec{m}$ in the first-order states. Reference to Table IV, where we have defined the above three systems - radiative, magnetic, and complex - with their wave functions, expectation values, and transition probabilities, will clarify the preceding discussion. In this chapter we do not attempt to evaluate the effect of the molecular perturbations. Thus the wave functions of the zero-order unperturbed system are not discussed or evaluated here. However, in the following chapters some of the influence on optical activity of vibration, substitution, and chromophore-chromophore interaction are analyzed. There we effectively expand the third-order radiative wave functions in terms of the zero-order wave functions. In anticipation of this procedure, we also define in Table IV the zero-order wave functions, expectation values and transition probabilities.

We first determine the form of the two wave function expansions used in the general theory. Referring to Table IV, we see that the time dependent perturbation by the radiative electromagnetic field ($\mathcal{H}_0^3 + \mathcal{H}_0^4$) expands the third-order wave functions $\psi_{Ra}^3(t)$ in the second-order wave function basis set $\psi_a^2(t)$. Following the standard techniques of time dependent perturbation theory, we have:

$$(2-63) \quad \psi_{Ra}^3(t) = \psi_a^2(t) + \sum_b C_{ab}(t) \psi_b^2(t)$$

Type of System	Example of System *	Order of States	Wave Function Notation and Hamiltonian	Perturbations Present	Expressions for Expectation Values	Expressions for Transition Probabilities
Radiative System		Radiative Third-order	$\Psi_{Ra}^3(t)$ $\mathcal{H} = \mathcal{H}'' + \mathcal{H}_0^3 + \mathcal{H}_0^4$	$\mathcal{H}_0^3 + \mathcal{H}_0^4$ $\mathcal{H}_M^2$ $\mathcal{H}_I^1 + \mathcal{H}_V^1 + \mathcal{H}_S^1$	${}^3\vec{\mu}_{Raa} = \langle \Psi_{Ra}^3 \vec{\mu} \Psi_{Ra}^3 \rangle$ ${}^3\vec{m}_{Raa} = \langle \Psi_{Ra}^3 \vec{m} \Psi_{Ra}^3 \rangle$	${}^3\vec{\mu}_{Rab} = \langle \Psi_{Ra}^3 \vec{\mu} \Psi_{Rb}^3 \rangle$ ${}^3\vec{m}_{Rab} = \langle \Psi_{Ra}^3 \vec{m} \Psi_{Rb}^3 \rangle$
Magnetic System		Magnetic Second-order	$\Psi_a^2(t)$ $= e^{-i\omega_a t} \psi_a^2$ $\mathcal{H}'' = \mathcal{H}' + \mathcal{H}_M^2$	$\mathcal{H}_M^2$ $\mathcal{H}_I^1 + \mathcal{H}_V^1 + \mathcal{H}_S^1$	${}^2\vec{\mu}_{aa} = \langle \Psi_a^2 \vec{\mu} \Psi_a^2 \rangle$ $= (\psi_a^2 \vec{\mu} \psi_a^2)$ ${}^2\vec{m}_{aa} = \langle \Psi_a^2 \vec{m} \Psi_a^2 \rangle$ $= (\psi_a^2 \vec{m} \psi_a^2)$	${}^2\vec{\mu}_{ab} e^{i\omega_{bat}} = \langle \psi_a^2 \vec{\mu} \psi_b^2 \rangle$ $\therefore {}^2\vec{\mu}_{ab} = (\psi_a^2 \vec{\mu} \psi_b^2)$ ${}^2\vec{m}_{ab} e^{i\omega_{bat}} = \langle \psi_a^2 \vec{m} \psi_b^2 \rangle$ $\therefore {}^2\vec{m}_{ab} = (\psi_a^2 \vec{m} \psi_b^2)$
Complex System		Complex First-order	ψ_a^1 $\mathcal{H}' = \mathcal{H}^0$ $+ \mathcal{H}_I^1 + \mathcal{H}_V^1 + \mathcal{H}_S^1$	$\mathcal{H}_I^1 + \mathcal{H}_V^1 + \mathcal{H}_S^1$	${}^1\vec{\mu}_{aa} = (\psi_a^1 \vec{\mu} \psi_a^1)$ ${}^1\vec{m}_{aa} = (\psi_a^1 \vec{m} \psi_a^1)$	${}^1\vec{\mu}_{ab} = (\psi_a^1 \vec{\mu} \psi_b^1)$ ${}^1\vec{m}_{ab} = (\psi_a^1 \vec{m} \psi_b^1)$
Simple System		Simple Zero-order	ψ_a^0 $\mathcal{H}^0$	None	$\vec{\mu}_{aa} = (\psi_a^0 \vec{\mu} \psi_a^0)$ $\vec{m}_{aa} = (\psi_a^0 \vec{m} \psi_a^0)$	$\vec{\mu}_{ab} = (\psi_a^0 \vec{\mu} \psi_b^0)$ $\vec{m}_{ab} = (\psi_a^0 \vec{m} \psi_b^0)$

TABLE IV

Table of wave functions, expectation values, and transition probabilities for the various systems and perturbations encountered in the derivation.

* The system examples are based on a simple system of benzene. Complexities shown here are substitution and chromophore-chromophore interaction. Vibration is also possible but is not shown here.

From equation (2-16), we have:

$$(2-64) \quad \mathcal{H} = \mathcal{H}'' + \mathcal{H}_0^3 + \mathcal{H}_0^4$$

$$(2-65) \quad \text{where} \quad \mathcal{H}'' = \mathcal{H}^0 + \mathcal{H}_I^1 + \mathcal{H}_S^1 + \mathcal{H}_V^1 + \mathcal{H}_M^2$$

$$(2-66) \quad \text{thus} \quad \mathcal{H} \Psi_{R_a}^3(t) = i\hbar \frac{\partial \Psi_{R_a}^3(t)}{\partial t}$$

$$(2-67) \quad \mathcal{H}'' \Psi_a^2(t) = i\hbar \frac{\partial \Psi_a^2(t)}{\partial t}$$

substituting equations (2-63) and (2-64) into equation (2-66)

$$\begin{aligned} [\mathcal{H}'' + \mathcal{H}_0^3 + \mathcal{H}_0^4] [\Psi_a^2(t) + \sum_b C_{ab}(t) \Psi_b^2(t)] \\ = i\hbar \frac{\partial}{\partial t} [\Psi_a^2(t) + \sum_b C_{ab}(t) \Psi_b^2(t)] \end{aligned}$$

expanding both left and right hand sides

$$\begin{aligned} (2-68) \quad & \mathcal{H}'' \Psi_a^2(t) + (\mathcal{H}_0^3 + \mathcal{H}_0^4) \Psi_a^2(t) \\ & + \mathcal{H}'' \sum_b C_{ab}(t) \Psi_b^2(t) + (\mathcal{H}_0^3 + \mathcal{H}_0^4) \sum_b C_{ab}(t) \Psi_b^2(t) \\ & = i\hbar \frac{\partial \Psi_a^2(t)}{\partial t} + i\hbar \sum_b C_{ab}(t) \frac{\partial \Psi_b^2(t)}{\partial t} + i\hbar \sum_b \frac{\partial C_{ab}(t)}{\partial t} \Psi_b^2(t) \end{aligned}$$

Using equation (2-67) and dropping the fourth term on the left hand side of (2-68) (as it is the product of two small quantities), we have:

$$\begin{aligned} & (\mathcal{H}_0^3 + \mathcal{H}_0^4) \Psi_a^2(t) + \sum_b C_{ab}(t) \mathcal{H}'' \Psi_b^2(t) \\ & = i\hbar \sum_b C_{ab}(t) \frac{\partial \Psi_b^2(t)}{\partial t} + i\hbar \sum_b \frac{\partial C_{ab}(t)}{\partial t} \Psi_b^2(t) \end{aligned}$$

from equation (2-67),, we see that the second term on the left hand side equals the first term on the right hand side. Thus we

have:

$$(2-69) \quad (\mathcal{H}_0^3 + \mathcal{H}_0^4) \Psi_a^2(t) = i\hbar \sum_b \frac{\partial C_{ab}(t)}{\partial t} \Psi_b^2(t)$$

multiplying both sides of equation (2-69) by $\Psi_c^{2*}(t)$ and integrating over all space yields:

$$\langle \Psi_c^2(t) | \mathcal{H}_0^3 + \mathcal{H}_0^4 | \Psi_a^2(t) \rangle = i\hbar \sum_b \frac{\partial C_{ab}(t)}{\partial t} \langle \Psi_c^2(t) | \Psi_b^2(t) \rangle$$

$$\text{as } \langle \Psi_c^2(t) | \Psi_b^2(t) \rangle = \delta_{bc}$$

$$\text{where } \delta_{bc} \text{ is the Dirac delta function } \delta_{bc} = \begin{cases} 0 & b \neq c \\ 1 & b = c \end{cases}$$

We therefore find:

$$i\hbar \frac{\partial C_{ab}(t)}{\partial t} = \langle \Psi_b^2(t) | \mathcal{H}_0^3 + \mathcal{H}_0^4 | \Psi_a^2(t) \rangle$$

$$(2-70) \quad C_{ab}(t) = \frac{1}{i\hbar} \int_0^\infty \langle \Psi_b^2(t) | \mathcal{H}_0^3 + \mathcal{H}_0^4 | \Psi_a^2(t) \rangle dt$$

Thus if we evaluate this integral giving the coefficients $C_{ab}(t)$ we have determined the expansion of the third-order radiative wave functions in terms of the second-order magnetic wave functions. This is done in Appendix IV. However, before we use the results of this appendix, we examine the second of the expansions, that of the second-order wave functions in the basis set of the first-order wave functions. This is a time independent perturbation expansion in the static magnetic field. Referring to equation (2-64), we specify the following Schroedinger equations for second-order and first-order systems.

$$(2-71) \quad \mathcal{H}'' = \mathcal{H}' + \mathcal{H}_M^2$$

(from equations (2-64))

$$(2-72) \quad \mathcal{H}' = \mathcal{H}^0 + \mathcal{H}_I^1 + \mathcal{H}_V^1 + \mathcal{H}_S^1$$

$$(2-67) \quad \mathcal{H}'' \Psi_a^2(t) = i\hbar \frac{\partial \Psi_a^2(t)}{\partial t}$$

substituting in $\Psi_a^2(t) = e^{-i\omega_a t} \psi_a^2$

$$e^{-i\omega_a t} \mathcal{H}'' \psi_a^2 = i\hbar \frac{\partial}{\partial t} [e^{-i\omega_a t} \psi_a^2] = \hbar\omega_a \psi_a^2 e^{-i\omega_a t}$$

Thus:

$$(2-73) \quad \mathcal{H}'' \psi_a^2 = \hbar\omega_a^2 \psi_a^2$$

$$(2-74) \quad \text{also} \quad \mathcal{H}' \psi_a^1 = \hbar\omega_a^1 \psi_a^1$$

where at this point we have differentiated the second-order energies $\hbar\omega_a^2$ from the first-order energies $\hbar\omega_a^1$. Throughout the derivations, we attempt to avoid having to make this differentiation as it could lead to confusion with the radian frequencies raised to powers. In the final results of this chapter only ω_a^1 appears, and it will be denoted by ω_a . All other confusing notation will be used only in places where the omission of same would lead to even more confusion. Using the standard techniques of time independent perturbation theory (27), we have:

$$(2-75) \quad \psi_a^2 = \psi_a^1 + \sum_d' \frac{(\psi_d^1 | \mathcal{H}_M^2 | \psi_a^1)}{\hbar\omega_{ad}} \psi_d^1 \quad \omega_{ad} = \omega_{ad}^1 = \omega_a^1 - \omega_d^1$$

$$(2-76) \quad \hbar\omega_a^2 = \hbar\omega_a^1 + (\psi_a^1 / \mathcal{H}_M^2 / \psi_a^1) = \hbar\omega_a + (\psi_a^1 / \mathcal{H}_M^2 / \psi_a^1)$$

We now must utilize the two wave function expansions to determine the average moments $\vec{\mu}$ and $\vec{m}$. Using the first expansion we determine the moments $\vec{\mu}_{Raa}$ and $\vec{m}_{Raa}$ in terms of the second-order functions. From Table IV, for an operator $\vec{O}$ ($\vec{\mu}$ or $\vec{m}$) we have:

$$(2-77) \quad \vec{O}_{Raa} = \langle \psi_{Ra}^3(t) | \vec{O} | \psi_{Ra}^3(t) \rangle$$

Substituting in equation (2-63)

$$\begin{aligned} \vec{O}_{Raa} = & \langle \psi_a^2(t) | \vec{O} | \psi_a^2(t) \rangle \\ & + \sum_b \left[c_{ab}^*(t) \langle \psi_b^2(t) | \vec{O} | \psi_a^2(t) \rangle + c_{ab}(t) \langle \psi_a^2(t) | \vec{O} | \psi_b^2(t) \rangle \right] \end{aligned}$$

Using the relations given in Table IV

$$(2-78) \quad \vec{O}_{Raa} = \vec{O}_{aa} + \sum_b \left[c_{ab}^*(t) e^{i\omega_{ba}t} \vec{O}_{ba} + c_{ab}(t) e^{-i\omega_{ba}t} \vec{O}_{ab} \right]$$

A complete evaluation of (2-78) for both $\vec{\mu}$ and $\vec{m}$ would lead to both circular dichroism and optical rotation. As previously discussed, we derive only the latter. The evaluation of the terms under the summation sign and the necessary approximations which lead to neglect of circular dichroism are set forth in Appendix IV. From this Appendix, we have (the radian frequencies are the second-order frequencies with the superscript 2 suppressed):

$$\begin{aligned}
(2-79) \quad C_{ab}^*(t) e^{i\omega_{ba}t} \vec{O}_{ba} + C_{ab}(t) e^{-i\omega_{ba}t} \vec{O}_{ab} \\
= \frac{2\omega_{ba}}{\hbar(\omega_{ba}^2 - \omega^2)} \operatorname{Re} \left\{ (\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) \vec{O}_{ab} \right\} \\
- \frac{2\omega_{ba}^2/\omega^2}{\hbar(\omega_{ba}^2 - \omega^2)} \operatorname{Im} \left\{ (\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) \vec{O}_{ab} \right\} \\
- \frac{2}{\hbar(\omega_{ba}^2 - \omega^2)} \operatorname{Im} \left\{ (\vec{m}_{ba} \cdot \dot{\vec{H}}_{Lo}) \vec{O}_{ab} \right\} \\
- \frac{2\omega_{ba}}{\hbar(\omega_{ba}^2 - \omega^2)} \operatorname{Re} \left\{ (\vec{m}_{ba} \cdot \vec{H}_{Lo}) \vec{O}_{ab} \right\}
\end{aligned}$$

Substituting into equation (2-78)

$$\begin{aligned}
\vec{O}_{Raa} = \vec{O}_{aa} + \frac{2}{\hbar} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \operatorname{Re} \left\{ (\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) \vec{O}_{ab} \right\} \right. \\
- \frac{\omega_{ba}^2/\omega^2}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \left\{ (\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) \vec{O}_{ab} \right\} \\
- \frac{1}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \left\{ (\vec{m}_{ba} \cdot \dot{\vec{H}}_{Lo}) \vec{O}_{ab} \right\} \\
\left. + \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \operatorname{Re} \left\{ (\vec{m}_{ba} \cdot \vec{H}_{Lo}) \vec{O}_{ab} \right\} \right]
\end{aligned}$$

We can simplify the second term under the summation if we

note that:

$$\begin{aligned}
\sum_b \frac{\omega_{ba}^2/\omega^2}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \left\{ (\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) \vec{O}_{ab} \right\} \\
= \frac{1}{\omega^2} \sum_b \operatorname{Im} \left\{ (\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) \vec{O}_{ab} \right\} + \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \left\{ (\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) \vec{O}_{ab} \right\}
\end{aligned}$$

The first term is easily seen to be zero.

$$\begin{aligned}
\frac{1}{\omega^2} \sum_b \operatorname{Im} \left\{ \vec{O}_{ab} (\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) \right\} &= \frac{1}{\omega^2} \operatorname{Im} \left\{ \left[\sum_b \vec{O}_{ab} \vec{\mu}_{ba} \right] \cdot \dot{\vec{E}}_{Lo} \right\} \\
&= \frac{1}{\omega^2} \operatorname{Im} \left\{ {}^2(\dot{\vec{\mu}})_{aa} \cdot \dot{\vec{E}}_{Lo} \right\}
\end{aligned}$$

but ${}^2(\vec{O}\vec{\mu})_{aa}$ is the diagonal element of a real observable and is thus real. Since $\vec{E}_{Lo}$ is real, this term is zero. Thus:

$$\sum_b \frac{\omega_{ba}^2/\omega^2}{\omega_{ba}^2 - \omega^2} \text{Im} \{ ({}^2\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) {}^2\vec{O}_{ab} \} = \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \text{Im} \{ ({}^2\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) {}^2\vec{O}_{ab} \}$$

Substituting into equation (2-79),

$$(2-80) \quad \begin{aligned} {}^3\vec{O}_{Raa} = {}^2\vec{O}_{aa} + \frac{2}{\hbar} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \text{Re} \{ ({}^2\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) {}^2\vec{O}_{ab} \} \right. \\ \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \text{Im} \{ ({}^2\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) {}^2\vec{O}_{ab} \} \right. \\ \left. + \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \text{Re} \{ ({}^2\vec{m}_{ba} \cdot \vec{H}_{Lo}) {}^2\vec{O}_{ab} \} \right. \\ \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \text{Im} \{ ({}^2\vec{m}_{ba} \cdot \vec{H}_{Lo}) {}^2\vec{O}_{ab} \} \right] \end{aligned}$$

We now average ${}^3\vec{O}_{Raa}$ over all states a which are occupied.

This yields:

$$\underline{\vec{O}} = \frac{1}{N_o} \sum_a N_a^2 {}^3\vec{O}_{Raa} = \sum_a \rho_a^2 {}^3\vec{O}_{Raa}$$

where N_a^2 is the number of molecules in state a (ψ_{Ra}^3 or ψ_a^2 as we assume that the incident radiation has no influence on the population), N_o is the total number of molecules, and ρ_a^2 is the fraction of molecules in state a .

$$(2-81) \quad \begin{aligned} \underline{\vec{O}} = \sum_a \rho_a^2 {}^2\vec{O}_{aa} + \frac{2}{\hbar} \sum_a \rho_a^2 \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \text{Re} \{ ({}^2\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) {}^2\vec{O}_{ab} \} \right. \\ \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \text{Im} \{ ({}^2\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) {}^2\vec{O}_{ab} \} \right. \\ \left. + \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \text{Re} \{ ({}^2\vec{m}_{ba} \cdot \vec{H}_{Lo}) {}^2\vec{O}_{ab} \} \right. \\ \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \text{Im} \{ ({}^2\vec{m}_{ba} \cdot \vec{H}_{Lo}) {}^2\vec{O}_{ab} \} \right] \end{aligned}$$

The second wave function expansion now is utilized to expand the second-order energies and operators in terms of the first-order energies and operators. Upon substitution of these expanded second-order quantities in equation (2-81), we can obtain the moments $\vec{O}$ in terms of first-order energies and moments. Combining equations (2-20) and (2-75), we have:

$$\psi_a^2 = \psi_a^1 - \sum_d' \frac{\vec{1}m_{da} \cdot \vec{H}'}{\hbar(\omega_a - \omega_d)} \psi_d^1 \quad \vec{H}' - \text{external magnetic field}$$

For the moment $\vec{O}_{ab}$ we have (noting that $\omega_{da} = -\omega_{ad}$):

$$\begin{aligned} \vec{O}_{ab}^2 &= (\psi_a^2 | \vec{O} | \psi_b^2) \\ (2-82) \quad &= (\psi_a^1 | \vec{O} | \psi_b^1) + \sum_d' \left[\frac{\vec{1}m_{ad} \cdot \vec{H}'}{\hbar \omega_{da}} (\psi_d^1 | \vec{O} | \psi_b^1) + (\psi_a^1 | \vec{O} | \psi_d^1) \frac{\vec{1}m_{db} \cdot \vec{H}'}{\hbar \omega_{db}} \right] \\ &= \vec{O}_{ab}^1 + \sum_d' \left[\frac{\vec{1}m_{ad} \cdot \vec{H}'}{\hbar \omega_{da}} \vec{O}_{db}^1 + \vec{O}_{ad}^1 \frac{\vec{1}m_{db} \cdot \vec{H}'}{\hbar \omega_{db}} \right] \end{aligned}$$

Similar expressions can be determined for $\vec{\mu}_{ab}^2$, $\vec{m}_{ab}^2$, $\vec{O}_{aa}^2$.

Now all the second-order energy functions in equation (2-81) can be expanded using equations (2-20) and (2-76).

$$(1)_a^2 = \omega_a - \frac{1}{\hbar} \vec{1}m_{aa} \cdot \vec{H}' \quad (2-83)$$

$$\omega_{ba}^2 = \omega_{ba} - \frac{1}{\hbar} (\vec{1}m_{bb} - \vec{1}m_{aa}) \cdot \vec{H}'$$

The functions ω_a^2 and ω_{ba}^2 are second-order radian frequencies.

The correction to ω_{ba} is the Zeeman shift. Assuming that the Zeeman shift is small compared with $\frac{\omega_{ba}^2 - \omega^2}{2\omega_{ba}}$ (always true for small fields and outside the region of absorption), we can expand $\frac{1}{\omega_{ba}^2 - \omega^2}$ and $\frac{\omega_{ba}^2}{\omega_{ba}^2 - \omega^2}$ as follows:

$$(2-84) \quad \frac{1}{\omega_{ba}^2 - \omega^2} \cong \frac{1}{\omega_{ba}^2 - \omega^2} + \frac{2}{\hbar} \frac{\omega_{ba}}{(\omega_{ba}^2 - \omega^2)^2} (\vec{m}_{bb} - \vec{m}_{aa}) \cdot \vec{H}'$$

$$(2-85) \quad \frac{\omega_{ba}^2}{\omega_{ba}^2 - \omega^2} \cong \frac{\omega_{ba}^2}{\omega_{ba}^2 - \omega^2} + \frac{1}{\hbar} \frac{\omega_{ba}^2 + \omega^2}{(\omega_{ba}^2 - \omega^2)^2} (\vec{m}_{bb} - \vec{m}_{aa}) \cdot \vec{H}'$$

Finally the number of molecules in the perturbed state ψ_a^2 varies with the temperature

$$N_a^2 = N_0 \rho_a^2 = \frac{N_0}{Z} e^{-\hbar \omega_a^2 / kT}$$

$$\therefore \rho_a^2 = \frac{1}{Z} e^{-\hbar \omega_a^2 / kT}$$

where Z is the partition function, k is Boltzman's constant.

$$\rho_a^2 = \frac{d_a}{Z d_a} e^{-\hbar \omega_a / kT} e^{-\hbar (\omega_a^2 - \omega_a) / kT} = \frac{\rho_a^1}{d_a} e^{-\hbar (\omega_a^2 - \omega_a) / kT}$$

where ρ_a^1 is the fraction of molecules in the first-order state ψ_a^1 and d_a is the degeneracy in the first order state ψ_a^1 (lifted by magnetic field).

Using equation (2-83), we have:

$$(2-86) \quad \rho_a^2 = \frac{\rho_a^1}{d_a} e^{\frac{1}{kT} (\vec{m}_{aa} \cdot \vec{H}')} \cong \frac{\rho_a^1}{d_a} \left[1 + \frac{\vec{m}_{aa} \cdot \vec{H}'}{kT} \right]$$

We must now substitute (2-82), (2-84), (2-85), and (2-86) into equation (2-81), keeping only terms linear in small corrections. The result is:

$$\begin{aligned}
\vec{O} = & \sum_a \frac{\rho_a^1}{\sigma_a} \left\{ \vec{O}_{aa} + \frac{1}{kT} (\vec{m}_{aa} \cdot \vec{H}') \vec{O}_{aa} \right. \\
& + \frac{2}{\hbar} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \operatorname{Re} \{ (\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) \vec{O}_{ab} \} \right. \\
& \quad - \frac{1}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \{ (\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) \vec{O}_{ab} \} \\
& \quad + \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \operatorname{Re} \{ (\vec{m}_{ba} \cdot \vec{H}_{Lo}) \vec{O}_{ab} \} \\
& \quad \left. \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \{ (\vec{m}_{ba} \cdot \dot{\vec{H}}_{Lo}) \vec{O}_{ab} \} \right] \right. \\
& + \frac{2}{\hbar kT} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \operatorname{Re} \{ (\vec{m}_{aa} \cdot \vec{H}') (\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) \vec{O}_{ab} \} \right. \\
& \quad - \frac{1}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \{ (\vec{m}_{aa} \cdot \vec{H}') (\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) \vec{O}_{ab} \} \\
& \quad + \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \operatorname{Re} \{ (\vec{m}_{aa} \cdot \vec{H}') (\vec{m}_{ba} \cdot \vec{H}_{Lo}) \vec{O}_{ab} \} \\
& \quad \left. \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \{ (\vec{m}_{aa} \cdot \vec{H}') (\vec{m}_{ba} \cdot \dot{\vec{H}}_{Lo}) \vec{O}_{ab} \} \right] \right. \\
& + \frac{2}{\hbar^2} \sum_b \left[\frac{\omega_{ba}^2 + \omega^2}{(\omega_{ba}^2 - \omega^2)^2} \operatorname{Re} \{ ([\vec{m}_{bb} - \vec{m}_{aa}] \cdot \vec{H}') (\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) \vec{O}_{ab} \} \right. \\
& \quad - \frac{2\omega_{ba}}{(\omega_{ba}^2 - \omega^2)^2} \operatorname{Im} \{ ([\vec{m}_{bb} - \vec{m}_{aa}] \cdot \vec{H}') (\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) \vec{O}_{ab} \} \\
& \quad + \frac{\omega_{ba}^2 + \omega^2}{(\omega_{ba}^2 - \omega^2)^2} \operatorname{Re} \{ ([\vec{m}_{bb} - \vec{m}_{aa}] \cdot \vec{H}') (\vec{m}_{ba} \cdot \vec{H}_{Lo}) \vec{O}_{ab} \} \\
& \quad \left. \left. - \frac{2\omega_{ba}}{(\omega_{ba}^2 - \omega^2)^2} \operatorname{Im} \{ ([\vec{m}_{bb} - \vec{m}_{aa}] \cdot \vec{H}') (\vec{m}_{ba} \cdot \dot{\vec{H}}_{Lo}) \vec{O}_{ab} \} \right] \right. \\
& + \frac{2}{\hbar^2} \sum_b \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{db}} \operatorname{Re} \{ (\vec{m}_{bd} \cdot \vec{H}') (\vec{\mu}_{da} \cdot \vec{E}_{Lo}) \vec{O}_{ab} \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{da}} \operatorname{Re} \{ (\vec{m}_{da} \cdot \vec{H}') (\vec{\mu}_{bd} \cdot \vec{E}_{Lo}) \vec{O}_{ab} \} \right]
\end{aligned}$$

$$\begin{aligned}
& + \frac{2}{\hbar^2} \sum_b \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{da}} \operatorname{Re} \{ (\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) (\vec{m}_{ad} \cdot \vec{H}') \vec{O}_{db} \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{db}} \operatorname{Re} \{ (\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) (\vec{m}_{db} \cdot \vec{H}') \vec{O}_{ad} \} \right] \\
& - \frac{2}{\hbar^2} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{db}} \operatorname{Im} \{ (\vec{m}_{bd} \cdot \vec{H}') (\vec{\mu}_{da} \cdot \vec{E}_{Lo}) \vec{O}_{ab} \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{da}} \operatorname{Im} \{ (\vec{m}_{da} \cdot \vec{H}') (\vec{\mu}_{bd} \cdot \vec{E}_{Lo}) \vec{O}_{ab} \} \right] \\
& - \frac{2}{\hbar^2} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{da}} \operatorname{Im} \{ (\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) (\vec{m}_{ad} \cdot \vec{H}') \vec{O}_{db} \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{db}} \operatorname{Im} \{ (\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) (\vec{m}_{db} \cdot \vec{H}') \vec{O}_{ad} \} \right] \\
& + \frac{2}{\hbar^2} \sum_b \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{db}} \operatorname{Re} \{ (\vec{m}_{bd} \cdot \vec{H}') (\vec{m}_{da} \cdot \vec{H}_{Lo}) \vec{O}_{ab} \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{da}} \operatorname{Re} \{ (\vec{m}_{da} \cdot \vec{H}') (\vec{m}_{bd} \cdot \vec{H}_{Lo}) \vec{O}_{ab} \} \right] \\
& + \frac{2}{\hbar^2} \sum_b \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{da}} \operatorname{Re} \{ (\vec{m}_{ba} \cdot \vec{H}_{Lo}) (\vec{m}_{ad} \cdot \vec{H}') \vec{O}_{db} \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{db}} \operatorname{Re} \{ (\vec{m}_{ba} \cdot \vec{H}_{Lo}) (\vec{m}_{db} \cdot \vec{H}') \vec{O}_{ad} \} \right] \\
& - \frac{2}{\hbar^2} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{db}} \operatorname{Im} \{ (\vec{m}_{bd} \cdot \vec{H}') (\vec{m}_{da} \cdot \vec{H}_{Lo}) \vec{O}_{ab} \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{da}} \operatorname{Im} \{ (\vec{m}_{da} \cdot \vec{H}') (\vec{m}_{bd} \cdot \vec{H}_{Lo}) \vec{O}_{ab} \} \right] \\
& - \frac{2}{\hbar^2} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{da}} \operatorname{Im} \{ (\vec{m}_{ba} \cdot \vec{H}_{Lo}) (\vec{m}_{ad} \cdot \vec{H}') \vec{O}_{db} \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{db}} \operatorname{Im} \{ (\vec{m}_{ba} \cdot \vec{H}_{Lo}) (\vec{m}_{db} \cdot \vec{H}') \vec{O}_{ad} \} \right] \Bigg\}
\end{aligned}$$

Here we have freely transferred the terms ${}^1\vec{m}_{aa} \cdot \vec{H}'$ and ${}^1\vec{m}_{bb} \cdot \vec{H}'$ from outside the $\text{Re}\{ \}$ and $\text{Im}\{ \}$ to inside them. These transfers are valid as the above terms are real. The sum over a is the sum over all non-degenerate states and/or members of degenerate states.

Dropping all terms in which the product of the magnetic moment $\vec{m}$ with itself appears yields a more simple expression for $\underline{\vec{O}}$

$$\begin{aligned}
 (2-87) \quad \underline{\vec{O}} = & \sum_a \frac{\rho_a^1}{d_a} \left\{ {}^1O_{aa} + \frac{1}{kT} ({}^1\vec{m}_{aa} \cdot \vec{H}') {}^1\vec{O}_{aa} \right. \\
 & + \frac{2}{\hbar} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \text{Re}\{({}^1\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) {}^1\vec{O}_{ab}\} \right. \\
 & \quad \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \text{Im}\{({}^1\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) {}^1\vec{O}_{ab}\} \right. \\
 & \quad \left. + \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \text{Re}\{({}^1\vec{m}_{ba} \cdot \vec{H}_{Lo}) {}^1\vec{O}_{ab}\} \right. \\
 & \quad \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \text{Im}\{({}^1\vec{m}_{ba} \cdot \dot{\vec{H}}_{Lo}) {}^1\vec{O}_{ab}\} \right] \\
 & + \frac{2}{\hbar kT} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \text{Re}\{({}^1\vec{m}_{aa} \cdot \vec{H}')({}^1\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) {}^1\vec{O}_{ab}\} \right. \\
 & \quad \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \text{Im}\{({}^1\vec{m}_{aa} \cdot \vec{H}')({}^1\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) {}^1\vec{O}_{ab}\} \right] \\
 & + \frac{2}{\hbar^2} \sum_b \left[\frac{\omega_{ba}^2 + \omega^2}{(\omega_{ba}^2 - \omega^2)^2} \text{Re}\{([{}^1\vec{m}_{bb} - {}^1\vec{m}_{aa}] \cdot \vec{H}')({}^1\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) {}^1\vec{O}_{ab}\} \right. \\
 & \quad \left. - \frac{2\omega_{ba}}{(\omega_{ba}^2 - \omega^2)^2} \text{Im}\{([{}^1\vec{m}_{bb} - {}^1\vec{m}_{aa}] \cdot \vec{H}')({}^1\vec{\mu}_{ba} \cdot \dot{\vec{E}}_{Lo}) {}^1\vec{O}_{ab}\} \right] \\
 & + \frac{2}{\hbar^2} \sum_b \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \left[\sum_d \frac{1}{\omega_{db}} \text{Re}\{({}^1\vec{m}_{bd} \cdot \vec{H}')({}^1\vec{\mu}_{da} \cdot \vec{E}_{Lo}) {}^1\vec{O}_{ab}\} \right.
 \end{aligned}$$

$$\begin{aligned}
& + \sum_d' \frac{1}{\omega_{da}} \operatorname{Re} \{ (\vec{m}_{da} \cdot \vec{H}') (\vec{\mu}_{bd} \cdot \vec{E}_{lo}) \vec{O}_{ab} \} \\
& + \frac{2}{\hbar^2} \sum_b \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{da}} \operatorname{Re} \{ (\vec{\mu}_{ba} \cdot \vec{E}_{lo}) (\vec{m}_{ad} \cdot \vec{H}') \vec{O}_{db} \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{db}} \operatorname{Re} \{ (\vec{\mu}_{ba} \cdot \vec{E}_{lo}) (\vec{m}_{db} \cdot \vec{H}') \vec{O}_{ad} \} \right] \\
& - \frac{2}{\hbar^2} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{db}} \operatorname{Im} \{ (\vec{m}_{bd} \cdot \vec{H}') (\vec{\mu}_{da} \cdot \vec{E}_{lo}) \vec{O}_{ab} \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{da}} \operatorname{Im} \{ (\vec{m}_{da} \cdot \vec{H}') (\vec{\mu}_{bd} \cdot \vec{E}_{lo}) \vec{O}_{ab} \} \right] \\
& - \frac{2}{\hbar^2} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{da}} \operatorname{Im} \{ (\vec{\mu}_{ba} \cdot \vec{E}_{lo}) (\vec{m}_{ad} \cdot \vec{H}') \vec{O}_{db} \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{db}} \operatorname{Im} \{ (\vec{\mu}_{ba} \cdot \vec{E}_{lo}) (\vec{m}_{db} \cdot \vec{H}') \vec{O}_{ad} \} \right] \}
\end{aligned}$$

We now must average over all molecular orientations. Upon inspection of equation (2-87), we see that this reduces to the determination of three types of averages. These averages are characterized by the averages of three types of vector products. They are:

$$\overline{\vec{a}} \quad ; \quad \overline{(\vec{a} \cdot \vec{U}) \vec{b}} \quad ; \quad \overline{(\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V}) \vec{c}}$$

where $\vec{a}, \vec{b}, \vec{c}$ are molecule fixed vectors; $\vec{U}, \vec{V}$ are space fixed vectors. The upper bars indicate the averages over all molecular orientations. It can be shown (Appendix V) that these three types of averages are given by:

$$\begin{aligned}
(2-88) \quad & \overline{\vec{a}} = 0 \\
& \overline{(\vec{a} \cdot \vec{U}) \vec{b}} = \frac{1}{3} (\vec{a} \cdot \vec{b}) \vec{U} \\
& \overline{(\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V}) \vec{c}} = \frac{1}{6} (\vec{a} \cdot \vec{b} \times \vec{c})(\vec{U} \times \vec{V})
\end{aligned}$$

The first average has no spatial reference and is therefore zero. The second average has as a reference the spatial vector $\vec{U}$ and therefore has a non-zero component only along the spatial direction defined by $\vec{U}$. The third average has as references, the spatial vectors $\vec{U}$ and $\vec{V}$. These two vectors define a plane, whose orientation in space is defined by the cross product $\vec{U} \times \vec{V}$. As the third average is referred to this plane, it therefore is referred to $\vec{U} \times \vec{V}$ and has a non-zero component only in the direction perpendicular to this plane (along the axial vector $\vec{U} \times \vec{V}$). Upon performing the above averages, we will find the results to be the following. From the second type of average, there will be a component of $\underline{\underline{\mu}}$ along $\vec{H}_{Lo}$, thus perpendicular to $\vec{E}_{Lo}$, and a component of $\underline{\underline{m}}$ along $\vec{E}_{Lo}$, thus perpendicular to $\vec{H}_{Lo}$. From the third type of average there will be a component of $\underline{\underline{\mu}}$ along $(\vec{E}_{Lo} \times \vec{H}')$ thus perpendicular to $\vec{E}_{Lo}$, and a component of $\underline{\underline{m}}$ along $(\vec{H}_{Lo} \times \vec{H}')$ thus perpendicular to $\vec{H}_{Lo}$. As emphasized in part A of this chapter and as shown here in detail the second type of average leads to natural optical rotation, and the third type of average to magnetically-induced optical rotation. Thus the tumbling of the molecule, which is the physical mechanism for the averaging, plays an extremely important role in the production of optical activity.

Taking the average of $\underline{\underline{O}}$ over all molecular orientations and substituting equations (2-88) yields:

$$\begin{aligned}
 (2-89) \quad \underline{\underline{O}} = \overline{\underline{\underline{O}}} = \sum_a \frac{\rho_a^1}{c_a} \left\{ \frac{1}{3kT} (\vec{m}_{aa} \cdot \vec{O}_{aa}) \vec{H}' \right. \\
 \left. + \frac{2}{3\hbar} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \operatorname{Re} \{ (\vec{\mu}_{ba} \cdot \vec{O}_{ab}) \vec{E}_{Lo} \} \right. \right. \\
 \left. \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \{ (\vec{\mu}_{ba} \cdot \vec{O}_{ab}) \vec{E}_{Lo} \} \right] \right\}
 \end{aligned}$$

$$\begin{aligned}
& + \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \operatorname{Re} \{ ({}^1\vec{m}_{ba} \cdot {}^1\vec{O}_{ab}) \vec{H}_{L0} \} \\
& - \frac{1}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \{ ({}^1\vec{m}_{ba} \cdot {}^1\vec{O}_{ab}) \dot{\vec{H}}_{L0} \} \\
& + \frac{2}{6\hbar kT} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \operatorname{Re} \{ ({}^1\vec{m}_{aa} \cdot {}^1\vec{O}_{ab} \times {}^1\vec{\mu}_{ba}) (\vec{E}_{L0} \times \vec{H}') \} \right. \\
& \quad \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \{ ({}^1\vec{m}_{aa} \cdot {}^1\vec{O}_{ab} \times {}^1\vec{\mu}_{ba}) (\dot{\vec{E}}_{L0} \times \vec{H}') \} \right] \\
& + \frac{2}{6\hbar^2} \sum_b \left[\frac{\omega_{ba}^2 + \omega^2}{(\omega_{ba}^2 - \omega^2)^2} \operatorname{Re} \{ ([{}^1\vec{m}_{bb} - {}^1\vec{m}_{aa}] \cdot {}^1\vec{O}_{ab} \times {}^1\vec{\mu}_{ba}) (\vec{E}_{L0} \times \vec{H}') \} \right. \\
& \quad \left. - \frac{2\omega_{ba}}{(\omega_{ba}^2 - \omega^2)^2} \operatorname{Im} \{ ([{}^1\vec{m}_{bb} - {}^1\vec{m}_{aa}] \cdot {}^1\vec{O}_{ab} \times {}^1\vec{\mu}_{ba}) (\dot{\vec{E}}_{L0} \times \vec{H}') \} \right] \\
& + \frac{2}{6\hbar^2} \sum_b \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{db}} \operatorname{Re} \{ ({}^1\vec{m}_{bd} \cdot {}^1\vec{O}_{ab} \times {}^1\vec{\mu}_{da}) (\vec{E}_{L0} \times \vec{H}') \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{da}} \operatorname{Re} \{ ({}^1\vec{m}_{da} \cdot {}^1\vec{O}_{ab} \times {}^1\vec{\mu}_{bd}) (\vec{E}_{L0} \times \vec{H}') \} \right] \\
& + \frac{2}{6\hbar^2} \sum_b \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{da}} \operatorname{Re} \{ ({}^1\vec{m}_{ad} \cdot {}^1\vec{O}_{db} \times {}^1\vec{\mu}_{ba}) (\vec{E}_{L0} \times \vec{H}') \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{db}} \operatorname{Re} \{ ({}^1\vec{m}_{db} \cdot {}^1\vec{O}_{ad} \times {}^1\vec{\mu}_{ba}) (\vec{E}_{L0} \times \vec{H}') \} \right] \\
& - \frac{2}{6\hbar^2} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{db}} \operatorname{Im} \{ ({}^1\vec{m}_{bd} \cdot {}^1\vec{O}_{ab} \times {}^1\vec{\mu}_{da}) (\dot{\vec{E}}_{L0} \times \vec{H}') \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{da}} \operatorname{Im} \{ ({}^1\vec{m}_{da} \cdot {}^1\vec{O}_{ab} \times {}^1\vec{\mu}_{bd}) (\dot{\vec{E}}_{L0} \times \vec{H}') \} \right] \\
& - \frac{2}{6\hbar^2} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \left[\sum_d' \frac{1}{\omega_{da}} \operatorname{Im} \{ ({}^1\vec{m}_{ad} \cdot {}^1\vec{O}_{db} \times {}^1\vec{\mu}_{ba}) (\dot{\vec{E}}_{L0} \times \vec{H}') \} \right. \\
& \quad \left. + \sum_d' \frac{1}{\omega_{db}} \operatorname{Im} \{ ({}^1\vec{m}_{db} \cdot {}^1\vec{O}_{ad} \times {}^1\vec{\mu}_{ba}) (\dot{\vec{E}}_{L0} \times \vec{H}') \} \right] \Bigg\}
\end{aligned}$$

We now use (2-89) to determine $\underline{\underline{\vec{m}}}$ and $\underline{\underline{\vec{\mu}}}$. The expression for $\underline{\underline{\vec{m}}}$ is particularly simple as we ignore terms where the magnetic moment $\vec{m}$ is multiplied by itself. We also ignore the term $(^1\vec{m}_{aa} \cdot ^1\vec{m}_{aa})\vec{H}$ as this is a magnetic susceptibility term and adds nothing to the optical activity.

$$(2-90) \quad \underline{\underline{\vec{m}}} \cong \frac{2}{3\hbar} \sum_a \frac{\rho_a^1}{d_a} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \operatorname{Re} \{ (^1\vec{\mu}_{ba} \cdot ^1\vec{m}_{ab}) \vec{E}_{L0} \} \right. \\ \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \{ (^1\vec{\mu}_{ba} \cdot ^1\vec{m}_{ab}) \vec{E}_{L0} \} \right]$$

The sums over a and b are over both all non-degenerate states, and all members of these degenerate states. If ψ_a^1 and ψ_b^1 are non-degenerate, then $^1\vec{\mu}_{ba}$ is real, $^1\vec{m}_{ab}$ is imaginary and $(^1\vec{\mu}_{ba} \cdot ^1\vec{m}_{ab})$ is imaginary. As $\vec{E}_{L0}$ and $\vec{E}_{L0}$ are real, the first term in (2-90) is zero, the only contribution being from the second term. If states ψ_a^1 and/or ψ_b^1 are degenerate, then the members of each set occur as complex conjugate states (if the degeneracy is odd then there are $\frac{d_a-1}{2}$ complex conjugate pairs, where d_a is the order of degeneracy, and one real state. If this is the case, arguments hold that are similar to those that follow). As all members of the degenerate states have the same energy, we can separate the sums so that equation (2-90) becomes:

$$(2-91) \quad \underline{\underline{\vec{m}}} \cong \frac{2}{3\hbar} \sum_a \frac{\rho_a^1}{d_a} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \operatorname{Re} \left\{ \sum_{a,b}^{\text{mem}} (^1\vec{\mu}_{ba} \cdot ^1\vec{m}_{ab}) \vec{E}_{L0} \right\} \right. \\ \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \operatorname{Im} \left\{ \sum_{a,b}^{\text{mem}} (^1\vec{\mu}_{ba} \cdot ^1\vec{m}_{ab}) \vec{E}_{L0} \right\} \right]$$

where now $\sum_a$, $\sum_b$ represents the sums over all degenerate sets and $\sum_{a,b}^{\text{mem}}$ represent the sums over all members of each degenerate set.

We can expand the member summations:

$$\begin{aligned}
\sum_{a,b}^{\text{mem}} ({}^1\vec{\mu}_{ba} \cdot {}^1\vec{m}_{ab}) &= (\psi_b^1 | \vec{\mu} | \psi_a^1) \cdot (\psi_a^1 | \vec{m} | \psi_b^1) \\
&+ (\psi_b^{1*} | \vec{\mu} | \psi_a^{1*}) \cdot (\psi_a^{1*} | \vec{m} | \psi_b^{1*}) \\
&+ (\psi_b^{1*} | \vec{\mu} | \psi_a^1) \cdot (\psi_a^1 | \vec{m} | \psi_b^{1*}) \\
&+ (\psi_b^1 | \vec{\mu} | \psi_a^{1*}) \cdot (\psi_a^{1*} | \vec{m} | \psi_b^1)
\end{aligned}$$

now $\vec{\mu}$ is purely real, $\vec{m}$ is purely imaginary.

Thus:

$$\begin{aligned}
(\psi_b^1 | \vec{\mu} | \psi_a^1) &= [(\psi_b^{1*} | \vec{\mu} | \psi_a^{1*})]^* \\
(\psi_b^{1*} | \vec{\mu} | \psi_a^1) &= [(\psi_b^1 | \vec{\mu} | \psi_a^{1*})]^* \\
(\psi_b^1 | \vec{m} | \psi_a^1) &= -[(\psi_b^{1*} | \vec{m} | \psi_a^{1*})]^* \\
(\psi_b^{1*} | \vec{m} | \psi_a^1) &= -[(\psi_b^1 | \vec{m} | \psi_a^{1*})]^*
\end{aligned}$$

$$\begin{aligned}
\therefore \sum_{a,b}^{\text{mem}} ({}^1\vec{\mu}_{ba} \cdot {}^1\vec{m}_{ab}) &= [(\psi_b^1 | \vec{\mu} | \psi_a^1) \cdot (\psi_a^1 | \vec{m} | \psi_b^1) \\
&+ (\psi_b^{1*} | \vec{\mu} | \psi_a^{1*}) (\psi_a^{1*} | \vec{m} | \psi_b^{1*})] \\
&- [\text{complex conjugate}]
\end{aligned}$$

This clearly shows that $\sum_{a,b}^{\text{mem}} ({}^1\vec{\mu}_{ba} \cdot {}^1\vec{m}_{ab})$ is purely imaginary and that the first term of equation (2-90) is zero.

Also:

$$(2-93) \quad \sum_{a,b}^{\text{mem}} ({}^1\vec{\mu}_{ba} \cdot {}^1\vec{m}_{ab}) = - \sum_{a,b}^{\text{mem}} ({}^1\vec{m}_{ba} \cdot {}^1\vec{\mu}_{ab})$$

The expression for $\underline{\vec{m}}$ now becomes:

$$(2-94) \quad \underline{\vec{m}} = -\frac{2}{3\hbar} \sum_a \frac{\rho_a}{d_a} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \text{Im} \{ {}^1\vec{\mu}_{ba} \cdot {}^1\vec{m}_{ab} \} \hat{E}_{\text{Lo}}$$

Here for simplicity of notation we drop the superscript on the population coefficient, setting $\rho_a^1 = \rho_a$. Also we have taken $\dot{\vec{E}}_{L0}$ outside the $\text{Im}\{\}$ as $\dot{\vec{E}}_{L0}$ is a real quantity and so can be treated. The expression for $\vec{\mu}$ is more complex. Substituting $\vec{\mu}$ for $\vec{O}$ in equation (2-89), dropping the first term as it adds nothing to the optical activity, and separating the sum over all states and members into separate sums over states and members, we obtain, again setting

$$\rho_a^1 = \rho_a :$$

$$\begin{aligned}
 (2-95) \quad \vec{\mu} = \sum_a \frac{A_a}{d_a} \Bigg\{ & \frac{2}{3\hbar} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \text{Re} \{ ({}^1\vec{\mu}_{ba} \cdot {}^1\vec{\mu}_{ab}) \dot{\vec{E}}_{L0} \} \right. \\
 & - \frac{1}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \text{Im} \{ ({}^1\vec{\mu}_{ba} \cdot {}^1\vec{\mu}_{ab}) \dot{\vec{E}}_{L0} \} \\
 & + \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \text{Re} \{ ({}^1\vec{m}_{ba} \cdot {}^1\vec{\mu}_{ab}) \vec{H}_{L0} \} \\
 & \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \text{Im} \{ ({}^1\vec{m}_{ba} \cdot {}^1\vec{\mu}_{ab}) \vec{H}_{L0} \} \right] \\
 & + \frac{2}{6\hbar K T} \sum_b \left[\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \text{Re} \{ ({}^1\vec{m}_{aa} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{ba}) (\vec{E}_{L0} \times \vec{H}') \} \right. \\
 & \left. - \frac{1}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \text{Im} \{ ({}^1\vec{m}_{aa} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{ba}) (\vec{E}_{L0} \times \vec{H}') \} \right] \\
 & + \frac{2}{6\hbar^2} \sum_b \left[\frac{\omega_{ba}^2 + \omega^2}{(\omega_{ba}^2 - \omega^2)^2} \sum_{a,b}^{\text{mem}} \text{Re} \{ ([{}^1\vec{m}_{bb} - {}^1\vec{m}_{aa}] \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{ba}) (\vec{E}_{L0} \times \vec{H}') \} \right. \\
 & \left. - \frac{2\omega_{ba}}{(\omega_{ba}^2 - \omega^2)} \sum_{a,b}^{\text{mem}} \text{Im} \{ ([{}^1\vec{m}_{bb} - {}^1\vec{m}_{aa}] \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{ba}) (\vec{E}_{L0} \times \vec{H}') \} \right] \\
 & + \frac{2}{6\hbar^2} \sum_b \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \left[\text{Re} \left\{ \sum_{d \neq b} \left(\frac{{}^1\vec{m}_{bd}}{\omega_{db}} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{da} \right) (\vec{E}_{L0} \times \vec{H}') \right. \right. \\
 & \quad + \sum_{d \neq a} \left(\frac{{}^1\vec{m}_{da}}{\omega_{da}} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{bd} \right) (\vec{E}_{L0} \times \vec{H}') \\
 & \quad \left. \left. + \sum_{d \neq a} \left(\frac{{}^1\vec{m}_{ad}}{\omega_{da}} \cdot {}^1\vec{\mu}_{db} \times {}^1\vec{\mu}_{ba} \right) (\vec{E}_{L0} \times \vec{H}') \right\} \right]
 \end{aligned}$$

$$\begin{aligned}
& + \sum_{d \neq b} \left(\frac{{}^1\vec{m}_{db}}{\omega_{db}} \cdot {}^1\vec{\mu}_{ad} \times {}^1\vec{\mu}_{ba} \right) (\vec{E}_{L0} \times \vec{H}') \Bigg] \\
& - \frac{2}{6\hbar^2} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{mem} \left[\text{Im} \left\{ \sum_{d \neq b} \left(\frac{{}^1\vec{m}_{bd}}{\omega_{db}} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{da} \right) (\vec{E}_{L0} \times \vec{H}') \right. \right. \\
& + \sum_{d \neq a} \left(\frac{{}^1\vec{m}_{da}}{\omega_{da}} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{bd} \right) (\vec{E}_{L0} \times \vec{H}') \\
& + \sum_{d \neq a} \left(\frac{{}^1\vec{m}_{ad}}{\omega_{da}} \cdot {}^1\vec{\mu}_{db} \times {}^1\vec{\mu}_{ba} \right) (\vec{E}_{L0} \times \vec{H}') \\
& \left. \left. + \sum_{d \neq b} \left(\frac{{}^1\vec{m}_{db}}{\omega_{db}} \cdot {}^1\vec{\mu}_{ad} \times {}^1\vec{\mu}_{ba} \right) (\vec{E}_{L0} \times \vec{H}') \right\} \right]
\end{aligned}$$

To simplify this expression for $\underline{\vec{\mu}}$ we need equations (2-92), and (2-93) plus several additional relations. We can show via reasoning parallel to that used for $\underline{\vec{m}}$, that of the first two terms of $\underline{\vec{\mu}}$, only the one involving the $\text{Re}\{\}$ contributes. Of the second two terms, only the one involving the $\text{Im}\{\}$ contributes and can be recast according to equation (2-93). To determine which of the next four terms should be kept, we note that:

${}^1\vec{m}_{aa}, {}^1\vec{m}_{bb}$ are real (diagonal elements of real observables)

Also $({}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{ba}) = -({}^1\vec{\mu}_{ba} \times {}^1\vec{\mu}_{ab}) = -({}^1\vec{\mu}_{ab}^* \times {}^1\vec{\mu}_{ba}^*) = -({}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{ba})^*$

$\therefore ({}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{ba})$ is purely imaginary.

Therefore ${}^1\vec{m}_{aa} \cdot ({}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{ba})$ and ${}^1\vec{m}_{bb} \cdot ({}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{ba})$ are purely imaginary and of the fifth to the eighth terms of (2-95), only the ones with $\text{Im}\{\}$, the sixth and eighth, contribute.

Finally, for the last eight terms of equation (2-95), terms nine through sixteen, we can show that the $\text{Re}\{\}$, terms nine through twelve, cancel in pairs, while the $\text{Im}\{\}$, terms thirteen through sixteen,

sum in pairs. For Example:

$$\begin{aligned}
 & \text{Re} \left\{ \sum_{d \neq b} \left(\frac{{}^1\vec{m}_{bd}}{\omega_{db}} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{da} \right) + \sum_{d \neq b} \left(\frac{{}^1\vec{m}_{db}}{\omega_{db}} \cdot {}^1\vec{\mu}_{ad} \times {}^1\vec{\mu}_{ba} \right) \right\} \\
 &= \text{Re} \left\{ \sum_{d \neq b} \frac{1}{\omega_{db}} \left[({}^1\vec{m}_{bd} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{da}) + ({}^1\vec{m}_{bd}^* \cdot {}^1\vec{\mu}_{da}^* \times {}^1\vec{\mu}_{ab}^*) \right] \right\} \\
 &= \text{Re} \left\{ \sum_{d \neq b} \frac{1}{\omega_{db}} \left[({}^1\vec{m}_{bd} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{da}) - ({}^1\vec{m}_{bd} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{da})^* \right] \right\}
 \end{aligned}$$

These obviously cancel, while if we took the imaginary part, they would sum. Applying all the above simplifications and setting $\vec{H}' = -\vec{H}$ (this is the same as reversing the convention we have chosen for the magnetic field and will only change the sign of the magnetically-induced optical activity. This will maintain consistency with the equations derived by other authors), we have for the moment $\underline{\underline{\vec{\mu}}}$:

$$\begin{aligned}
 (2-96) \quad \underline{\underline{\vec{\mu}}} &= \frac{2}{3\hbar} \sum_a \frac{\rho_a}{d_a} \sum_b \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \text{Re} \{ {}^1\vec{\mu}_{ba} \cdot {}^1\vec{\mu}_{ab} \} \vec{E}_{L0} \\
 &+ \frac{2}{3\hbar} \sum_a \frac{\rho_a}{d_a} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \text{Im} \{ {}^1\vec{\mu}_{ba} \cdot {}^1\vec{r}_{lab} \} \dot{\vec{H}}_{L0} \\
 &+ \frac{2}{6\hbar kT} \sum_a \frac{\rho_a}{d_a} \sum_b \frac{1}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \text{Im} \{ {}^1\vec{m}_{aa} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{ba} \} (\dot{\vec{E}}_{L0} \times \vec{H}') \\
 &+ \frac{2}{6\hbar^2} \sum_a \frac{\rho_a}{d_a} \sum_b \frac{2\omega_{ba}}{(\omega_{ba}^2 - \omega^2)^2} \sum_{a,b}^{\text{mem}} \text{Im} \{ ({}^1\vec{m}_{bb} - {}^1\vec{m}_{aa}) \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{ba} \} (\dot{\vec{E}}_{L0} \times \vec{H}') \\
 &+ \frac{2}{6\hbar^2} \sum_a \frac{\rho_a}{d_a} \sum_b \frac{2}{\omega_{ba}^2 - \omega^2} \sum_{a,b}^{\text{mem}} \text{Im} \left\{ \sum_d' \left(\frac{{}^1\vec{m}_{da}}{\omega_{da}} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{bd} \right) \right. \\
 &\quad \left. + \sum_d' \left(\frac{{}^1\vec{m}_{bd}}{\omega_{db}} \cdot {}^1\vec{\mu}_{ab} \times {}^1\vec{\mu}_{da} \right) \right\} (\dot{\vec{E}}_{L0} \times \vec{H}')
 \end{aligned}$$

We may write equations (2-94) and (2-96) in a more concise form:

$$\begin{aligned}
 (2-97) \quad \underline{\underline{\vec{\mu}}} &= \alpha \vec{E}_{L0} - \beta \dot{\vec{H}}_{L0} - \eta (\dot{\vec{E}}_{L0} \times \vec{H}') \\
 \underline{\underline{\vec{m}}} &= \beta \dot{\vec{E}}_{L0}
 \end{aligned}$$

where ,

$$(2-98) \quad \alpha = \frac{2}{3\hbar\omega^2} \sum_a \rho_a \sum_b \omega_{ba} f_2^0(\omega, \omega_{ba}) D_{ab}$$

$$\beta = -\frac{2}{3\hbar\omega^2} \sum_a \rho_a \sum_b f_2^0(\omega, \omega_{ba}) R_{ab}$$

$$\eta = -\frac{2}{3\hbar\omega^2} \sum_a \rho_a \sum_b \left[f_1^0(\omega, \omega_{ba}) A_{ab} + f_2^0(\omega, \omega_{ba}) B_{ab} + \frac{1}{kT} f_2^0(\omega, \omega_{ba}) C_{ab} \right]$$

where

$$(2-99) \quad f_1^0(\omega, \omega_{ba}) = \frac{2\omega_{ba}\omega^2}{\hbar(\omega_{ba}^2 - \omega^2)^2}$$

$$f_2^0(\omega, \omega_{ba}) = \frac{\omega^2}{\omega_{ba}^2 - \omega^2}$$

and

$$D_{ab} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Re} \{ \vec{\mu}_{ba} \cdot \vec{\mu}_{ab} \}$$

$$(2-100) \quad R_{ab} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Im} \{ \vec{\mu}_{ba} \cdot \vec{m}_{ba} \}$$

$$A_{ab} = \frac{1}{2d_a} \sum_{a,b}^{\text{mem}} (\vec{m}_{bb} - \vec{m}_{aa}) \cdot \text{Im} \{ \vec{\mu}_{ab} \times \vec{\mu}_{ba} \}$$

$$B_{ab} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Im} \left\{ \sum_d' \frac{\vec{m}_{da}}{\hbar\omega_{da}} \cdot \vec{\mu}_{ab} \times \vec{\mu}_{bd} + \sum_d' \frac{\vec{m}_{bd}}{\hbar\omega_{db}} \cdot \vec{\mu}_{ab} \times \vec{\mu}_{da} \right\}$$

$$C_{ab} = \frac{1}{2d_a} \sum_{a,b}^{\text{mem}} \vec{m}_{aa} \cdot \text{Im} \{ \vec{\mu}_{ab} \times \vec{\mu}_{ba} \}$$

Here we have dropped the left superscript on the various matrix elements. They will only be of importance in Chapters 4 and 5 where they can easily be reestablished. For now, we ignore them and just remember that the matrix elements are those of the complex system and therefore that the equations for optical activity are for the complex system.

The frequency functions $f_1^o(\omega, \omega_{ba})$ and $f_2^o(\omega, \omega_{ba})$ have zero bandwidths and have singularities at $\omega = \omega_{ba}$. To avoid these non-physical conditions, we follow the lead of other authors (6), (23), and (29) and assume a band shape. Here we choose a damped oscillator form, (1) and (23), and we write the new frequency functions as f_1 , replacing f_1^o , and f_2 , replacing f_2^o .

$$(2-101) \quad f_1(\omega, \omega_{ba}) = \frac{2\omega_{ba}\omega^2 [(\omega_{ba}^2 - \omega^2)^2 - \omega^2 \Gamma_{ba}^2]}{\hbar [(\omega_{ba}^2 - \omega^2)^2 + \omega^2 \Gamma_{ba}^2]}$$

$$f_2(\omega, \omega_{ba}) = \frac{\omega^2 (\omega_{ba}^2 - \omega^2)}{(\omega_{ba}^2 - \omega^2)^2 + \omega^2 \Gamma_{ba}^2}$$

and our coefficients α , β , η become

$$\alpha = \frac{2}{3\hbar\omega^2} \sum_a \rho_a \sum_b \omega_{ba} f_2(\omega, \omega_{ba}) D_{ab}$$

$$(2-102) \quad \beta = -\frac{2}{3\hbar\omega^2} \sum_a \rho_a \sum_b f_2(\omega, \omega_{ba}) R_{ab}$$

$$\eta = -\frac{2}{3\hbar\omega^2} \sum_a \rho_a \sum_b \left[f_1(\omega, \omega_{ba}) A_{ab} + f_2(\omega, \omega_{ba}) B_{ab} + \frac{1}{kT} f_2(\omega, \omega_{ba}) C_{ab} \right]$$

Finally, in the determination of $\underline{\underline{m}}$ from equation (2-89), we ignored terms where the magnetic moment was multiplied by itself. If we had included those terms, we would have obtained a form for $\underline{\underline{m}}$ which

would give the expressions for $\underline{\vec{u}}$ and $\underline{\vec{m}}$ a more symmetrical appearance.

$$(2-103) \quad \underline{\vec{u}} = \alpha \vec{E}_{L0} - \beta \dot{\vec{H}}_{L0} - \eta (\vec{E}_{L0} \times \vec{H}')$$

$$\underline{\vec{m}} = \chi \vec{H}_{L0} + \beta \dot{\vec{E}}_{L0} - \xi (\dot{\vec{H}}_{L0} \times \vec{H}')$$

As the evaluation of χ and ξ is not necessary for the evaluation of optical activity (they do not appear in equation (2-62)), we do not calculate them in this thesis. Those interested in their calculation should refer to Stephens (22).

The final results for optical rotation, natural and magnetically-induced, are embodied in equations (2-103) or (2-97), equation (2-101), equation (2-102), equation (2-100), and equation (2-62). Circular dichroism is obtained via the Kronig Kramers transform as described in part A of this chapter.

FOOTNOTES

1. It shall be assumed that unless otherwise specified the phrase "optical activity" shall include both natural and magnetically-induced optical activity.
2. The mathematical transform known by the name Kronig-Kramers is a specialized form of the Hilbert transform. If one has a physical quantity represented by a complex function, the Hilbert transform states that if one knows the real part, the imaginary part is uniquely determined and visa-versa. In the formulation for complex optical activity ORD (MORD) is the real part and CD (MCD) the imaginary part. See Appendix VI for more details.
3. Thus we distinguish magnetically-induced optical activity from such phenomena as the Cotton-Mouton effect which results from components of the external magnetic field which are perpendicular to the direction of propagation.
4. The restriction that the helical molecular orbital be fixed in space is not imperative to demonstrate the production of the small corrections on $\vec{D}_L$ and $\vec{B}_L$. However, to consider it not fixed and to be required to average over all positions would result in complexities which add nothing to the physical picture presented by this model.
5. In general, both solute and solvent molecules can contribute electronic and magnetic oscillators. Since we normally either choose optically inactive solvents or measure in such a way so as to eliminate solvent optical activity, we ignore the solvent contribution

contribution in our derivation. We also assume that the absorption bands of the solvent are in regions of the spectrum removed from those of the solute, thus effectively eliminating any effects due to optical activity induced in the solvent by an asymmetric solute. All discussion therefore, is understood to refer to solute optical activity. For a further discussion of solvent-solute interactions, see Appendix VIII.

6. The relation of the local to the macroscopic fields is complex. The assumption that they are equal can be adequate for a gas but the difference can be significant in the condensed phase, especially for the electric field. A common procedure is to equate the local electric field to the Lorentz effective field

$$\vec{E}_L = \vec{E}_0 + \frac{4\pi}{3} \vec{P}_L$$

However, the assumptions leading to this are rather crude (36), and there is no reason to believe that this is much better than the simple equality relation, especially since the more complex relation gives poor agreement with experiment in many cases (See references (37), (38), and (39)). Furthermore, it greatly complicates the solution of Maxwell's equations. Further discussion and the application of the Lorentz correction can be found in references (23) and (40).

7. The molecular system, in the absence of all perturbations, external field and molecular, is termed the zero-order simple system. Treatment of both the zero-order system and the molecular perturbations is reserved for Chapters 3, 4, and 5.
8. See Footnote 8, Chapter 1.

Chapter 3

OPTICAL ACTIVITY OF COMPLEX SYSTEMS

In Chapter 2, we derived equations for the natural and magnetically-induced optical activity of a molecular system. At that time, there was no specification of this system as to number of chromophores, excitation of modes of vibration, or existence of patterns of substitution. The assumption was that, regardless of the nature of the molecular system, one could determine the appropriate wave functions and energies, and thus the pertinent rotational strengths. Unfortunately, this assumption is, for many molecular systems, a poor one, in that the direct determination of the eigenfunctions is not feasible. In these situations one must use the principles of perturbation theory -- or its more general parent, diagonalization of the matrix representation of the Hamiltonian -- to develop solutions of the complex molecular system in terms of known solutions of a similar but simpler molecular system.

In the remaining chapters of this dissertation, we shall examine the complications that arise in the equations for optical activity when any or all of three types of molecular complexity are present. These complexities are (i) chromophore-chromophore interaction, leading to the equations for the optical activity of polymers, (ii) vibrational perturbations, leading to the equations for vibronic structuring of optical activity and (iii) substitutional perturbations, leading to the equations describing substitutional influences on optical activity.

In this chapter we lay down the theoretical foundations

required for the analysis of these three complexities. First, given the complex molecular system and its Hamiltonian,, one must choose the most appropriate simple molecular system with which to approximate the complex system. The determination of what constitutes the most appropriate approximate system, given a particular complex system, is one of the goals of this chapter. Having specified both complex and simple systems, one then determines the matrix representation of the Hamiltonian of the complex molecular system in the eigenfunctions of the simple molecular system. This matrix representation, when diagonalized, yields the eigenfunctions and eigenvalues of the complex system in terms of those of the simple system. Under appropriate conditions, this procedure of diagonalization reduces to a simpler and more useful perturbation expansion of the eigenfunctions of the complex system in those eigenfunctions of the simple system. These complex eigenfunctions, whether evaluated by matrix diagonalization or perturbation theory, can be directly utilized in the equations for optical activity derived in Chapter 2.

A. Formalism to Relate Complex System to Simple System

In Chapter 2, we expressed the equations for optical activity in terms of the electric and magnetic dipole matrix elements in the representation defined by the wave functions of the molecular system of interest, which we termed the complex molecular system. These wave functions are eigenfunctions of the total molecular Hamiltonian and are designated as first-order states. They are, in actuality, the stationary states of the complex molecular system (Footnote 1). If

this complex system is in reality quite simple, say an isolated, unsubstituted, non-vibrating chromophore, then generally it is practicable to determine these stationary states. Here we have a single, simple, non-moving (nuclear) framework in which the electrons move. The stationary states of this system are identical to the eigenstates of the electronic Hamiltonian and, upon making the many assumptions common to molecular orbital theory (for example, see Salem (41)), these eigenstates can be determined and used in the basic equations for optical activity (Footnote 2). If, however, we now add the complexities normally found in a molecular system -- i.e. the molecular perturbations of vibration, substitution and chromophore-chromophore interaction -- the stationary states of the system become more numerous, more complex, more difficult to attach physical meaning to, and their direct calculation rapidly becomes impracticable. Because of this, the general approach to the solution of these more complex cases is to obtain the stationary states of the complex system as expansions of the stationary states of a simple, more determined system -- in general, the complex system minus certain of the complexities (Footnote 3).

As preparation for the determination of these expansions, we briefly outline the notation we shall use in the remainder of this chapter. Following Table IV of Chapter 2, we write the first-order, stationary states of the total (complex) molecular system as ψ_a^1 and the zero-order, stationary states of the approximate (simple) molecular system (non-stationary states of the total molecular system) as ψ_a^0 (Footnote 4). Referring to equation (2-72) we may write the total, first-order Hamiltonian as:

$$(2-72) \quad \mathcal{H}' = \mathcal{H}^0 + \mathcal{H}_I^1 + \mathcal{H}_V^1 + \mathcal{H}_S^1$$

where $\mathcal{H}^0$ is the zero-order, approximate Hamiltonian and $\mathcal{H}_I^1, \mathcal{H}_V^1, \mathcal{H}_S^1$

have been defined respectively as any chromophore-chromophore interaction, any vibrational perturbation, and any substitutional perturbation, not included in the zero-order Hamiltonian. The first-order wave functions are related to the first-order Hamiltonian via the Schroedinger equation (using bra-ket notation, see appendix I):

$$(3-1) \quad \mathcal{H}' |\psi_a^1\rangle = E_a^1 |\psi_a^1\rangle \quad E_a^1 = \hbar\omega_a^1 - \hbar\omega_a$$

Similarly for the zero-order quantities

$$(3-2) \quad \mathcal{H}^0 |\psi_a^0\rangle = E_a^0 |\psi_a^0\rangle \quad E_a^0 = \hbar\omega_a^0$$

In most cases it is possible to determine the proper expansions of the ψ_a^1 in the ψ_a^0 via standard time independent perturbation theory. However, as there are situations in which the perturbation expansion is invalid, in this chapter we will discuss a more general approach, one which not only reduces to the perturbation expansion under the conditions where perturbation theory is applicable but, in the general form, will still be valid where perturbation theory is not. The general method is that of the diagonalization of the matrix representation of the Hamiltonian $\mathcal{H}'$ in the basis set ψ_a^0 , and the nature of the perturbation theory validity criteria will be brought out during the development of the general method.

The first step in the development of the general method is to write the representation of the first-order wave functions ψ_a^1 in the zero-order basis set ψ_a^0 . From Appendix I, we can write (using bra-ket notation):

$$(3-3) \quad |\psi_a^1\rangle = \sum_b (\psi_b^0 | \psi_a^1) |\psi_b^0\rangle$$

Here of course, we have assumed that the ψ_b° are the N members of a complete orthonormal basis set. We now substitute equation (3-3) into equation (3-1). This gives:

$$(3-4) \quad \sum_b^N (\psi_b^\circ | \psi_a^1) \mathcal{H}' | \psi_b^\circ) = E_a^1 \sum_b^N (\psi_b^\circ | \psi_a^1) | \psi_b^\circ)$$

Multiplying both sides of equation (3-4) by $(\psi_c^\circ |$ and noting that the ψ_b° are an orthonormal set, i.e. $(\psi_b^\circ | \psi_c^\circ) = \delta_{bc}$, we have:

$$(3-5) \quad \begin{aligned} \sum_b^N (\psi_c^\circ | \mathcal{H}' | \psi_b^\circ) (\psi_b^\circ | \psi_a^1) &= E_a^1 \sum_b^N (\psi_c^\circ | \psi_b^\circ) (\psi_b^\circ | \psi_a^1) \\ &= E_a^1 \sum_b^N (\psi_b^\circ | \psi_a^1) \delta_{bc} \end{aligned}$$

or

$$(3-6) \quad \sum_b^N (\psi_c^\circ | \mathcal{H}' - E_a^1 \delta_{bc} | \psi_b^\circ) (\psi_b^\circ | \psi_a^1) = 0$$

As there are N of the ψ_c° , there are N of these equations.

We now use a more compact notation and equation (3-6) becomes:

$$(3-7) \quad \sum_b^N (H_{cb}^1 - E_a^1 \delta_{cb}) C_{ba} = 0$$

where

$$(3-8) \quad H_{cb}^1 = (\psi_c^\circ | \mathcal{H}' | \psi_b^\circ)$$

$$(3-9) \quad C_{ba} = (\psi_b^\circ | \psi_a^1)$$

Using equation (3-9), equation (3-3) can be written:

$$(3-10) \quad |\psi_a^1) = \sum_b^N C_{ba} |\psi_b^\circ)$$

The N equations given by equations (3-7) can be written in matrix notation

$$(3-11) \quad \begin{bmatrix} H_{11}^1 - E_a^1 & H_{12}^1 & \cdots & H_{1N}^1 \\ H_{21}^1 & H_{22}^1 - E_a^1 & \cdots & H_{2N}^1 \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1}^1 & H_{N2}^1 & \cdots & H_{NN}^1 - E_a^1 \end{bmatrix} \begin{bmatrix} C_{1a} \\ C_{2a} \\ \vdots \\ C_{Na} \end{bmatrix} = 0$$

We note two facts. First of all, if the above matrix representation of the Hamiltonian is diagonal, i.e. all off-diagonal elements H_{ij}^1 , $i \neq j$ are zero, then the chosen first-order wavefunctions ψ_a^1 are identical with the zero-order basis set ψ_a^0 . This can readily be shown. Setting the off-diagonal elements in equation (3-11) equal to zero, we have:

$$\begin{bmatrix} H_{11}^1 - E_a^1 & 0 & \cdots & 0 \\ 0 & H_{22}^1 - E_a^1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & H_{NN}^1 - E_a^1 \end{bmatrix} \begin{bmatrix} C_{1a} \\ C_{2a} \\ \vdots \\ C_{Na} \end{bmatrix} = 0$$

This is equivalent to the N equations

$$(H_{ii}^1 - E_a^1) C_{ia} = 0 \quad i = 1, N$$

and leads to the N equations

$$H_{ii}^1 - E_a^1 = 0$$

or $(\psi_i^\circ | \mathcal{H}' | \psi_i^\circ) = E_a^1$

This will be true only if $|\psi_i^\circ\rangle = |\psi_a^1\rangle$. Thus using equation (3-9), we have for the C_{ia}

$$(3-12) \quad C_{ia} = (\psi_i^\circ | \psi_a^1) = (\psi_i^\circ | \psi_i^\circ) = (\psi_a^1 | \psi_a^1) = 1$$

Thus the ψ_i° are eigenfunctions of $\mathcal{H}'$ and there is a one-to-one correspondence between the ψ_a^1 and the ψ_i° .

The second thing we can show is that if we represent the matrix equation (3-11) in the shorthand

$$(3-13) \quad HC = 0$$

then if the matrix H , the representation of the Hamiltonian, is not diagonal, then there is a unitary matrix S (satisfying $SS^{-1} = I$ where I is the unit matrix) which will diagonalize H by a similarity transformation. Thus we write:

$$(3-14) \quad SHC = SHS^{-1} SC = 0$$

where SHS^{-1} is diagonal. According to what we initially showed, the elements of the column matrix SC will be unity if SHS^{-1} is diagonal.

Thus we have:

$$SC = \begin{bmatrix} S_{11} & S_{12} & \cdots & S_{1N} \\ S_{21} & S_{22} & \cdots & S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N1} & S_{N2} & \cdots & S_{NN} \end{bmatrix} \begin{bmatrix} C_{1a} \\ C_{2a} \\ \vdots \\ C_{Na} \end{bmatrix} = \begin{bmatrix} S_{11}C_{1a} + S_{12}C_{2a} + \cdots + S_{1N}C_{Na} \\ S_{21}C_{1a} + S_{22}C_{2a} + \cdots + S_{2N}C_{Na} \\ \vdots \\ S_{N1}C_{1a} + S_{N2}C_{2a} + \cdots + S_{NN}C_{Na} \end{bmatrix} \begin{bmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{bmatrix}$$

This means that for all i

$$S_{i1} C_{1a} + S_{i2} C_{2a} + \dots + S_{iN} C_{Na} = 1 \quad i = 1, N$$

Substituting from equation (3-9), we have:

$$(3-15) \quad S_{i1} (\psi_1^0 | \psi_a^1) + S_{i2} (\psi_2^0 | \psi_a^1) + \dots + S_{iN} (\psi_N^0 | \psi_a^1) = 1 \quad i = 1, N$$

But for equation (3-15) to hold, we must have:

$$(3-16) \quad |\psi_a^1\rangle = S_{1i} |\psi_1^0\rangle + S_{2i} |\psi_2^0\rangle + \dots + S_{Ni} |\psi_N^0\rangle \quad i = 1, N$$

Thus the N first-order wave functions ψ_a^1 are given by the N equations specified by equation (3-16). We therefore note that if we determine the elements S_{ij} of the matrix S , the matrix that diagonalizes the matrix representation of the Hamiltonian, then we can determine the N linear combinations of the zero order basis functions that form the correct first-order eigenfunctions of $\mathcal{H}'$.

We note that diagonalization of H , the matrix representation of the Hamiltonian $\mathcal{H}'$ in the zero-order basis set ψ_a^0 , is the most general method of determining the correct eigenfunctions of $\mathcal{H}'$. However, this is usually a difficult task, so one looks for easier methods. Under certain special conditions, namely

$$(3-17) \quad (H_{ii}^1 - H_{jj}^1) \gg H_{ij}^1$$

diagonalization of H reduces to standard time independent perturbation theory. This is shown in Appendix I. When this condition does not hold,

such as for degenerate or near degenerate states, perturbation theory breaks down and one is forced to use the more general diagonalization procedure.

B. Choice of the Approximate Zero-order system and
Specification of Zero-order basis functions

The choice of the most appropriate approximate zero-order system will depend on the nature of the total first-order system. We postulate two limiting forms for the approximate system. The first would identify the complex molecular system itself with the approximate system. The second limiting case assumes for the approximate system an isolated, unsubstituted, non-vibrating chromophore, denoted here as the electronic system. In the first instance, we have a trivial identification and the adjective "approximate" is not even applicable. The second case is the simplest we can present and in most situations makes the discrepancy between the total and approximate systems so great that any advantage inherent in this approach to the problem is lost. Although in special instances, this second limiting case can be useful, usually the approximate system of choice lies somewhere between the two limiting cases.

In a quantum mechanical sense, specification of the wave functions of a system completely determines the physical properties of that system. Thus we shall specify the approximate systems by specifying their wave functions. There are many types of approximations that have been used, but most can be considered to be derived from two main classes; the electronic approximation (the second limiting case discussed above) and the vibronic (vibrational - electronic) approximation.

Each of these can be further subdivided according to whether or not the electronic portion of the wave function depends on the nuclear coordinate. If it does not, we term the approximation harmonic; if it does, we term it adiabatic (Footnote 5). Thus we have four basic approximations: harmonic electronic, adiabatic electronic, harmonic vibronic, and adiabatic vibronic. These are tabulated, along with the form of their wave functions, in Table V. In this Table

χ and q are the electronic and nuclear coordinates respectively, q^0 is the equilibrium nuclear position, $\phi_e^0(\chi, q^0)$ and $\phi_e^0(\chi, q)$ are the electronic wave functions, $\chi_{en}^0(q)$ are the nuclear wave functions. The subscripts e and n denote electronic and nuclear quantum numbers. A full description of these wave functions is found in Appendix VII.

Note that the form of the wave function of the electronic approximation includes no nuclear wave function. Thus if nuclear terms are included in the Hamiltonian $\mathcal{H}'$, the consequence is the occurrence of off-diagonal matrix elements in the representation of the Hamiltonian. These matrix elements may or may not be appreciable. In contrast, the form of the wave function of the vibronic approximation includes a nuclear wave function, and any off-diagonal matrix elements resulting from nuclear terms in $\mathcal{H}'$, are more likely to be small corrections. The harmonic vibronic approximation and the adiabatic vibronic approximation are commonly known as the two principle approximations of Born and Oppenheimer. Because of their importance, a rather detailed derivation and description is given in Appendix VII.

In Table VI, we list the various approximations most often used for zero-order basis functions. We include the basic electronic

TABLE V

Basic Wave Function Approximations

<div>Subtype</div> <div>Type</div>	Harmonic	Vibronic
Electronic	$\varphi_e^0(x, q^0)$	$\varphi_e^0(x, q)$
Vibronic	$\varphi_e^0(x, q^0) \chi_{en}^0(q)$	$\varphi_e^0(x, q) \chi_{en}^0(q)$

Type of Approximation	References Harmonic $\varphi_e^\circ = \varphi_e^\circ(x, q)$ Adiabatic $\varphi_e^\circ = \varphi_e^\circ(x, q)$		Zero-order Basis Functions	First-order Hamiltonian	Systems Appropriate For	Weakness of Approximation
Electronic	many workers	-----	φ_e°	$T_E(x) + V_E(x) + V_{EN}(x, q)$	Non-vibrating Monomer	Breaks Down for vibrating molecules
Excitonic	45,46,47 48,49,50 51	-----	$\frac{1}{N} \sum_i e^{-i\vec{k} \cdot \vec{r}_i} \varphi_e^{o(i)} \prod_{j \neq i} \varphi_e^{o(j)}$	$\sum_i [T_{Ei}(x_i) + V_{Ei}(x_i) + V_{EiNi}(x_i, q_i)]$ $+ \sum_{i,j} \sum_{N_i, N_j} V_{EiEj}(x_i, x_j)$	Non-vibrating Ordered Polymer	Breaks Down for Vibrating Molecules
Product	52,53 54,55	52,56	$\varphi_e^\circ \chi_{en}^\circ$	$T_E(x) + V_E(x) + V_{EN}(x, q)$ $+ T_N(q) + V_N(q)$	Non-degenerate Vibrating Monomers	Breaks Down for Degeneracy, Near Degeneracy
Sum of Products	-----	52,57,58 59,60,61 62,63,64	$\frac{1}{\sqrt{K}} \sum_i \varphi_e^{o(i)} \chi_{en}^{o(i)}$	$T_E(x) + V_E(x) + V_{EN}(x, q)$ $+ T_N(q) + V_N(q)$	Monomers and Dimers with Degenerate States	Unwieldy for N-mers higher than Dimers
Weak Coupling	65,66,67 68,69,70	71,72	$\frac{1}{N} \sum_i e^{-i\vec{k} \cdot \vec{r}_i} \varphi_e^{o(i)} \chi_{en}^{o(i)} \prod_{j \neq i} \varphi_e^{o(j)} \chi_{en}^{o(j)}$	$\sum_i [T_{Ei}(x_i) + V_{Ei}(x_i) + V_{EiNi}(x_i, q_i)$ $+ T_{Ni}(q_i) + V_{Ni}(q_i)]$ $+ \sum_{i,j} \sum_{N_i, N_j} [V_{EiEj}(x_i, x_j) + V_{NiNj}(q_i, q_j)]$	Polymers with Degenerate States and Weak Interactions	Breaks Down for Strong Intermolecular Coupling
Strong Coupling	68,69,70 73,74	71,75,76 77,78,79 80,81,82 45	$\frac{1}{N} \left[\sum_i e^{-i\vec{k} \cdot \vec{r}_i} \varphi_e^{o(i)} \prod_{j \neq i} \varphi_e^{o(j)} \right]$ $\times \left\{ \sum_i \left[e^{-i\vec{q} \cdot \vec{r}_i} \chi_{en}^{o(i)} \prod_{j \neq i} \chi_{en}^{o(j)} \right] \right.$ $\left. + \chi_{en}^{o(i)} \sum_{j \neq i} e^{-i\vec{q} \cdot \vec{r}_j} \chi_{en}^{o(j)} \prod_{k \neq i,j} \chi_{en}^{o(k)} \right\}$	$\sum_i [T_{Ei}(x_i) + V_{Ei}(x_i) + V_{EiNi}(x_i, q_i)$ $+ T_{Ni}(q_i) + V_{Ni}(q_i)]$ $+ \sum_{i,j} \sum_{N_i, N_j} [V_{EiEj}(x_i, x_j) + V_{NiNj}(q_i, q_j)]$	Polymers with Degenerate States and Strong Interactions	Breaks Down for Vibronic Coupling Comparable to Intermolecular Coupling
Strong Coupling, Second Quantization	-----	71,77,79 81,82	$(e, e_2, \dots, e_N\rangle p, p_2, \dots, p_N\rangle)$ where e_i, p_i represent the occupation numbers of the i^{th} exciton, i^{th} phonon modes	Modification of Rashba's Hamiltonian (82)	N exciton and/or phonon transitions where $N \geq 2$	Same as for Standard Strong Coupling Approximation

TABLE VI

Most Common Zero-order Systems

and vibronic approximations plus other more complex approximations stemming from extensions of the more basic ones. Each of these approximations can be subdivided, as mentioned previously, into harmonic and adiabatic approximations. These subdivisions can be identified by the arguments of the electronic parts of the zero-order wave functions as is indicated in Table V. Along with the form of the zero-order wave functions, we list in Table VI the references to workers who have used the harmonic and/or adiabatic subtypes of each approximation, the complex molecular system each approximation is most appropriate for, the first-order Hamiltonian $\mathcal{H}'$ of that system, and lastly the weakness and point of breakdown for each approximation.

Although Table VI is in general self-explanatory and can be an aid to proper selection of an appropriate zero-order approximating molecular system, a few comments are in order. First of all, in the formulae for the basis functions the unprimed subscripts e and n indicate the ground electronic and nuclear states while the primed subscripts e' and n' indicate the excited electronic state and the nuclear state of the excited electronic state. Secondly, a particularly good description of weak coupling, strong coupling, and the occupation number representation is given in Young's thesis (77). Finally, the development of the various first-order Hamiltonians are given in part C of this chapter.

C. Specification of first-order Hamiltonians

The first-order Hamiltonians given in Table VI can be considered as various simplifications of the complete solute Hamiltonian derived in Appendix VIII (Footnote 6). There the formalism for treating

solute-solvent interactions as well as the more familiar inter- and intra- solute effects are developed. As we are not concerned with solvent effects in this thesis, we may use equation (VIII-18) from Appendix VIII for the first-order Hamiltonian. Thus:

$$(3-18) \quad \mathcal{H}' = \sum_i^{\text{groups}} \left[T_{Ei} + V_{Ei} + V_{EiNi} + T_{Ni} + V_{Ni} \right] \\ + \sum_i^{\text{groups}} \sum_{j>i}^{\text{groups}} \left[V_{EiEj} + V_{NiNj} \right] + \sum_i^{\text{groups}} \sum_{j \neq i}^{\text{groups}} V_{EiNj}$$

Here the electrons and nuclei are assigned to particular groups and exchange among groups (such as charge transfer phenomena) is not considered. In general, we may substitute the term "chromophore" for the term "group". The various terms in $\mathcal{H}'$ are defined as follows:

$$T_{Ei} = T_{Ei}(\chi_i) \quad - \quad \text{electronic kinetic energy of chromophore } i$$

$$T_{Ni} = T_{Ni}(q_i) \quad - \quad \text{nuclear kinetic energy of chromophore } i$$

$$V_{Ei} = V_{Ei}(\chi_i) \quad - \quad \text{electron-electron potential of chromophore } i$$

$$V_{Ni} = V_{Ni}(q_i) \quad - \quad \text{nuclear-nuclear potential of chromophore } i$$

$$V_{EiNi} = V_{EiNi}(\chi_i, q_i) \quad - \quad \text{interactions between electrons and nuclei of chromophore } i$$

$$V_{EiEj} = V_{EiEj}(\chi_i, \chi_j) \quad - \quad \text{interactions between the electrons of chromophore } i \text{ and those of chromophore } j$$

$$V_{NiNj} = V_{NiNj}(q_i, q_j) \quad - \quad \text{interaction between the nuclei of chromophore } i \text{ and those of chromophore } j$$

$$V_{EiNj} = V_{EiNj}(\chi_i, q_j) \quad - \quad \text{interaction between the electrons of chromophore } i \text{ and the nuclei of chromophore } j$$

Here χ_i and q_i are the sets of electronic and nuclear

coordinates for the chromophore i .

It is worthwhile to discuss briefly the significance of the various terms in equation (3-18). The terms T_{Ei} , T_{Ni} , V_{Ei} , V_{Ni} are self-explanatory. The term V_{EiNi} leads to electron-nuclear coupling in each monomer (chromophore) and is responsible for the breakdown of the Born-Oppenheimer approximation in monomers. The term V_{EiEj} is the interaction responsible for polymer excitons and the term V_{NiNj} for polymer phonons. The relative magnitudes of V_{EiEj} and V_{EiNi} determine whether one is dealing with weak, intermediate, or strong coupling in the Simpson-Peterson definition (70), see also Young's thesis (77) for an excellent description of the various types of coupling). The interaction term V_{EiNj} also can cause breakdown of the Born-Oppenheimer approximation in polymers, but its effect is usually negligible compared to the combination of V_{EiEj} , V_{NiNj} and V_{EiNi} . Therefore, it is not included in any of the first-order Hamiltonians listed in Table VI.

D. Evaluation of Matrix Elements of Hamiltonian Representation

Having specified the zero-order basis functions of the approximate systems and the first-order Hamiltonians of the total systems, we now proceed with the evaluation of the matrix elements of the representations for the Hamiltonians of all cases, excepting those for weak and strong coupling. These latter two approximations are not evaluated, as such evaluation is quite complex and not of interest to us in this dissertation.

The matrix elements, diagonal and off-diagonal, for the various representations are evaluated in Appendix IX and tabulated in

Table VII. From inspection of the matrix elements listed in this table, we may draw several conclusions. First, in comparing the harmonic and adiabatic subtypes of each approximation, we see that while the wave functions of the harmonic approximations are more easily calculated than those of the adiabatic approximations, in general, the wave functions of the adiabatic approximations lead to representation matrices with fewer and simpler off-diagonal elements. Secondly, inspection of the various harmonic approximations indicate that the off-diagonal matrix elements are minimized when the quantities

$$V'_{EN} = \left. \frac{\partial V_{EN}(x, q)}{\partial q} \right|_{q=q^0}$$

$$V''_{EN} = \left. \frac{\partial^2 V_{EN}(x, q)}{\partial q^2} \right|_{q=q^0}$$

are minimized. The first parameter is important when discussing phenomena such as the Jahn-Teller effect, but in other cases is small. The second parameter, commonly known as the force constant, is more important. The smaller it is, the more shallow the molecular potential well, and the more valid is the harmonic approximation. Comparison of these harmonic approximations with the parallel adiabatic approximations indicate that only for the vibronic approximations do the matrices of the harmonic subtypes appear as complicated as those of the adiabatic subtypes. This is illusory however, as the only requirement that the off-diagonal elements be negligible in the adiabatic approximations, is that the electronic states be non-degenerate, while for the off-diagonal elements to be negligible in the harmonic approximation, we have the additional requirement on the size of the force constant. These factors

Approximate System	First-order Hamiltonian, Zero-order Wave Functions	Matrix Elements
Electronic Harmonic	$\mathcal{H}' = T_E(x) + V_E(x) + V_{EN}(x, q)$ $\Phi(e) = \varphi_e^0(x, q)$	<u>Diagonal</u> $(\Phi(e) \mathcal{H}' \Phi(e)) = E_e^0(q) + (q - q^0)^2 (\varphi_e^0 V_{EN}'' \varphi_e^0)$ <u>Off-diagonal</u> $(\Phi(e) \mathcal{H}' \Phi(e')) = (q - q^0) (\varphi_e^0 V_{EN}' \varphi_{e'}^0) + (q - q^0)^2 (\varphi_e^0 V_{EN}'' \varphi_{e'}^0)$
Electronic Adiabatic	$\mathcal{H}' = T_E(x) + V_E(x) + V_{EN}(x, q)$ $\Phi(e) = \varphi_e^0(x, q)$	<u>Diagonal</u> $(\Phi(e) \mathcal{H}' \Phi(e)) = E_e^0(q)$ <u>Off-diagonal</u> None
Excitonic Harmonic	$\mathcal{H}' = \sum_i [T_{E_i}(x_i) + V_{E_i}(x_i) + V_{E_i N_i}(x_i, q_i)] + \sum_{i,j} \sum_{i \neq j} V_{E_i E_j}(x_i, x_j)$ $\Phi(k, e) = \frac{1}{N!} \sum_i e^{-i\hat{k} \cdot \hat{r}_i} \varphi_e^{(i)} \prod_{j \neq i} \varphi_e^{(j)}$ $\varphi_e^{(i)} = \varphi_e^0(x_i, q_i)$	<u>Diagonal</u> $(\Phi(k, e) \mathcal{H}' \Phi(k, e)) = E_0^0(q) + (N-1) E_e^0(q) + \sum_i (q_i - q_i^0)^2 (\varphi_e^{(i)} V_{E_i N_i}'' \varphi_e^{(i)})$ $+ \frac{1}{N} \sum_i (q_i - q_i^0)^2 [(\varphi_e^{(i)} V_{E_i N_i}'' \varphi_e^{(i)}) - (\varphi_e^{(i)} V_{E_i N_i}'' \varphi_e^{(i)})]$ $+ \frac{1}{N} \sum_i \sum_{j \neq i} [(\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)}) - (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)})]$ $+ \frac{1}{N} \sum_i \sum_{j \neq i} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)}) + \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i\hat{k} \cdot (\hat{r}_i - \hat{r}_j)} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)})$ <u>Off-diagonal</u> $(\Phi(k, e) \mathcal{H}' \Phi(k', e')) = \frac{1}{N} \sum_i (q_i - q_i^0) (\varphi_e^{(i)} V_{E_i N_i}' \varphi_{e'}^{(i)}) + \frac{1}{N} \sum_i (q_i - q_i^0)^2 (\varphi_e^{(i)} V_{E_i N_i}'' \varphi_{e'}^{(i)})$ $+ \frac{1}{N} \sum_i \sum_{j \neq i} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_{e'}^{(i)} \varphi_{e'}^{(j)}) - \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i\hat{k} \cdot (\hat{r}_i - \hat{r}_j)} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_{e'}^{(i)} \varphi_{e'}^{(j)})$ $(\Phi(k, e) \mathcal{H}' \Phi(k', e')) = \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \hat{r}_i} (q_i - q_i^0)^2 [(\varphi_e^{(i)} V_{E_i N_i}'' \varphi_{e'}^{(i)}) - (\varphi_e^{(i)} V_{E_i N_i}'' \varphi_{e'}^{(i)})]$ $+ \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \hat{r}_i} \sum_{j \neq i} [(\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_{e'}^{(i)} \varphi_{e'}^{(j)}) - (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_{e'}^{(i)} \varphi_{e'}^{(j)})]$ $+ \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i(\hat{k} \cdot \hat{r}_i - \hat{k}' \cdot \hat{r}_j)} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_{e'}^{(i)} \varphi_{e'}^{(j)})$

TABLE VII

Matrix Elements of Various Representations of the Hamiltonian

Approximate System	First-order Hamiltonian, Zero-order Wave Functions	Matrix Elements
Excitonic Harmonic (cont.)		<u>Off-diagonal (cont.)</u> $(\Phi(\hat{k}, e') \mathcal{H}' \Phi(\hat{k}, e'')) = \frac{1}{N} \sum_i e^{-i(\hat{k}-\hat{k}') \cdot \hat{r}_i} [(q_i - q_i^0)(\varphi_e^{(i)} V_{E_i N_i}' \varphi_e^{(i)}) + (q_i - q_i^0)^2 (\varphi_e^{(i)} V_{E_i N_i}'' \varphi_e^{(i)})]$ $+ \frac{1}{N} \sum_i e^{-i(\hat{k}-\hat{k}') \cdot \hat{r}_i} \sum_{j \neq i} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)}) + \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i(\hat{k} \cdot \hat{r}_i - \hat{k}' \cdot \hat{r}_j)} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)})$
Excitonic Adiabatic	$\mathcal{H}' = \sum_i [T_{E_i}(x_i) + V_{E_i}(x_i) + V_{E_i N_i}(x_i, q_i)]$ $+ \sum_i \sum_{j \neq i} V_{E_i E_j}(x_i, x_j)$ $\Phi(\hat{k}, e') = \frac{1}{N} \sum_i e^{-i\hat{k} \cdot \hat{r}_i} \varphi_e^{(i)} \prod_{j \neq i} \varphi_e^{(j)}$ $\varphi_e^{(j)} = \varphi_e^{(j)}(x_j, q_j)$	<u>Diagonal</u> $(\Phi(\hat{k}, e') \mathcal{H}' \Phi(\hat{k}, e')) = \frac{1}{N} \sum_i [E_e^{(i)}(q_i) + \sum_{j \neq i} E_e^{(j)}(q_j)]$ $+ \frac{1}{N} \sum_i \sum_{j \neq i} [(\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)}) - (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)})]$ $+ \frac{1}{N} \sum_i \sum_{j \neq i} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)}) + \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i\hat{k}(\hat{r}_i - \hat{r}_j)} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)})$ <u>Off-diagonal</u> $(\Phi(\hat{k}, e') \mathcal{H}' \Phi(\hat{k}, e'')) = \frac{1}{N} \sum_i \sum_{j \neq i} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)}) + \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i\hat{k}(\hat{r}_i - \hat{r}_j)} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)})$ $(\Phi(\hat{k}, e') \mathcal{H}' \Phi(\hat{k}', e')) = \frac{1}{N} \sum_i e^{-i(\hat{k}-\hat{k}') \cdot \hat{r}_i} \sum_{j \neq i} [(\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)}) - (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)})]$ $+ \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i(\hat{k} \cdot \hat{r}_i - \hat{k}' \cdot \hat{r}_j)} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)})$ $(\Phi(\hat{k}, e') \mathcal{H}' \Phi(\hat{k}, e'')) = \frac{1}{N} \sum_i e^{-i(\hat{k}-\hat{k}') \cdot \hat{r}_i} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)})$ $+ \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i(\hat{k} \cdot \hat{r}_i - \hat{k}' \cdot \hat{r}_j)} (\varphi_e^{(i)} \varphi_e^{(j)} V_{E_i E_j} \varphi_e^{(i)} \varphi_e^{(j)})$
Vibronic Product Harmonic	$\mathcal{H}' = T_E(x) + V_E(x) + V_{EN}(x, q)$ $+ V_N(q) + T_N(q)$ $\Phi(e, n) = \varphi_e^0 \chi_{en}^0$ $\varphi_e^0 = \varphi_e^0(x, q)$ $\chi_{en}^0 = \chi_{en}^0(q)$	<u>Diagonal</u> $(\Phi(e, n) \mathcal{H}' \Phi(e, n)) = E_{en}^0 + (\varphi_e^0 V_{EN}'' \varphi_e^0)(\chi_{en}^0 (q - q^0)^2 \chi_{en}^0)$ <u>Off-diagonal</u> $(\Phi(e, n) \mathcal{H}' \Phi(e, n')) = (\varphi_e^0 V_{EN}'' \varphi_e^0)(\chi_{en}^0 (q - q^0)^2 \chi_{en'}^0)$ $(\Phi(e, n) \mathcal{H}' \Phi(e', n')) = (\varphi_e^0 V_{EN}' \varphi_e^0)(\chi_{en}^0 (q - q^0) \chi_{e'n'}^0) + (\varphi_e^0 V_{EN}'' \varphi_e^0)(\chi_{en}^0 (q - q^0)^2 \chi_{e'n'}^0)$

TABLE VII (cont.)

Approximate System	First-order Hamiltonian, Zero-order Wave Functions	Matrix Elements
Vibronic Product Adiabatic	$\mathcal{H}' = T_E(x) + V_E(x) + V_{EN}(x, q)$ $+ V_N(q) + T_N(q)$ $\Phi(e, n) = \varphi_e^0 \chi_{en}^0$ $\varphi_e^0 = \varphi_e^0(x, q)$ $\chi_{en}^0 = \chi_{en}^0(q)$	<u>Diagonal</u> $(\Phi(e, n) \mathcal{H}' \Phi(e, n)) = E_{en}^0 + (\chi_{en}^0 \{(\varphi_e^0 T_N \varphi_e^0)\} \chi_{en}^0)$ <u>Off-diagonal</u> $(\Phi(e, n) \mathcal{H}' \Phi(e, n')) = (\chi_{en}^0 \{(\varphi_e^0 T_N \varphi_e^0)\} \chi_{en'}^0)$ $(\Phi(e, n) \mathcal{H}' \Phi(e', n')) = (\chi_{en}^0 \{(\varphi_e^0 T_N \varphi_{e'}^0)\} \chi_{en'}^0) + \frac{1}{2M} (\chi_{en}^0 \{(\varphi_e^0 P_N \varphi_{e'}^0) P_N\} \chi_{en'}^0)$
Vibronic Sum of Products Harmonic	$\mathcal{H}' = T_E(x) + V_E(x) + V_{EN}(x, q)$ $+ V_N(q) + T_N(q)$ $\Phi(e, n, \kappa) = \frac{1}{\sqrt{\kappa}} \sum_i \varphi_e^{o(i)} \chi_{en}^{o(i)}$ $\varphi_e^{o(i)} = \varphi_e^{o(i)}(x, q^o)$ $\chi_{en}^{o(i)} = \chi_{en}^{o(i)}(q)$	<u>Diagonal</u> $(\Phi(e, n, \kappa) \mathcal{H}' \Phi(e, n, \kappa)) = \frac{1}{\kappa} \sum_i E_{en}^{o(i)} + \frac{1}{\kappa} \sum_i (\varphi_e^{o(i)} V_{EN}'' \varphi_e^{o(i)}) (\chi_{en}^{o(i)} (q - q^o)^2 \chi_{en}^{o(i)})$ <u>Off-diagonal</u> $(\Phi(e, n, \kappa) \mathcal{H}' \Phi(e, n', \kappa)) = \frac{1}{\kappa} \sum_i (\varphi_e^{o(i)} V_{EN}'' \varphi_e^{o(i)}) (\chi_{en}^{o(i)} (q - q^o)^2 \chi_{en'}^{o(i)})$ $(\Phi(e, n, \kappa) \mathcal{H}' \Phi(e', n', \kappa')) = (\frac{1}{\kappa \kappa'})^{1/2} \sum_i \sum_j^{K'} (\varphi_e^{o(i)} V_{EN}' \varphi_{e'}^{o(j)}) (\chi_{en}^{o(i)} q - q^o \chi_{e'n'}^{o(j)})$ $+ (\frac{1}{\kappa \kappa'})^{1/2} \sum_i \sum_j^{K'} (\varphi_e^{o(i)} V_{EN}'' \varphi_{e'}^{o(j)}) (\chi_{en}^{o(i)} (q - q^o)^2 \chi_{e'n'}^{o(j)})$
Vibronic Sum of Products Adiabatic	$\mathcal{H}' = T_E(x) + V_E(x) + V_{EN}(x, q)$ $+ V_N(q) + T_N(q)$ $\Phi(e, n, \kappa) = \frac{1}{\sqrt{\kappa}} \sum_i \varphi_e^{o(i)} \chi_{en}^{o(i)}$ $\varphi_e^{o(i)} = \varphi_e^{o(i)}(x, q)$ $\chi_{en}^{o(i)} = \chi_{en}^{o(i)}(q)$	<u>Diagonal</u> $(\Phi(e, n, \kappa) \mathcal{H}' \Phi(e, n, \kappa)) = \frac{1}{\kappa} \sum_i E_{en}^{o(i)} + \frac{1}{\kappa} \sum_i (\chi_{en}^{o(i)} \{(\varphi_e^{o(i)} T_N \varphi_e^{o(i)})\} \chi_{en}^{o(i)})$ <u>Off-diagonal</u> $(\Phi(e, n, \kappa) \mathcal{H}' \Phi(e, n', \kappa)) = \frac{1}{\kappa} \sum_i (\chi_{en}^{o(i)} \{(\varphi_e^{o(i)} T_N \varphi_e^{o(i)})\} \chi_{en'}^{o(i)})$ $(\Phi(e, n, \kappa) \mathcal{H}' \Phi(e', n', \kappa')) = (\frac{1}{\kappa \kappa'})^{1/2} \sum_i \sum_j^{K'} (\chi_{en}^{o(i)} \{(\varphi_e^{o(i)} T_N \varphi_{e'}^{o(j)})\} \chi_{e'n'}^{o(j)})$ $+ (\frac{1}{\kappa \kappa'})^{1/2} \sum_i \sum_j^{K'} (\chi_{en}^{o(i)} \frac{1}{2M} (\varphi_e^{o(i)} P_N \varphi_{e'}^{o(j)}) P_N \chi_{e'n'}^{o(j)})$

TABLE VII (cont.)

are discussed in more detail in Appendix VII.

Having obtained the matrix elements of the chosen representation of the Hamiltonian, one can proceed to diagonalize the matrix. This is, in almost all instances, a very difficult task. Therefore, it is important to determine when the more simple procedure of perturbation theory is valid. The main factor in this determination is the magnitude of the off-diagonal matrix elements compared with the magnitude of the diagonal elements. This was discussed in Appendix I and part A of this chapter. In the extensions of optical activity, it is convenient to choose our representation so that perturbation theory is valid. We will base our choice of representation on the size and number of off-diagonal matrix elements as listed in Table VII.

E. Perturbation Theory and Extensions of the Theory of Optical Activity.

In Chapter 4, we use a perturbation expansion to extend the theory of optical activity to the investigation of some of the effects of vibrational and substitutional perturbations on the phenomena of absorption, natural optical activity, and magnetically-induced optical activity, determining the symmetry patterns that alter, enhance and allow the various electronic transitions for molecules in the point group C_{4v} . Here we find that previous authors investigating these systems had chosen their approximate systems without a critical examination of the magnitude of the various off-diagonal matrix elements. This led to the implicit ignoring of certain

off-diagonal matrix elements of the representation of the Hamiltonians, and these matrix elements were never proven negligible. It is entirely possible, and in some cases even more likely, that this neglect of the off-diagonal elements was justified. However, it is important to confirm such approximations, and it is for this reason that the tabulation of the matrix elements, such as is done in Table VII, is important.

In conclusion, this chapter provides a basic formalism upon which to base future extensions of the theory of optical activity. It offers a guide to choosing the most appropriate approximate system and a method to determine whether perturbation theory is a valid technique for the problem under investigation. Finally, if perturbation theory is valid, the information needed to generate the perturbation expansions is supplied in Tables VI and VII.

FOOTNOTES - Chapter 3

1. The adjective "stationary" derives from the fact that these states, in the absence of an external perturbation, are invariant with time.
2. It is worth noting here that for an unsubstituted, isolated, chromophore, only the magnetically-induced optical activity will be non-zero, unless the chromophore is inherently asymmetric.
3. It is, of course, evident that the stationary states of the simple system are not stationary states of the more complex system. The complex molecular system, placed in one of these non-stationary states (through radiative or other means) can undergo non-radiative transitions to other non-stationary states under the influence of those molecular perturbations that mix these states. This is the basis of the radiationless transition process.
4. In the remainder of Chapter 3 we shall use the terms -- complex, total, and first-order -- interchangeably, as also the terms -- simple, approximate, and zero-order.
5. The meaning of the terms, harmonic and adiabatic, as applied to the vibronic approximation are explained fully in Appendix VII. Their meaning, when applied to the electronic approximation, is of similar nature.
6. The first-order 2nd quantization Hamiltonian for one exciton-one phonon transitions can be derived from the complete solute Hamiltonian

developed in Appendix VIII. However, the derivation is not as simple as that of the other first-order Hamiltonians listed in Table VI; these latter being obtained simply by keeping or discarding terms of equation (VIII-18) or Appendix VIII. For a clear derivation of the occupation number representation and the 2nd quantization Hamiltonian, see Young (77). The 2nd quantization procedure has the advantages that one can most easily treat multi-phonon and multi-exciton problems.

Chapter 4

THE SYMMETRY PATTERNS OF VIBRATIONAL
AND SUBSTITUTIONAL PERTURBATIONS ON ABSORPTION,
NATURAL OPTICAL ACTIVITY AND MAGNETICALLY-INDUCED
OPTICAL ACTIVITY

A. Introduction and Definition of the Problem

In the previous chapters, we have developed the general theory of optical activity and the formalism necessary to extend this theory to various complex systems. In this chapter, we consider one such extension, namely the analysis of vibrational and substitutional structuring in natural and magnetically-induced optical activity. For comparison we also consider such structuring in absorption.

A complete accounting of vibrational and substitutional structuring would include a detailed analysis of not only the type, but also the magnitude, of the various perturbations. However, such a quantitative treatment would be very complex, and sufficient groundwork has not been done in the qualitative aspects to justify such an undertaking. We therefore restrict ourselves to the classification of type of perturbation, and in particular, to the symmetry patterns that are important to the character of absorption and optical activity.

Although this approach may appear to limit us, there is a great deal of information about molecular systems to be obtained through the basic application of the symmetry rules of group theory. In general, symmetry rules yield two classes of information. First, the number and kinds of energy levels (states) which an atom or molecule may have are rigorously and precisely determined by the symmetry of the

molecule or of the environment of the atom. Secondly, symmetry tells us whether or not transitions between these states are allowed. These two types of information, and their various applications, form powerful tools for the determination of the nature of molecular systems (Footnote 1). In this chapter, we shall deal primarily with the second type of information and attempt to determine the specific vibrational and substitutional symmetry patterns that alter, enhance, and allow the various electronic transitions in the three types of molecular spectra of interest -- i.e. absorption, natural optical activity, and magnetically-induced optical activity.

The analysis proceeds in the following manner. First, there is a selection of the most appropriate approximate system and its associated zero-order wave functions. This choice depends on the nature of the complex system to be approximated -- in this case, a vibrating substituted chromophore -- and gives due consideration to the diagonalization problem discussed in Chapter 3. Next, the first-order wave functions (of the complex system) are expanded, via perturbation theory, in the zero-order wave functions. These wave function expansions are then substituted into the various matrix elements of the oscillator strength D_{ab} , the natural rotational strength R_{ab} , and the magnetic rotational strengths A_{ab} , B_{ab} , C_{ab} . Whereas the oscillator and rotational strengths were previously expressed in terms of matrix elements of the first-order wave functions, they are now expressed in terms of matrix elements of the zero-order wave functions. This resultant expansion is maintained to third-order in the perturbations for absorption and natural optical activity and to second-order for magnetically-induced optical activity. The resultant terms of these perturbation expansions

are then symmetry analyzed, initially on a preliminary basis which eliminates many terms from consideration, and finally, by a computer analysis, which applies the rules of group theory and tabulates the important symmetry patterns. The need for a computer program for such calculations becomes most evident when considering molecular systems belonging to point groups having degenerate representations, i.e. those molecular systems with a three-fold or higher axis of symmetry. The degeneracy introduces complexities which make the task of evaluating symmetry patterns next to impossible without a computer. These complexities are discussed in the latter part of this chapter.

In part B of this chapter, we attempt to clarify what the problems are in determining the important symmetry patterns. This is best done by reference to simplified examples, in this case, first-order perturbation expansions, in vibration and substitution, for the oscillator strength and the natural rotational strength, of a molecule belonging to a point group with no degenerate representations. In addition to point out the difficulties and the need for a computer program, we obtain several "symmetry conclusions" which are general statements about the symmetry properties of the vibrational and electronic wave functions of the various molecular states involved in vibronic transitions. In the final part of this chapter, part C, we investigate the symmetry patterns of vibrational and substitutional perturbations of the three optical phenomena for a particular point group C_{4v} that contains degenerate representations.

B. Illustrative Examples of Symmetry Analysis

The basic examples we use in order to illustrate the general

procedure of symmetry analysis are first-order perturbation expansions in vibration and substitution, of the oscillator strength and the natural rotational strength. As examples, we use only molecules belonging to point groups with no degenerate representations, thereby avoiding all the problems associated with degeneracy; the treatment of these being reserved for part C of this chapter. Before we begin, it is well to note that many of the symmetry conclusions developed in this part of the chapter were first pointed out either by Albrecht (53) in his work on vibronic structuring in absorption, by Weigang (33) in his investigation into vibronic structuring in circular dichroism, or by Schellman (31) in his symmetry treatment of substitutional influences in natural optical activity.

We first develop the first-order perturbation equations for the oscillator strength and for the natural rotational strength. From equation (2-100) of Chapter 2, we have:

$$D_{ab} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Re} \{ \vec{\mu}_{ba} \cdot \vec{\mu}_{ab} \} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Re} \{ (\psi_b^1 | \vec{\mu} | \psi_a^1) \cdot (\psi_a^1 | \vec{\mu} | \psi_b^1) \}$$

$$R_{ab} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Im} \{ \vec{\mu}_{ba} \cdot \vec{m}_{ab} \} = \frac{1}{d_a} \sum_{a,b}^{\text{mem}} \text{Im} \{ (\psi_b^1 | \vec{\mu} | \psi_a^1) \cdot (\psi_a^1 | \vec{m} | \psi_b^1) \}$$

where a is our first-order initial state and b our first-order final state. As will be shown in part C of this chapter, we can choose as our first-order wave functions, the Born-Oppenheimer adiabatic vibronic approximations, and as our zero-order wave functions, the Born-Oppenheimer harmonic vibronic approximations. We shall henceforth label our ground state by the index j , our excited state by the index k , and any other states of interest by the indices l, m, n . Furthermore,

we condense our notation so that the first-order adiabatic states appear as:

$$(4-1) \quad \begin{aligned} (\psi_a^1| \Rightarrow (\psi_j^1| &= (\varphi_j^1|(\chi_{ja}| = (J|(j| = (J_j| \\ (\psi_b^1| \Rightarrow (\psi_k^1| &= (\varphi_k^1|(\chi_{ks}| = (K|(k| = (K_k| \end{aligned}$$

and the zero-order harmonic states appear as:

$$(4-2) \quad \begin{aligned} (\psi_a^0| \Rightarrow (\psi_j^0| &= (\varphi_j^0|(\chi_{ja}| = (J^0|(j| = (J_j^0| \\ (\psi_b^0| \Rightarrow (\psi_k^0| &= (\varphi_k^0|(\chi_{ks}| = (K^0|(k| = (K_k^0| \end{aligned}$$

where $(J|$ and $(K|$ are the adiabatic ground and excited electronic wave functions, $(J^0|$ and $(K^0|$ are the harmonic ground and excited electronic wave functions, and $(j|$ and $(k|$ represent the product wave function description of vibration in the ground state and in the excited state.

The states $(j|$ and $(k|$ are written as:

$$(4-3) \quad \begin{aligned} (j| &= (j_1|(j_2| \cdots (j_n| \cdots \\ (k| &= (k_1|(k_2| \cdots (k_n| \cdots \end{aligned}$$

where $(j_n|$ and $(k_n|$ are the j^{TH} and k^{TH} quantum of the $\mathcal{N}^{\text{TH}}$ normal mode in the ground and excited state respectively (Footnote 2).

Now substituting equations (4-1) into the equation for we have for the specific transition $j \rightarrow k$:

$$(4-4) \quad \begin{aligned} D_{jk} &= \frac{1}{d_j} \sum_{j,k}^{\text{mem}} \text{Re} \{ (K_k|\vec{\mu}|J_j) \cdot (J_j|\vec{\mu}|K_k) \} \\ R_{jk} &= \frac{1}{d_j} \sum_{j,k}^{\text{mem}} \text{Im} \{ (K_k|\vec{\mu}|J_j) \cdot (J_j|\vec{m}|K_k) \} \end{aligned}$$

Expanding the dot products and considering the x components

(Footnote 3):

$$D_{jk}(x) = \frac{1}{d_j} \sum_{j,k}^{\text{mem}} \text{Re} \{ (K_k | \mu_x | J_j) (J_j | \mu_x | K_k) \}$$

(4-5)

$$R_{jk}(x) = \frac{1}{d_j} \sum_{j,k}^{\text{mem}} \text{Im} \{ (K_k | \mu_x | J_j) (J_j | m_x | K_k) \}$$

We now apply first-order perturbation theory to the wave functions $(K_k |$ and $(J_j |$. These wave functions appear only in the matrix elements in equation (4-5) and therefore, we consider only these matrix elements in our analysis. We now present without proof the first-order perturbation expansions of the matrix element products of equation (4-5). See (Footnote 4).

$$\begin{aligned} (K_k | \mu_x | J_j) (J_j | \mu_x | K_k) &= (K^0 | \mu_x | J^0) (J^0 | \mu_x | K^0) (k | j) (j | k) \\ &+ \sum_l \sum_{L^0 \neq K^0} F_{L^0 K^0}^1 (K^0 | \mu_x | J^0) (J^0 | \mu_x | L^0) (k | j) (j | l) + [\text{c.c.}] \\ &+ \sum_m \sum_{M^0 \neq J^0} F_{M^0 J^0}^1 (K^0 | \mu_x | M^0) (J^0 | \mu_x | K^0) (k | m) (j | k) + [\text{c.c.}] \end{aligned}$$

(4-6)

$$\begin{aligned} (K_k | \mu_x | J_j) (J_j | m_x | K_k) &= (K^0 | \mu_x | J^0) (J^0 | m_x | K^0) (k | j) (j | k) \\ &+ \sum_l \sum_{L^0 \neq K^0} F_{L^0 K^0}^1 (K^0 | \mu_x | J^0) (J^0 | m_x | L^0) (k | j) (j | l) + [\text{c.c.}] \\ &+ \sum_m \sum_{M^0 \neq J^0} F_{M^0 J^0}^1 (K^0 | \mu_x | M^0) (J^0 | m_x | K^0) (k | m) (j | k) + [\text{c.c.}] \end{aligned}$$

where [c.c.] indicates the complex conjugate of the preceding expression, and we have used the notation of equation (4-2) for the zero-order harmonic wave functions. States (L^0) and (M^0) are "mixing" states whose character is borrowed by the ground and the excited states.

As we need only one of the four first-order terms in each of equation (4-6a) and (4-6b) to illustrate the various steps of the analysis, we choose the second term of each equation, and we define the coefficient F_{LK}^1 , again without proof, as:

$$(4-7) \quad F_{LK}^1 = \frac{1}{\hbar(\omega_K^0 - \omega_L^0)} \left\{ (L^0 | V_a | K^0) (l | k) + \sum_n^R (L^0 | \mathcal{H}_n | K^0) (l | Q_n | k) \right\}$$

Here the first term in the brackets is the substitutional contribution, and the remaining R terms are the vibrational contributions, where R is the number of modes of the vibrating system. V_a is the potential energy of the substitutional perturbation, Q_n is the normal mode coordinate, $\mathcal{H}_n = \left(\frac{\partial \mathcal{H}'}{\partial Q_n} \right)_0$ (Footnote 5), $\mathcal{H}_n Q_n$ is the Hamiltonian of the n^{th} vibrational perturbation, the $\sum_n^R$ is over all normal modes, and ω_K^0, ω_L^0 are the zero-order frequencies corresponding to the energies of the zero-order states $E_K^0 = \hbar \omega_K^0$, $E_L^0 = \hbar \omega_L^0$.

Substituting the above expression for F_{LK}^1 into the second term of equations (4-6a) and into the second term of equation (4-6b) and isolating these terms, we have:

$$(4-8) \quad \begin{aligned} & \left[(K_k | \vec{\mu} | J_j) \cdot (J_j | \vec{\mu} | K_k) \right] \substack{\text{x component, 2nd term,} \\ \text{substitutional and vibrational contribution}} \\ &= \sum_l \sum_{L^0+K^0} \frac{1}{\hbar(\omega_K^0 - \omega_L^0)} \left\{ (K^0 | \mu_x | J^0) (J^0 | \mu_x | L^0) (L^0 | V_a | K^0) (k | j) (j | l) (l | k) \right. \\ & \quad \left. + \sum_n^R (K^0 | \mu_x | J^0) (J^0 | \mu_x | L^0) (L^0 | \mathcal{H}_n | K^0) (k | j) (j | l) (l | Q_n | k) \right\} \end{aligned}$$

$$\begin{aligned}
 & \left[(K_k | \vec{\mu} | J_j) \cdot (J_j | \vec{m} | K_k) \right] \times \text{component, 2nd term,} \\
 & \quad \text{substitutional and vibrational contribution} \\
 (4-9) \quad & = \sum_k \sum_{L^0 \neq K^0} \frac{1}{\hbar(\omega_k^0 - \omega_{L^0}^0)} \left\{ (K^0 | \mu_x | J^0) (J^0 | m_x | L^0) (L^0 | V_a | K^0) (k | j) (j | l) (l | k) \right. \\
 & \quad \left. + \sum_{\lambda} (K^0 | \mu_x | J^0) (J^0 | m_x | L^0) (L^0 | \mathcal{Q}_{\lambda} | K^0) (k | j) (j | l) (l | Q_{\lambda} | k) \right\}
 \end{aligned}$$

We must now describe the basic principles underlying the symmetry arguments to follow. First, in order for any term of any component to have a non-zero vibrational or substitutional contribution, all matrix elements in that contribution must be non-zero. In each of equations (4-8) and (4-9) we have $R+1$ contributions: one substitutional contribution and R vibrational contributions. With each contribution are associated six matrix elements, three of which involve the electronic wave functions and three of which involve the vibrational wave functions. For any one of these $R+1$ contributions to be non-zero, all of its associated six matrix elements must be non-zero. Or, in other words, if any one of these matrix elements is zero, then the vibrational or substitutional contribution to which it belongs is zero. With this in mind, in the following discussion we specify a condition on each matrix element which, if not satisfied, is sufficient to set that matrix element equal to zero, and thus to eliminate from further consideration the associated contribution.

All of the symmetry operations -- rotations, inversions, translations -- which take the molecular system into itself, make up the elements of the point group of the molecular system (Footnote 6). Each of these symmetry elements operating on a matrix element multiplies that matrix element by some factor (Footnote 7). As a matrix element represents a property of the molecular system, it must be invariant under

each of these symmetry elements. Therefore, either all of the multiplying factors are $+1$ or the matrix element is zero. As the matrix element must belong to the totally symmetric representation for all the factors to be $+1$, if it is not totally symmetric, it must be zero. Thus, if not all of the matrix elements of a particular vibrational or substitutional contribution are totally symmetric, then that contribution is zero. This is the basic formula we shall continually follow as we proceed through the simple illustrative symmetry examples in this part of Chapter 3 and through the more complex analysis in part C. However, it must be noted that the condition that all matrix elements be totally symmetric is necessary but not sufficient to ensure that the vibrational or substitutional contribution containing these matrix elements is non-zero. This is because a totally symmetric matrix element can still be zero if the integral to which it is equivalent calculates to be zero.

We now apply the symmetry principles described above to the substitutional contributions to equations (4-8) and (4-9). We immediately conclude (from either equation) that for the three vibrational matrix elements to be non-zero, the relation $\Gamma_f = \Gamma_l = \Gamma_k$ must hold, where Γ_f is the symmetry representation of the vibrational wave function $|f\rangle$, Γ_l that of $|l\rangle$, and Γ_k that of $|k\rangle$. The basis of this conclusion is that all three matrix elements must be totally symmetric and therefore the following direct product relations must hold (Footnote 8):

$$\begin{aligned}
 (4-10) \quad & \Gamma_f \otimes \Gamma_l = \Gamma_0 & \therefore \Gamma_f = \Gamma_l \\
 & \Gamma_f \otimes \Gamma_k = \Gamma_0 & \therefore \Gamma_f = \Gamma_k \\
 & \Gamma_k \otimes \Gamma_l = \Gamma_0 & \therefore \Gamma_k = \Gamma_l
 \end{aligned}$$

where Γ_0 is the totally symmetric representation. We may, however, make an even stronger statement. Using equation (4-3) to expand $\langle k|f\rangle$, we

have:

$$(4-11) \quad (k|j) = (k_1|j_1)(k_2|j_2) \cdots (k_n|j_n) \cdots$$

Following the same reasoning as above and extending the results to the matrix elements $(j|l)$ and $(l|k)$ we have:

$$(4-12) \quad \begin{aligned} \Gamma_{k_n} &= \Gamma_{j_n} \\ \Gamma_{j_n} &= \Gamma_{l_n} \\ \Gamma_{l_n} &= \Gamma_{k_n} \end{aligned} \quad n = 1, 2, \cdots, R$$

Therefore, we have reached our first conclusion, which will hold for all orders of perturbation.

Conclusion 1. Substitutional perturbations induce mixing and allow transitions only between vibronic states whose vibrational wave functions have the same symmetry. Furthermore, for individual normal mode vibrations, symmetry must be conserved in the transitions or mixing. Therefore, the selection rule is that the change of quantum number for each normal mode must be even.

The symmetry requirements specified in this conclusion are a necessary but not sufficient condition that the vibrational matrix elements of the substitutional contributions be non-zero. The natures of the potential energy surfaces in the ground and the excited states are also a factor. We consider two cases (also discussed by Weigang (33)):

(i) the case of vertical potential surfaces, where the potential energy surfaces of the ground and excited states differ only by a constant and are otherwise identical; (ii) and the case of nonvertical potential surfaces, where the potential energy surfaces of the ground and excited state can also differ in equilibrium position, force constant, degree of anharmonicity, etc. For the first case, vertical potential surfaces,

we can replace all $(k_n|$ in equation (4-11) with $(j'_n|$, as the vibrational wave functions of the ground state also serve as those of the excited state. Thus:

$$(4-13) \quad (k|f) = (j'_1|f_1)(j'_2|f_2) \cdots (j'_n|f_n) \cdots$$

Only if all $j'_n = j_n$, the case of no vibrational excitation, is the matrix element $(k|f)$ non-zero. This is a result of the orthogonality of the wave functions. For non-vertical potential surfaces, we may not make the substitution $(k_n| = (j'_n|$ in equation (4-11), and the value of $(k|f)$ is determined by the various French-Condon factors $(k_n|j_n)$. The above discussion of the two cases for potential energy surfaces applies to other matrix elements than $(k|f)$. It also applies to $(f|l)$ and $(l|k)$, and we may therefore write a corollary of Conclusion 1.

Conclusion 1a. For vertical potential surfaces, there must be, in addition to the symmetry requirement, no vibrational change from ground to excited state. The same requirement holds for both the ground and for the excited states with respect to the mixing states. For non-vertical potential surfaces, the strengths of the transitions and of the mixing is determined by the value of Franck-Condon factors.

It should be noted that conclusions drawn from study of the vibrational elements of either the substitutional or vibrational contributions hold for absorption, natural optical activity, and magnetically-induced optical activity, regardless of which of the three phenomena the conclusions were developed from. In contrast, conclusions drawn from the electronic matrix elements are specific for that particular optical phenomenon investigated, and one must consider

separately the electronic matrix elements of absorption, natural optical activity, and magnetically-induced optical activity.

With this in mind, we turn to consideration of the electronic matrix elements of the substitutional contributions to the absorption. From equation (4-8), we see that the symmetry representation of the substitutional perturbation is given by $\Gamma_{V_a} = \Gamma_L \otimes \Gamma_K$, as obtained from the requirement that the electronic matrix element $\langle L^0 | V_a | K^0 \rangle$ be totally symmetric. From the remaining two electronic matrix elements, we have:

$$(4-14) \quad \begin{aligned} \Gamma_L &= \Gamma_{\mu_x} \otimes \Gamma_J \\ \Gamma_{\mu_x} &= \Gamma_J \otimes \Gamma_K \end{aligned}$$

Combining these two equations and noting that $\Gamma_J \otimes \Gamma_J = \Gamma_0$

we have:

$$(4-15) \quad \Gamma_L = \Gamma_K$$

Substituting this into the previous equation $\Gamma_{V_a} = \Gamma_L \otimes \Gamma_K$

we find that:

$$(4-16) \quad \Gamma_{V_a} = \Gamma_0$$

This can be shown to be true for the substitutional contributions of other terms and of other components of the absorption. We therefore have our second conclusion.

Conclusion 2. For absorption, only totally symmetric substitutions act as first-order perturbations.

As an example, hexamethyl benzene is benzene that has a totally symmetric substitution pattern. We can also show for our third conclusion that:

Conclusion 3. For absorption, substitutional first-order perturbations stimulate borrowing only from states whose symmetry is identical to that of either the ground or excited states.

The electronic matrix elements of the substitutional contributions

to the natural optical activity, given in equation (4-9), follow different symmetry rules than do those of the substitutional contributions to absorption. Here the restriction that each matrix element must be totally symmetric yields:

$$(4-17) \quad \Gamma_{\mu_x} = \Gamma_K \otimes \Gamma_J$$

$$\Gamma_{m_x} = \Gamma_L \otimes \Gamma_J$$

$$\Gamma_{V_a} = \Gamma_L \otimes \Gamma_K$$

Combining the first two of these three equations, we have:

$$\Gamma_L \otimes \Gamma_K = \Gamma_{\mu_x} \otimes \Gamma_{m_x}$$

Substituting into the third equation of (4-17), we have:

$$(4-18) \quad \Gamma_{V_a} = \Gamma_{\mu_x} \otimes \Gamma_{m_x}$$

Thus, a part of V_a must transform as $\mu_x m_x$ for there to be a possible first-order substitutional contribution to natural optical activity. It is well known that the scalar product of a polar and an axial vector, such as $\vec{\mu} \cdot \vec{m}$, is a pseudoscalar, i.e. it behaves like a scalar under all transformations except those of reflection and inversion, where it changes sign. In any point group other than the pure rotation groups, there is always a representation for pseudoscalar functions. This representation has been termed the pseudoscalar representation by Schellman (31) and is denoted by Γ_S in this dissertation. We see that V_a must belong to, or contain a part which belongs to, the pseudoscalar representation. This conclusion has been shown to apply to point groups with degenerate representations as well (31). Therefore, we have our fourth conclusion.

Conclusion 4. For natural optical activity, only substitutional symmetry patterns transforming as the pseudoscalar representation, act as first-order perturbations.

Benzene with an asymmetric carbon substituted at one position is an example of such a pseudoscalar substitutional symmetry pattern..

We may also make some statements about the symmetry of the mixing states. From the relation $\Gamma_{V_a} = \Gamma_S$ and the third equation of (4-17), we have:

$$(4-19) \quad \Gamma_L = \Gamma_S \otimes \Gamma_K$$

The third first-order term of equation (4-6b) yields a similar equation.

$$(4-20) \quad \Gamma_L = \Gamma_S \otimes \Gamma_J$$

Thus for our fifth conclusion, we have:

Conclusion 5. For natural optical activity, substitutional perturbations stimulate borrowing in first-order only from states whose symmetry representation is given by direct multiplying of the ground or excited state symmetry representation by the pseudoscalar representation.

We now evaluate the vibrational contributions of equations (4-8) and (4-9). For the $\mathcal{L}^{TH}$ vibrational perturbation, we can determine from the vibrational matrix elements that

$$(4-21) \quad \begin{aligned} \Gamma_J &= \Gamma_L \\ \Gamma_J &= \Gamma_K \end{aligned} \quad \therefore \Gamma_K = \Gamma_L$$

This in association with $\Gamma_{Q_a} = \Gamma_L \otimes \Gamma_K$ yields

$$\Gamma_{Q_a} = \Gamma_0$$

and we have our sixth conclusion.

Conclusion 6. Only totally symmetric vibrations act as first-order vibrational perturbations.

In analogy to the reasoning following Conclusion 1, we note that the symmetry requirement of Conclusion 6 is a necessary but not a sufficient condition that the vibrational matrix elements of the

vibrational contributions of equations (4-8) and (4-9) be non-zero. As before, we consider the cases of vertical and non-vertical potential surfaces.

With vertical potential surfaces, if there is a vibrational change from ground to excited state, the matrix element $(k|j)$ is zero, and therefore, the vibrational contributions are zero. The reasoning is identical to that used for the analysis of the substitutional contributions. In this case, however, we may also show that there is no vibrational contribution under the conditions of no vibrational change. Making use of the sum rule and equation (4-3), we have for the remaining vibrational matrix elements

$$(4-21) \quad \sum_l (j|l)(l|Q_n|k) = (j|Q_n|k) = (j_1|k_1)(j_2|k_2) \cdots (j_n|Q_n|k_n) \cdots$$

As we are considering vertical potential surfaces and no vibrational change, we may replace all $|k_n\rangle$ by $|j_n\rangle$. Then using $(j_n|j_n) = 1$ we have:

$$(4-22) \quad \sum_l (j|l)(l|Q_n|k) = (j_n|Q_n|j_n)$$

the expectation value of Q_n in the state $|j_n\rangle$. If the potential wells are harmonic, this is identically zero as we have chosen the equilibrium value of Q_n to be zero (Footnote 9). Although for deviations from harmonic wells, the value of equation (4-22) will be non-zero, for a normal degree of anharmonicity and commonly encountered temperatures and force constants, the value can be considered negligible. Thus, from the above discussion of vertical potential surfaces, we may consider the vibrational contribution of equations (4-8) and (4-9) to be zero, regardless of whether or not there is vibrational change between the

ground and the excited state. Again, for non-vertical surfaces, we must determine Franck-Condon integrals. We therefore, have the corollary to Conclusion 6.

Conclusion 6a. For vertical potential surfaces, we may assume that even totally symmetric vibrational perturbations do not contribute in first-order. For non-vertical potential surfaces, the contribution is evaluated via the Franck-Condon integrals.

We may now consider the electronic matrix elements of the vibrational contributions of equations (4-8) and (4-9). For all cases, $\mathcal{H}_n Q_n$ is totally symmetric (Footnote 9), and thus the symmetry of $\mathcal{H}_n$ is the same as that of Q_n . In the case of first-order perturbations, Q_n is totally symmetric, and therefore, $\mathcal{H}_n$ is also.

$$(4-22) \quad \Gamma_{\mathcal{H}_n} = \Gamma_{Q_n} = \Gamma_0$$

Applied to equation (4-8) for absorption, this indicates that for a non-zero vibrational contribution, the mixing state must be the same symmetry as the excited state

$$\Gamma_L = \Gamma_0 \otimes \Gamma_K = \Gamma_K$$

Other first-order terms of the absorption yield $\Gamma_L = \Gamma_J$. Therefore, we have our seventh conclusion.

Conclusion 7. In absorption, only states having the same symmetry as the ground or excited states can be borrowed from by first-order vibrational perturbations.

Applied to equation (4-9) for natural optical activity, equation (4-22) combines with an equation analogous to equation (4-18)

to yield a contradiction for point groups other than the pure rotation groups. Thus

$$\Gamma_{\chi_n} = \Gamma_{\mu_x} \otimes \Gamma_{m_x} = \Gamma_s$$

$$\Gamma_{\chi_n} = \Gamma_{\phi_n} = \Gamma_o$$

This can only be satisfied for the pure rotation groups where $\Gamma_s = \Gamma_o$. We therefore have our eighth conclusion.

Conclusion 8. For molecular systems belonging to point groups other than the pure rotation groups, there can be no first-order vibrational contribution to natural optical activity.

Finally, we can show that if the transition is forbidden, i.e. the zero-order absorption is zero, then there is no vibrational or substitutional contribution in first-order. This is readily seen, as reference to equation (4-6a) indicates only two conditions under which the zero-order term will be zero.

$$(J^o | \mu_x | K^o) = 0$$

$$(j | k) = 0$$

Since satisfaction of either of these conditions also sets all first-order terms equal to zero, we can state our ninth conclusion:

Conclusion 9. If there is no zero-order absorption -- a forbidden transition -- then there is no first-order vibrational or substitutional contribution to absorption.

The nine conclusions presented above are examples of the type of information available from a straightforward symmetry analysis. At this point, we have ignored point groups with degenerate representations and only investigated two simple cases, first-order absorption and first-order natural optical activity. In part C of this chapter, we will

consider groups with degenerate representations and develop the more complex expansions of third-order absorption, third-order natural optical activity, and second-order magnetically-induced optical activity. In the process of analyzing these expansions, we attempt to expand our list of symmetry conclusions. Various factors make this extension a non-trivial process. First, as one goes to higher orders of perturbation, the number of terms to be considered increases greatly. Secondly, consideration of magnetically-induced optical activity involves a vector triple product and does not readily separate into "components" as does absorption and natural optical activity. Finally, as long as the analysis is restricted to point groups with no degenerate representations, things remain comparatively simple. However, the introduction of degeneracy greatly complicates matters from two standpoints (to be discussed in part C), and the symmetry analysis of any one of the three optical phenomena is next to impossible without a computer analysis.

C. SYMMETRY PATTERNS OF VIBRATIONAL AND SUBSTITUTIONAL
PERTURBATIONS ON ABSORPTION, NATURAL OPTICAL ACTIVITY, AND MAGNETICALLY-
INDUCED OPTICAL ACTIVITY FOR THE POINT GROUP C_{4v} .

In this last part of Chapter 4, we attempt to deal with the formidable problems of symmetry analysis arising from higher order perturbations, magnetically-induced optical activity and degeneracy. Part C is divided into four sections. The first develops the perturbation expansions, to third-order in absorption and natural optical activity, to second-order in magnetically-induced optical activity. The second section reduces these extremely complex expansions to more tractable expressions, using symmetry arguments similar to those of part B to accomplish this. The third section presents a computer program which can perform the

symmetry analysis for point groups containing degenerate representations. Finally, in the fourth section, the results of this analysis are presented for the point group C_{4v} . These results, when combined with the nine symmetry conclusions developed in part B, give the most comprehensive set of symmetry rules yet presented for this type of problem.

1. Perturbation Expansions for Absorption, Natural Optical Activity, and Magnetically-Induced Optical Activity.

We will need perturbation expansions to third-order in absorption, to third-order in natural optical activity, and to second order in magnetically-induced optical activity. As will become clear as the derivation progresses, this enables us to investigate the influence of vibration and substitution on absorption, and on both types of optical activity. As we are particularly concerned with the effects of degeneracy, we must use degenerate perturbation theory for these expansions. Fortunately, the formulae for such expansions are available in Table 5.1 of the book by Carson (88). In Appendix X, we develop in a general perturbation $\mathcal{P}$, the third-order degenerate perturbation expansions for the ground and excited states, starting with the formulae of Carson. In this appendix, we simplify the formulae by suppressing the notation indicating members of a degenerate set. This will not result in any erroneous conclusions as long as one remembers that if an electronic state is degenerate, one must sum over all members of that degenerate set. This will become important when performing the symmetry analysis. We thus have from Appendix X for the expanded ground and excited states (we use here, and in the remainder of Chapter 4, the bra-ket notation):

$$\begin{aligned}
(J| &= (J^0| + \sum_{M^0 \neq J^0} \frac{(J^0|P|M^0)}{E_J^0 - E_M^0} (M^0| \\
&+ \sum_{M^0 \neq J^0} \left\{ \left[\sum_{N^0 \neq J^0} \frac{(N^0|P|M^0)(J^0|P|N^0)}{(E_J^0 - E_M^0)(E_J^0 - E_N^0)} \right] - \frac{(J^0|P|J^0)(J^0|P|M^0)}{(E_J^0 - E_M^0)^2} \right\} (M^0| \\
&+ \sum_{M^0 \neq J^0} \left\{ \left[\sum_{N^0 \neq J^0} \left[\sum_{L^0 \neq J^0} \frac{(N^0|P|M^0)(L^0|P|N^0)(J^0|P|L^0)}{(E_J^0 - E_M^0)(E_J^0 - E_N^0)(E_J^0 - E_L^0)} \right] \right. \right. \\
&\quad \left. \left. - 2 \left(E_J^0 - \frac{E_M^0 + E_N^0}{2} \right) \frac{(N^0|P|M^0)(J^0|P|N^0)(J^0|P|J^0)}{(E_J^0 - E_M^0)^2 (E_J^0 - E_N^0)^2} \right. \right. \\
&\quad \left. \left. - \frac{3}{2} \left(E_J^0 - \frac{E_M^0 + 2E_N^0}{2} \right) \frac{(J^0|P|M^0)|(J^0|P|N^0)|^2}{(E_J^0 - E_M^0)^2 (E_J^0 - E_N^0)^2} \right] \right\} \\
&\quad \left. + \frac{(J^0|P|J^0)(J^0|P|M^0)}{(E_J^0 - E_M^0)^3} \right\} (M^0|
\end{aligned}
\tag{4-23}$$

$$\begin{aligned}
|K\rangle &= |K^0\rangle + \sum_{L^0 \neq K^0} \frac{(L^0|P|K^0)}{E_K^0 - E_L^0} |L^0\rangle \\
&+ \sum_{L^0 \neq K^0} \left\{ \left[\sum_{M^0 \neq K^0} \frac{(L^0|P|M^0)(M^0|P|K^0)}{(E_K^0 - E_L^0)(E_K^0 - E_M^0)} \right] - \frac{(K^0|P|K^0)(L^0|P|K^0)}{(E_K^0 - E_L^0)^2} \right\} |L^0\rangle \\
&+ \sum_{L^0 \neq K^0} \left\{ \left[\sum_{M^0 \neq K^0} \left[\sum_{N^0 \neq K^0} \frac{(L^0|P|M^0)(M^0|P|N^0)(N^0|P|K^0)}{(E_K^0 - E_L^0)(E_K^0 - E_M^0)(E_K^0 - E_N^0)} \right] \right. \right. \\
&\quad \left. \left. - 2 \left(E_K^0 - \frac{E_L^0 + E_M^0}{2} \right) \frac{(L^0|P|M^0)(M^0|P|K^0)(K^0|P|K^0)}{(E_K^0 - E_L^0)^2 (E_K^0 - E_M^0)^2} \right. \right. \\
&\quad \left. \left. - \frac{3}{2} \left(E_K^0 - \frac{E_L^0 + 2E_M^0}{3} \right) \frac{(L^0|P|K^0)|(K^0|P|M^0)|^2}{(E_K^0 - E_L^0)^2 (E_K^0 - E_M^0)^2} \right] \right\} \\
&\quad \left. + \frac{(K^0|P|K^0)^2 (L^0|P|K^0)}{(E_K^0 - E_L^0)^3} \right\} |L^0\rangle
\end{aligned}
\tag{4-24}$$

It should be noted that we have also suppressed the vibrational wave functions. Thus, we should replace $|k\rangle$ by $|k\rangle|k\rangle$, $(J|$ by $(J|(j|$, $|k^0\rangle$ by $|k^0\rangle|k\rangle$, $|L^0\rangle$ by $|L^0\rangle|L\rangle$ etc. That we do not do so is for the sake of convenience in notation. However, it is important to note that it is not the first-order electronic wave functions that are expanded in the zero-order electronic wave functions, but the first-order vibronic wave functions that are expanded in the zero-order vibronic wave functions. This is important in that if the former expansion is used, as is done by Weigang (33) and Albrecht (53), then the expansion is really not in the complete set of electronic zero-order functions, but in the over-complete set of mixed vibronic functions. Examples of such mixed vibronic functions are $|M^0\rangle|k\rangle$, $(L^0|(j|$, etc. This could lead to incorrect symmetry conclusions. Therefore, in the analysis of this chapter, we use the vibronic harmonic approximations for the zero-order wave functions and the vibronic adiabatic approximation for the first-order wave functions. There is an additional reason for using the harmonic approximation. The analysis is a symmetry analysis and, as the harmonic electronic wave functions are the electronic wave functions at the equilibrium position of the molecule, they can be unambiguously assigned a symmetry representation. The same cannot be said for the adiabatic electronic wave functions.

We may now write the general matrix element $(J|\hat{O}|K)$ for the operator $\hat{O}$. Using equations (4-23) and (4-24), (still suppressing the vibrational wave functions) and dropping all terms in order higher than third) we have:

$$\begin{aligned}
 (4-25) \quad (J|\hat{O}|K) &= (J^0|\hat{O}|K^0) + \sum_{L^0 \neq K^0} F_{LK} (J^0|\hat{O}|L^0) \\
 &\quad + \sum_{M^0 \neq J^0} F_{JM} (M^0|\hat{O}|K^0) + \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq J^0}} F_{ML}^{JK} (M^0|\hat{O}|L^0)
 \end{aligned}$$

where

$$\begin{aligned}
 (4-26) \quad F_{LK} &= F_{LK}^1 + F_{LK}^2 + F_{LK}^3 \\
 F_{JM} &= F_{JM}^1 + F_{JM}^2 + F_{JM}^3 \\
 F_{ML}^{JK} &= F_{ML}^{JK2} + F_{ML}^{JK3}
 \end{aligned}$$

and

$$(4-27) \quad F_{LK}^1 = \frac{(L^0 | P | K^0)}{(E_K^0 - E_L^0)}$$

$$F_{LK}^2 = \left[\sum_{M^0 \neq K^0} \frac{(L^0 | P | M^0)(M^0 | P | K^0)}{(E_K^0 - E_L^0)(E_K^0 - E_M^0)} \right] - \frac{(K^0 | P | K^0)(L^0 | P | K^0)}{(E_K^0 - E_L^0)^2}$$

$$\begin{aligned}
 F_{LK}^3 = & \left[\sum_{M^0 \neq K^0} \left\{ \left[\sum_{N^0 \neq K^0} \frac{(L^0 | P | M^0)(M^0 | P | N^0)(N^0 | P | K^0)}{(E_K^0 - E_L^0)(E_K^0 - E_M^0)(E_K^0 - E_N^0)} \right] \right. \right. \\
 & - 2 \left(E_K^0 - \frac{E_L^0 + E_M^0}{2} \right) \frac{(L^0 | P | M^0)(M^0 | P | K^0)(K^0 | P | K^0)}{(E_K^0 - E_L^0)^2 (E_K^0 - E_M^0)^2} \\
 & \left. \left. - \frac{3}{2} \left(E_K^0 - \frac{E_L^0 + 2E_M^0}{3} \right) \frac{(L^0 | P | K^0)(K^0 | P | M^0)^2}{(E_K^0 - E_L^0)^2 (E_K^0 - E_M^0)^2} \right\} \right] \\
 & + \frac{(K^0 | P | K^0)^2 (L^0 | P | K^0)}{(E_K^0 - E_L^0)^3}
 \end{aligned}$$

$$F_{JM}^1 = \frac{(J^0 | P | M^0)}{E_J^0 - E_M^0}$$

$$F_{JM}^2 = \left[\sum_{L^0 \neq J^0} \frac{(J^0 | P | L^0)(L^0 | P | M^0)}{(E_J^0 - E_L^0)(E_J^0 - E_M^0)} \right] - \frac{(J^0 | P | J^0)(J^0 | P | M^0)}{(E_J^0 - E_M^0)^2}$$

$$F_{JM}^3 = \left[\sum_{L^0 \neq J^0} \left\{ \left[\sum_{N^0 \neq J^0} \frac{(J^0 | P | N^0)(N^0 | P | L^0)(L^0 | P | M^0)}{(E_J^0 - E_L^0)(E_J^0 - E_N^0)(E_J^0 - E_M^0)} \right. \right. \right. \\ \left. \left. - 2 \left(E_K^0 - \frac{E_M^0 + E_L^0}{2} \right) \frac{(J^0 | P | J^0)(J^0 | P | L^0)(L^0 | P | M^0)}{(E_J^0 - E_M^0)^2(E_J^0 - E_L^0)^2} \right. \right. \\ \left. \left. - \frac{3}{2} \left(E_K^0 - \frac{E_M^0 + 2E_L^0}{3} \right) \frac{(J^0 | P | M^0)(J^0 | P | L^0)^2}{(E_J^0 - E_M^0)^2(E_J^0 - E_L^0)^2} \right\} \right] \\ + \frac{(J^0 | P | J^0)^2(J^0 | P | M^0)}{(E_J^0 - E_M^0)^3}$$

$$F_{ML}^{JK2} = \frac{(L^0 | P | K^0)(J^0 | P | M^0)}{(E_K^0 - E_L^0)(E_J^0 - E_M^0)}$$

$$F_{ML}^{JK3} = \frac{(L^0 | P | K^0)}{E_K^0 - E_L^0} \left\{ \left[\sum_{N^0 \neq J^0} \frac{(J^0 | P | N^0)(N^0 | P | M^0)}{(E_J^0 - E_M^0)(E_J^0 - E_N^0)} \right] - \frac{(J^0 | P | J^0)(J^0 | P | M^0)}{(E_J^0 - E_M^0)^2} \right\} \\ + \frac{(J^0 | P | M^0)}{E_J^0 - E_M^0} \left\{ \left[\sum_{N^0 \neq K^0} \frac{(L^0 | P | N^0)(N^0 | P | K^0)}{(E_K^0 - E_L^0)(E_K^0 - E_N^0)} \right] - \frac{(K^0 | P | K^0)(L^0 | P | K^0)}{(E_K^0 - E_L^0)^2} \right\}$$

We now explicitly define our perturbation $\mathcal{P}$.

$$(4-28) \quad \mathcal{P} = V_a + \sum_n \mathcal{H}_n Q_n$$

where the quantities V_a and $\mathcal{H}_a Q_a$ have been previously defined as the substitutional perturbation and the vibrational perturbation of the $\mathcal{N}^{\text{TH}}$ normal mode. We shall make the assumption that vibrational and substitutional perturbations are of the same order of magnitude (see Appendix II), and therefore, a simultaneous perturbation approach must be employed. Substituting equation (4-28) into equations (4-27) and making use of the sum rule

$$\sum_m |m\rangle\langle m| = 1$$

we have:

$$F_{LK}^1 = \frac{1}{E_K^0 - E_L^0} \left\{ (L^0 | V_a | K^0) (L | k) + \sum_n (L^0 | \mathcal{H}_n | K^0) (L | Q_n | k) \right\}$$

(4-29)

$$\begin{aligned} F_{LK}^2 = \frac{1}{E_K^0 - E_L^0} & \left\{ \left[\sum_{M \neq K^0} \frac{1}{E_K^0 - E_M^0} \left\{ (L^0 | V_a | M^0) (M^0 | V_b | K^0) (L | k) \right. \right. \right. \\ & + \sum_n (L^0 | V_a | M^0) (M^0 | \mathcal{H}_n | K^0) (L | Q_n | k) \\ & + \sum_n (L^0 | \mathcal{H}_n | M^0) (M^0 | V_b | K^0) (L | Q_n | k) \\ & \left. \left. + \sum_{n,s} (L^0 | \mathcal{H}_n | M^0) (M^0 | \mathcal{H}_s | K^0) (L | Q_n Q_s | k) \right\} \right] \\ & - \left[\frac{1}{E_K^0 - E_L^0} \left\{ (K^0 | V_a | K^0) (L^0 | V_b | K^0) (L | k) \right. \right. \\ & + \sum_n (K^0 | V_a | K^0) (L^0 | \mathcal{H}_n | K^0) (L | Q_n | k) \\ & + \sum_n (K^0 | \mathcal{H}_n | K^0) (L^0 | V_b | K^0) (L | Q_n | k) (L | k) \\ & \left. \left. + \sum_{n,s} (K^0 | \mathcal{H}_n | K^0) (L^0 | \mathcal{H}_s | K^0) (L | Q_n | k) (L | Q_s | k) \right\} \right] \end{aligned}$$

$$\begin{aligned}
F_{LK}^3 = & \frac{1}{E_K^0 - E_L^0} \left\{ \left[\sum_{M^0 \neq K^0} \frac{1}{E_K^0 - E_M^0} \left\{ \sum_{N^0 \neq K^0} \frac{1}{E_K^0 - E_N^0} \left\{ (L^0 | V_a | M^0) (M^0 | V_b | N^0) (N^0 | V_c | K^0) (l | k) \right. \right. \right. \right. \\
& + \sum_{\lambda} (L^0 | V_a | M^0) (M^0 | V_b | N^0) (N^0 | \mathcal{V}_{\lambda} | K^0) (l | Q_{\lambda} | k) \\
& + \sum_{\lambda} (L^0 | V_a | M^0) (M^0 | \mathcal{V}_{\lambda} | N^0) (N^0 | V_c | K^0) (l | Q_{\lambda} | k) \\
& + \sum_{\lambda} (L^0 | \mathcal{V}_{\lambda} | M^0) (M^0 | V_b | N^0) (N^0 | V_c | K^0) (l | Q_{\lambda} | k) \\
& + \sum_{\lambda, S} (L^0 | V_a | M^0) (M^0 | \mathcal{V}_{\lambda} | N^0) (N^0 | \mathcal{V}_S | K^0) (l | Q_{\lambda} Q_S | k) \\
& + \sum_{\lambda, S} (L^0 | \mathcal{V}_{\lambda} | M^0) (M^0 | V_b | N^0) (N^0 | \mathcal{V}_S | K^0) (l | Q_{\lambda} Q_S | k) \\
& + \sum_{\lambda, S} (L^0 | \mathcal{V}_{\lambda} | M^0) (M^0 | \mathcal{V}_S | N^0) (N^0 | V_c | K^0) (l | Q_{\lambda} Q_S | k) \\
& \left. \left. + \sum_{\lambda, S, t} (L^0 | \mathcal{V}_{\lambda} | M^0) (M^0 | \mathcal{V}_S | N^0) (N^0 | \mathcal{V}_t | K^0) (l | Q_{\lambda} Q_S Q_t | k) \right\} \right] \\
& - \left[\frac{2(E_K^0 - \frac{E_L^0 + E_M^0}{2})}{(E_K^0 - E_L^0)(E_K^0 - E_M^0)} \left\{ (L^0 | V_a | M^0) (M^0 | V_b | K^0) (K^0 | V_c | K^0) (l | k) \right. \right. \\
& + \sum_{\lambda} (L^0 | V_a | M^0) (M^0 | V_b | K^0) (K^0 | \mathcal{V}_{\lambda} | K^0) (l | k) (k | Q_{\lambda} | k) \\
& + \sum_{\lambda} (L^0 | V_a | M^0) (M^0 | \mathcal{V}_{\lambda} | K^0) (K^0 | V_c | K^0) (l | Q_{\lambda} | k) \\
& + \sum_{\lambda} (L^0 | \mathcal{V}_{\lambda} | M^0) (M^0 | V_b | K^0) (K^0 | V_c | K^0) (l | Q_{\lambda} | k) \\
& \left. \left. + \sum_{\lambda, S} (L^0 | V_a | M^0) (M^0 | \mathcal{V}_{\lambda} | K^0) (K^0 | \mathcal{V}_S | K^0) (l | Q_{\lambda} | k) (k | Q_S | k) \right\} \right]
\end{aligned}$$

$$\begin{aligned}
& + \sum_{\lambda, s} (L^0 | \mathcal{H}_\lambda | M^0) (M^0 | V_b | K^0) (K^0 | \mathcal{H}_s | K^0) (\ell | Q_\lambda | k) (k | Q_s | k) \\
& + \sum_{\lambda, s} (L^0 | \mathcal{H}_\lambda | M^0) (M^0 | \mathcal{H}_s | K^0) (K^0 | V_c | K^0) (\ell | Q_\lambda | Q_s | k) \\
& + \sum_{\lambda, s, t} (L^0 | \mathcal{H}_\lambda | M^0) (M^0 | \mathcal{H}_s | K^0) (K^0 | \mathcal{H}_t | K^0) (\ell | Q_\lambda | Q_s | k) (k | Q_t | k) \Big] \\
& - \left[\frac{\frac{1}{2} (E_K^0 - E_L^0 + 2E_H^0)}{(E_K^0 - E_L^0)(E_K^0 - E_H^0)} \left\{ (L^0 | V_a | K^0) (K^0 | V_b | M^0) (M^0 | V_c | K^0) (\ell | k) \right. \right. \\
& + \sum_{\lambda} (L^0 | V_a | K^0) (K^0 | V_b | M^0) (M^0 | \mathcal{H}_\lambda | K^0) (\ell | k) (k | Q_\lambda | k) \\
& + \sum_{\lambda} (L^0 | V_a | K^0) (K^0 | \mathcal{H}_\lambda | M^0) (M^0 | V_c | K^0) (\ell | k) (k | Q_\lambda | k) \\
& + \sum_{\lambda} (L^0 | \mathcal{H}_\lambda | K^0) (K^0 | V_b | M^0) (M^0 | V_c | K^0) (\ell | Q_\lambda | k) \\
& + \sum_{\lambda, s} (L^0 | V_a | K^0) (K^0 | \mathcal{H}_\lambda | M^0) (M^0 | \mathcal{H}_s | K^0) (\ell | k) (k | Q_\lambda | Q_s | k) \\
& + \sum_{\lambda, s} (L^0 | \mathcal{H}_\lambda | K^0) (K^0 | V_b | M^0) (M^0 | \mathcal{H}_s | K^0) (\ell | Q_\lambda | k) (k | Q_s | k) \\
& + \sum_{\lambda, s} (L^0 | \mathcal{H}_\lambda | K^0) (K^0 | \mathcal{H}_s | M^0) (M^0 | V_c | K^0) (\ell | Q_\lambda | k) (k | Q_s | k) \\
& \left. + \sum_{\lambda, s, t} (L^0 | \mathcal{H}_\lambda | K^0) (K^0 | \mathcal{H}_s | M^0) (M^0 | \mathcal{H}_t | K^0) (\ell | Q_\lambda | k) (k | Q_s | Q_t | k) \right\} \\
& - \left[\frac{1}{(E_K^0 - E_L^0)^2} \left\{ (K^0 | V_a | K^0) (K^0 | V_b | K^0) (L^0 | V_c | K^0) (\ell | k) \right. \right.
\end{aligned}$$

$$\begin{aligned}
& + \sum_n (K^0 | V_a | K^0) (K^0 | V_b | K^0) (L^0 | \mathcal{X}_n | K^0) (l | Q_n | k) \\
& + 2 \sum_n (K^0 | \mathcal{X}_n | K^0) (K^0 | V_a | K^0) (L^0 | V_c | K^0) (k | Q_n | k) (l | k) \\
& + 2 \sum_{n,s} (K^0 | \mathcal{X}_n | K^0) (K^0 | V_a | K^0) (L^0 | \mathcal{X}_s | K^0) (k | Q_n | k) (l | Q_s | k) \\
& + \sum_{\lambda, s} (K^0 | \mathcal{X}_\lambda | K^0) (K^0 | \mathcal{X}_s | K^0) (L^0 | V_c | K^0) (k | Q_\lambda | k) (k | Q_s | k) (l | k) \\
& + \sum_{\lambda, s, t} (K^0 | \mathcal{X}_\lambda | K^0) (K^0 | \mathcal{X}_s | K^0) (L^0 | \mathcal{X}_t | K^0) (k | Q_\lambda | k) (k | Q_s | k) (l | Q_t | k) \} \} \}
\end{aligned}$$

$$\begin{aligned}
F_{ML}^{JK2} = \frac{1}{(E_K^0 - E_L^0)(E_J^0 - E_M^0)} & \left\{ (J^0 | V_a | M^0) (L^0 | V_b | K^0) (j | m) (l | k) \right. \\
& + \sum_n (J^0 | V_a | M^0) (L^0 | \mathcal{X}_n | K^0) (j | m) (l | Q_n | k) \\
& + \sum_n (J^0 | \mathcal{X}_n | M^0) (L^0 | V_b | K^0) (j | Q_n | m) (l | k) \\
& \left. + \sum_{\lambda, s} (J^0 | \mathcal{X}_\lambda | M^0) (L^0 | \mathcal{X}_s | K^0) (j | Q_\lambda | m) (l | Q_s | k) \right\}
\end{aligned}$$

$$\begin{aligned}
F_{ML}^{JK3} = \frac{1}{(E_K^0 - E_L^0)(E_J^0 - E_M^0)} & \left\{ \sum_{N^0 \neq J^0} \frac{1}{E_J^0 - E_N^0} \left\{ (J^0 | V_a | N^0) (N^0 | V_b | M^0) (L^0 | V_c | K^0) (j | m) (l | k) \right. \right. \\
& + \sum_n (J^0 | V_a | N^0) (N^0 | V_b | M^0) (L^0 | \mathcal{X}_n | K^0) (j | m) (l | Q_n | k) \\
& + \sum_n (J^0 | V_a | N^0) (N^0 | \mathcal{X}_n | M^0) (L^0 | V_c | K^0) (j | Q_n | m) (l | k) \\
& \left. \left. + \sum_n (J^0 | \mathcal{X}_n | N^0) (N^0 | V_b | M^0) (L^0 | V_c | K^0) (j | Q_n | m) (l | k) \right\} \right\}
\end{aligned}$$

$$\begin{aligned}
& + \sum_{\lambda, s} (J^0 | V_a | N^0) (N^0 | \mathcal{H}_\lambda | M^0) (L^0 | \mathcal{H}_s | K^0) (j | Q_\lambda | m) (l | Q_s | k) \\
& + \sum_{\lambda, s} (J^0 | \mathcal{H}_\lambda | N^0) (N^0 | V_b | M^0) (L^0 | \mathcal{H}_s | K^0) (j | Q_\lambda | m) (l | Q_s | k) \\
& + \sum_{\lambda, s} (J^0 | \mathcal{H}_\lambda | N^0) (N^0 | \mathcal{H}_s | M^0) (L^0 | V_c | K^0) (j | Q_\lambda Q_s | m) (l | k) \\
& + \sum_{\lambda, s, t} (J^0 | \mathcal{H}_\lambda | N^0) (N^0 | \mathcal{H}_s | M^0) (L^0 | \mathcal{H}_t | K^0) (j | Q_\lambda Q_t | m) (l | Q_s Q_t | k) \Big] \\
& + \left[\sum_{N^0, K^0} \frac{1}{E_K^0 - E_N^0} \left\{ (J^0 | V_a | M^0) (L^0 | V_b | N^0) (N^0 | V_c | K^0) (j | m) (l | k) \right. \right. \\
& + \sum_{\lambda} (J^0 | V_a | M^0) (L^0 | V_b | N^0) (N^0 | \mathcal{H}_\lambda | K^0) (j | m) (l | Q_\lambda | k) \\
& + \sum_{\lambda} (J^0 | V_a | M^0) (L^0 | \mathcal{H}_\lambda | N^0) (N^0 | V_c | K^0) (j | m) (l | Q_\lambda | k) \\
& + \sum_{\lambda} (J^0 | \mathcal{H}_\lambda | M^0) (L^0 | V_b | N^0) (N^0 | V_c | K^0) (j | Q_\lambda | m) (l | k) \\
& + \sum_{\lambda, s} (J^0 | V_a | M^0) (L^0 | \mathcal{H}_\lambda | N^0) (N^0 | \mathcal{H}_s | K^0) (j | m) (l | Q_\lambda Q_s | k) \\
& + \sum_{\lambda, s} (J^0 | \mathcal{H}_\lambda | M^0) (L^0 | V_b | N^0) (N^0 | \mathcal{H}_s | K^0) (j | Q_\lambda | m) (l | Q_s | k) \\
& + \sum_{\lambda, s} (J^0 | \mathcal{H}_\lambda | M^0) (L^0 | \mathcal{H}_s | N^0) (N^0 | V_c | K^0) (j | Q_\lambda | m) (l | Q_s | k) \\
& \left. + \sum_{\lambda, s, t} (J^0 | \mathcal{H}_\lambda | M^0) (L^0 | \mathcal{H}_s | N^0) (N^0 | \mathcal{H}_t | K^0) (j | Q_\lambda | m) (l | Q_s Q_t | k) \right\} \Big] \\
& - \left[\frac{1}{E_J^0 - E_M^0} \left\{ (J^0 | V_a | J^0) (J^0 | V_b | M^0) (L^0 | V_c | K^0) (j | m) (l | k) \right. \right. \\
& + \sum_{\lambda} (J^0 | V_a | J^0) (J^0 | V_b | M^0) (L^0 | \mathcal{H}_\lambda | K^0) (j | m) (l | Q_\lambda | k)
\end{aligned}$$

$$\begin{aligned}
& + \sum_{\lambda} (J^0 | V_a | J^0) (J^0 | \mathcal{X}_\lambda | M^0) (L^0 | V_c | K^0) (j | Q_\lambda | m) (\ell | k) \\
& + \sum_{\lambda} (J^0 | \mathcal{X}_\lambda | J^0) (J^0 | V_b | M^0) (L^0 | V_c | K^0) (j | Q_\lambda | j) (j | m) (\ell | k) \\
& + \sum_{\lambda, s} (J^0 | V_a | J^0) (J^0 | \mathcal{X}_\lambda | M^0) (L^0 | \mathcal{X}_s | K^0) (j | Q_\lambda | m) (\ell | Q_s | k) \\
& + \sum_{\lambda, s} (J^0 | \mathcal{X}_\lambda | J^0) (J^0 | V_b | M^0) (L^0 | \mathcal{X}_s | K^0) (j | Q_\lambda | j) (j | m) (\ell | Q_s | k) \\
& + \sum_{\lambda, s} (J^0 | \mathcal{X}_\lambda | J^0) (J^0 | \mathcal{X}_s | M^0) (L^0 | V_c | K^0) (j | Q_\lambda | j) (j | Q_s | m) (\ell | k) \\
& + \sum_{\lambda, s, t} (J^0 | \mathcal{X}_\lambda | J^0) (J^0 | \mathcal{X}_s | M^0) (L^0 | \mathcal{X}_t | K^0) (j | Q_\lambda | j) (j | Q_s | m) (\ell | Q_t | k) \Big]
\end{aligned}$$

$$\begin{aligned}
& - \left[\frac{1}{E_K^0 - E_L^0} \left\{ (J^0 | V_a | M^0) (K^0 | V_b | K^0) (L^0 | V_c | K^0) (j | m) (\ell | k) \right. \right. \\
& + \sum_{\lambda} (J^0 | V_a | M^0) (K^0 | V_b | K^0) (L^0 | \mathcal{X}_\lambda | K^0) (j | m) (\ell | Q_\lambda | k) \\
& + \sum_{\lambda} (J^0 | V_a | M^0) (K^0 | \mathcal{X}_\lambda | K^0) (L^0 | V_c | K^0) (j | m) (k | Q_\lambda | k) (\ell | k) \\
& + \sum_{\lambda} (J^0 | \mathcal{X}_\lambda | M^0) (K^0 | V_b | K^0) (L^0 | V_c | K^0) (j | Q_\lambda | m) (\ell | k) \\
& + \sum_{\lambda, s} (J^0 | V_a | M^0) (K^0 | \mathcal{X}_\lambda | K^0) (L^0 | \mathcal{X}_s | K^0) (j | m) (k | Q_\lambda | k) (\ell | Q_s | k) \\
& + \sum_{\lambda, s} (J^0 | \mathcal{X}_\lambda | M^0) (K^0 | V_b | K^0) (L^0 | \mathcal{X}_s | K^0) (j | Q_\lambda | m) (\ell | Q_s | k) \\
& + \sum_{\lambda, s} (J^0 | \mathcal{X}_\lambda | M^0) (K^0 | \mathcal{X}_s | K^0) (L^0 | V_c | K^0) (j | Q_\lambda | m) (k | Q_s | k) (\ell | k) \\
& \left. \left. + \sum_{\lambda, s, t} (J^0 | \mathcal{X}_\lambda | M^0) (K^0 | \mathcal{X}_s | K^0) (L^0 | \mathcal{X}_t | K^0) (j | Q_\lambda | m) (k | Q_s | k) (\ell | Q_t | k) \right\} \right]
\end{aligned}$$

Similar equations can be written for the coefficients F_{JM}^1 , F_{JM}^2 , and F_{JM}^3 by substituting (J°) for (K°) , (M°) for (L°) , and using the following relations (good for all orders 1, 2, 3).

$$(4-30) \quad \begin{aligned} F_{LK} &= F_{KL}^* \\ F_{JM} &= F_{MJ}^* \\ F_{ML}^{JK} &= F_{LM}^{KJ*} \end{aligned} \quad \begin{array}{l} * \text{ denotes complex conjugates} \end{array}$$

where the permutations LK to KL , JM to MJ apply to the wave functions but not to the energy denominators. Following the lead of part B of this chapter, we need consider for the perturbation expansions, only the pertinent matrix element products of the oscillator strength, natural rotational strength, and magnetic rotational strengths. Extracting these products from equations (2-100) of Chapter 2 and designating them P_D , P_R , P_A , P_B , and P_C (their origin being D_{jk} , R_{jk} , A_{jk} , B_{jk} and C_{jk} respectively), we have:

$$(4-31) \quad \begin{aligned} a) \quad P_D &= (K_k | \vec{\mu} | J_j) \cdot (J_j | \vec{\mu} | K_k) \\ b) \quad P_R &= (K_k | \vec{\mu} | J_j) \cdot (J_j | \vec{m} | K_k) \\ c) \quad P_A &= [(K_k | \vec{m} | K_k) - (J_j | \vec{m} | J_j)] \cdot (J_j | \vec{\mu} | K_k) \times (K_k | \vec{\mu} | J_j) \\ d) \quad P_B &= (N_n | \vec{m} | J_j) \cdot (J_j | \vec{\mu} | K_k) \times (K_k | \vec{\mu} | N_n) \\ e) \quad P_C &= (J_j | \vec{m} | J_j) \cdot (J_j | \vec{\mu} | K_k) \times (K_k | \vec{\mu} | J_j) \end{aligned}$$

There are two factors that should be noted. First, if we determine the symmetry rules for P_A in the proper manner, we will at the same time determine those for P_C . This can be used to advantage in the writing of our computer program. Secondly, in the expression for P_B

we have not listed the second matrix product found in equation (2-100) for the "B" magnetic rotational strength. This presents no problem as the symmetry analysis for this second matrix product can be determined from the analysis of P_B by interchanging the symmetries of (J_f) and (K_f) . The symmetry pattern for the "B" magnetic rotational strength will then be the union of these two symmetry patterns.

Before we develop the expansions for the five matrix element products of equation (4-31), we digress to discuss the "component" concept (See part B of this chapter; also Footnote 3.). We use the word, component, in the sense that each "component" will have its own individual symmetry patterns. The classification will be different for groups with degenerate representations than for groups without degenerate representations.

Consider first, molecules belonging to point groups containing no degenerate representations. For absorption and natural optical activity, the x, y and z components are readily identified. For magnetically-induced optical activity, this component specification is more complex as we have, rather than a simple scalar product, the dot-cross product commonly known as the triple product. Thus, there are expressions such as (Footnote 10):

$$\begin{aligned}
 \vec{m} \cdot \vec{\mu} \times \vec{\mu} &= m_x (\mu_y \mu_z - \mu_z \mu_y) \\
 (4-32) \qquad &+ m_y (\mu_z \mu_x - \mu_x \mu_z) \\
 &+ m_z (\mu_x \mu_y - \mu_y \mu_x)
 \end{aligned}$$

Here there are six distinguishable "components", corresponding to the six terms of equation (4-32), and we designate them as xy_z , xzy , yzx , yxz , zxy and zyx .

We may now consider molecules having a three-fold or higher

axis of symmetry. For these molecules, χ and γ form the members of a degenerate representation and z transforms as a non-degenerate representation. For absorption and natural optical activity, the components are given by:

$$(4-33) \quad \begin{aligned} \vec{\mu} \cdot \vec{\mu} &= (\mu_x \mu_x + \mu_y \mu_y) + \mu_z \mu_z \\ \vec{\mu} \cdot \vec{m} &= (\mu_x m_x + \mu_y m_y) + \mu_z m_z \end{aligned}$$

and are designated as the $\chi\gamma$ and z components. To determine the components for magnetically-induced optical activity, we must rearrange equation (4-32). Thus:

$$\begin{aligned} \vec{m} \cdot \vec{\mu} \times \vec{\mu} &= (m_x \mu_y - m_y \mu_x) \mu_z \\ &\quad + m_z (\mu_x \mu_y - \mu_y \mu_x) \\ &\quad + m_y \mu_z \mu_x - m_x \mu_z \mu_y \end{aligned}$$

Since χ and γ are the members of a degenerate representation, we have three components from this triple product:

$$(4-34) \quad \begin{aligned} & (m_x \mu_y - m_y \mu_x) \mu_z \\ & m_z (\mu_x \mu_y - \mu_y \mu_x) \\ & m_y \mu_z \mu_x - m_x \mu_z \mu_y \end{aligned}$$

which we designate as the $\chi\gamma z$, $z\chi\gamma$ and $\gamma z\chi$ components. The results of the computer symmetry analysis that are presented in section 4 of this part of the chapter clearly demonstrate that these are components, in the sense that they have their own unique symmetry patterns.

We now develop the expansions for P_R , P_B , P_C from the basic expansions of the matrix elements. These latter expansions are

either given by, or can be developed from, equation (4-25). We do not show here the expansion for P_A or P_D as they are readily obtained from those of P_C and P_R respectively. Substituting the matrix element expansions into equations (4-31b), we find for P_R , again suppressing vibrational wave functions:

$$\begin{aligned}
 P_R &= (K|\mu|J)(J|m|K) \\
 (4-35) \quad &= (K^0|\mu|J^0)(J^0|m|K^0) \\
 &+ \sum_{L^0 \neq K^0} \left[F_{LK}(K^0|\mu|J^0)(J^0|m|L^0) \right. \\
 &\quad \left. + F_{LK}^*(L^0|\mu|J^0)(J^0|m|K^0) \right] \\
 &+ \sum_{M^0 \neq J^0} \left[F_{MJ}(K^0|\mu|M^0)(J^0|m|K^0) \right. \\
 &\quad \left. + F_{MJ}^*(K^0|\mu|J^0)(M^0|m|K^0) \right] \\
 &+ \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq J^0}} \left[F_{ML}^{JK}(K^0|\mu|J^0)(M^0|m|L^0) \right. \\
 &\quad \left. + F_{ML}^{JK*}(L^0|\mu|M^0)(J^0|m|K^0) \right] \\
 &+ \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq J^0}} \left[F_{LK}F_{MJ}(K^0|\mu|M^0)(J^0|m|L^0) \right. \\
 &\quad \left. + F_{LK}^*F_{MJ}^*(L^0|\mu|J^0)(M^0|m|K^0) \right] \\
 &+ \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq K^0}} F_{LK}F_{MK}^*(M^0|\mu|J^0)(J^0|m|L^0) \\
 &+ \sum_{\substack{L^0 \neq J^0 \\ M^0 \neq J^0}} F_{MJ}^*F_{LJ}(K^0|\mu|L^0)(M^0|m|K^0)
 \end{aligned}$$

$$\begin{aligned}
& + \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq J^0 \\ N^0 \neq K^0}} \left[F_{LK} F_{MN}^{KJ} (M^0 | \mu | N^0) (J^0 | m | L^0) \right. \\
& \quad \left. + F_{LK}^* F_{MN}^{KJ*} (L^0 | \mu | J^0) (N^0 | m | M^0) \right] \\
& + \sum_{\substack{L^0 \neq J^0 \\ M^0 \neq J^0 \\ N^0 \neq K^0}} \left[F_{MJ} F_{LN}^{JK} (K^0 | \mu | M^0) (L^0 | m | N^0) \right. \\
& \quad \left. + F_{MJ}^* F_{LN}^{JK*} (N^0 | \mu | L^0) (M^0 | m | K^0) \right]
\end{aligned}$$

We have not designated which of the P_R components we are dealing with, but this is easily done by adding the proper subscripts to μ and m in the above equation.

We note here that to obtain P_D , we simply replace all the m by μ . For P_B , to second-order, we have:

$$\begin{aligned}
(4-36) \quad P_B &= (N | m | J) (J | \mu | K) (K | \mu | N) \\
&= (N^0 | m | J^0) (J^0 | \mu | K^0) (K^0 | \mu | N^0) \\
&+ \sum_{L^0 \neq K^0} \left[F_{LK} (N^0 | m | J^0) (J^0 | \mu | L^0) (K^0 | \mu | N^0) \right. \\
& \quad \left. + F_{LK}^* (N^0 | m | J^0) (J^0 | \mu | K^0) (L^0 | \mu | N^0) \right] \\
&+ \sum_{M^0 \neq J^0} \left[F_{MJ} (N^0 | m | M^0) (J^0 | \mu | K^0) (K^0 | \mu | N^0) \right. \\
& \quad \left. + F_{MJ}^* (N^0 | m | J^0) (M^0 | \mu | K^0) (K^0 | \mu | N^0) \right] \\
&+ \sum_{L^0 \neq N^0} \left[F_{LN} (N^0 | m | J^0) (J^0 | \mu | K^0) (K^0 | \mu | L^0) \right. \\
& \quad \left. + F_{LN}^* (L^0 | m | J^0) (J^0 | \mu | K^0) (K^0 | \mu | N^0) \right]
\end{aligned}$$

$$\begin{aligned}
& + \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq J^0}} F_{ML}^{JK} (N^0 | m | J^0) (M^0 | \mu | L^0) (K^0 | \mu | N^0) \\
& + \sum_{\substack{L^0 \neq J^0 \\ M^0 \neq N^0}} F_{ML}^{NJ} (M^0 | m | L^0) (J^0 | \mu | K^0) (K^0 | \mu | N^0) \\
& + \sum_{\substack{L^0 \neq N^0 \\ M^0 \neq K^0}} F_{ML}^{KN} (N^0 | m | J^0) (J^0 | \mu | K^0) (M^0 | \mu | L^0) \\
& + \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq J^0}} \left[F_{LK} F_{MJ} (N^0 | m | M^0) (J^0 | \mu | L^0) (K^0 | \mu | N^0) \right. \\
& \quad + F_{LK}^* F_{MJ}^* (N^0 | m | J^0) (M^0 | \mu | K^0) (L^0 | \mu | N^0) \\
& \quad \left. + F_{LK}^* F_{MJ} (N^0 | m | M^0) (J^0 | \mu | K^0) (L^0 | \mu | N^0) \right] \\
& + \sum_{\substack{L^0 \neq J^0 \\ M^0 \neq N^0}} \left[F_{LJ} F_{MN} (N^0 | m | L^0) (J^0 | \mu | K^0) (K^0 | \mu | M^0) \right. \\
& \quad + F_{LJ}^* F_{MN}^* (M^0 | m | J^0) (L^0 | \mu | K^0) (K^0 | \mu | N^0) \\
& \quad \left. + F_{LJ}^* F_{MN} (N^0 | m | J^0) (L^0 | \mu | K^0) (K^0 | \mu | M^0) \right] \\
& + \sum_{\substack{L^0 \neq N^0 \\ M^0 \neq K^0}} \left[F_{LN} F_{MK} (N^0 | m | J^0) (J^0 | \mu | M^0) (K^0 | \mu | L^0) \right. \\
& \quad + F_{LN}^* F_{MK}^* (L^0 | m | J^0) (J^0 | \mu | K^0) (M^0 | \mu | N^0) \\
& \quad \left. + F_{LN}^* F_{MK} (L^0 | m | J^0) (J^0 | \mu | M^0) (K^0 | \mu | N^0) \right] \\
& + \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq J^0}} F_{LK} F_{MK}^* (N^0 | m | J^0) (J^0 | \mu | L^0) (M^0 | \mu | N^0) \\
& + \sum_{\substack{L^0 \neq J^0 \\ M^0 \neq N^0}} F_{LJ} F_{MJ}^* (N^0 | m | L^0) (M^0 | \mu | K^0) (K^0 | \mu | N^0) \\
& + \sum_{\substack{L^0 \neq N^0 \\ M^0 \neq K^0}} F_{LN} F_{MN}^* (M^0 | m | J^0) (J^0 | \mu | K^0) (K^0 | \mu | L^0)
\end{aligned}$$

Finally, for P_c , to second-order, we have:

$$\begin{aligned}
 (4-37) \quad P_c &= (J|m|J)(J|\mu|K)(K|\mu|J) \\
 &= (J^0|m|J^0)(J^0|\mu|K^0)(K^0|\mu|J^0) \\
 &\quad + \sum_{L^0 \neq K^0} \left[F_{LK}(J^0|m|J^0)(J^0|\mu|L^0)(K^0|\mu|J^0) \right. \\
 &\quad \left. + F_{LK}^*(J^0|m|J^0)(J^0|\mu|K^0)(L^0|\mu|J^0) \right] \\
 &\quad + \sum_{M^0 \neq J^0} \left[F_{MJ}(J^0|m|J^0)(J^0|\mu|K^0)(K^0|\mu|J^0) \right. \\
 &\quad \left. + F_{MJ}^*(J^0|m|J^0)(M^0|\mu|K^0)(K^0|\mu|M^0) \right] \\
 &\quad + \sum_{\substack{M^0 \neq J^0 \\ L^0 \neq K^0}} \left[F_{MJ}(J^0|m|M^0)(J^0|\mu|K^0)(K^0|\mu|J^0) \right. \\
 &\quad \left. + F_{MJ}^*(M^0|m|J^0)(J^0|\mu|K^0)(K^0|\mu|J^0) \right] \\
 &\quad + \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq J^0}} \left[F_{ML}^{JK}(J^0|m|J^0)(M^0|\mu|L^0)(K^0|\mu|J^0) \right. \\
 &\quad \left. + F_{ML}^{JK*}(J^0|m|J^0)(J^0|\mu|K^0)(L^0|\mu|M^0) \right] \\
 &\quad + \sum_{\substack{L^0 \neq J^0 \\ M^0 \neq J^0}} F_{ML}^{JJ}(M^0|m|L^0)(J^0|\mu|K^0)(K^0|\mu|J^0)
 \end{aligned}$$

$$+ \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq J^0}} \left[F_{LK} F_{MJ} (J^0 | m | J^0) (J^0 | \mu | L^0) (K^0 | \mu | M^0) \right. \\ \left. + F_{LK}^* F_{MJ}^* (J^0 | m | J^0) (M^0 | \mu | K^0) (L^0 | \mu | J^0) \right]$$

$$+ \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq J^0}} \left[F_{LK} F_{MJ} (J^0 | m | M^0) (J^0 | \mu | L^0) (K^0 | \mu | J^0) \right. \\ \left. + F_{LK}^* F_{MJ}^* (M^0 | m | J^0) (J^0 | \mu | K^0) (L^0 | \mu | J^0) \right]$$

$$+ \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq J^0}} \left[F_{LK} F_{MJ}^* (M^0 | m | J^0) (J^0 | \mu | L^0) (K^0 | \mu | J^0) \right. \\ \left. + F_{LK}^* F_{MJ} (J^0 | m | M^0) (J^0 | \mu | K^0) (L^0 | \mu | J^0) \right]$$

$$+ \sum_{\substack{L^0 \neq J^0 \\ M^0 \neq J^0}} \left[F_{LJ} F_{MJ} (J^0 | m | L^0) (J^0 | \mu | K^0) (K^0 | \mu | M^0) \right. \\ \left. + F_{LJ}^* F_{MJ}^* (L^0 | m | J^0) (M^0 | \mu | K^0) (K^0 | \mu | J^0) \right]$$

$$+ \sum_{\substack{L^0 \neq J^0 \\ M^0 \neq J^0}} \left[F_{LJ} F_{MJ}^* (J^0 | m | L^0) (M^0 | \mu | K^0) (K^0 | \mu | J^0) \right. \\ \left. + F_{LJ}^* F_{MJ} (L^0 | m | J^0) (J^0 | \mu | K^0) (K^0 | \mu | M^0) \right]$$

$$+ \sum_{\substack{L^0 \neq J^0 \\ M^0 \neq J^0}} F_{LJ} F_{MJ}^* (J^0 | m | J^0) (M^0 | \mu | K^0) (K^0 | \mu | L^0)$$

$$+ \sum_{\substack{L^0 \neq K^0 \\ M^0 \neq K^0}} F_{LK} F_{MK}^* (J^0 | m | J^0) (J^0 | \mu | L^0) (M^0 | \mu | J^0)$$

These three expansions -- equations (4-35), (4-36), and (4-37) -- along with corresponding expressions for P_D and P_A , reveal the complexity inherent in considering these higher-order perturbations. This complexity becomes most evident when the coefficients F_{LK} , F_{MJ} , F_{ML}^{JK} , etc. are substituted from equations (4-29). However, actual substitution will only produce a morass of terms which do little else but confuse the situation. Fortunately, there are some preliminary simplifications which eliminate the majority of these terms. These simplifications fall into two categories. First, as we deal with no higher than third-order expansions in absorption and natural optical activity and with no higher than second-order in magnetically-induced optical activity, we may simplify many of the coefficient products appearing in the equations for P_R , P_B , and P_C . For example, the product $F_{LK}F_{MJ}$ from equation (4-35) can be rewritten, using equations (4-26), as:

$$\begin{aligned} F_{LK}F_{MJ} &= (F_{LK}^1 + F_{LK}^2 + F_{LK}^3)(F_{MJ}^1 + F_{MJ}^2 + F_{MJ}^3) \\ &= F_{LK}^1F_{MJ}^1 + (F_{LK}^1F_{MJ}^2 + F_{LK}^2F_{MJ}^1) \\ &\quad + (F_{LK}^1F_{MJ}^3 + F_{LK}^2F_{MJ}^2 + F_{LK}^3F_{MJ}^1) \\ &\quad + (F_{LK}^2F_{MJ}^3 + F_{LK}^3F_{MJ}^2) + F_{LK}^3F_{MJ}^3 \end{aligned}$$

but, as we take natural optical activity only to third-order, we may approximate

$$F_{LK}F_{MJ} \cong F_{LK}^1F_{MJ}^1 + F_{LK}^1F_{MJ}^2 + F_{LK}^2F_{MJ}^1$$

Similar restrictions can be made for absorption and magnetically-induced optical activity, and for their coefficient products. The second type of preliminary simplification involves the application of basic symmetry arguments to the vibrational matrix elements. These

symmetry arguments are similar to those presented in part B of this chapter. In the next section, we discuss the simplifications of the expansion for P_R , P_B and P_C .

2. Preliminary Symmetry Analysis and the Resulting Simplification of the Equations for P_D , P_R , P_A , P_B and P_C

The first type of simplification described at the conclusion of the previous section is readily understood and implemented. The second type, the preliminary analysis, is not as straightforward and entails a great deal of algebra. For two reasons, it is impractical to elaborate each step of the simplification. First, the number of pages needed to completely describe the analysis is prohibitive. Second, the multitude of algebraic manipulations would only detract from the continuity of the presentation. Therefore, the reader will have to be content with a description of the general rules of simplification, with the simplified expansions and with the knowledge that the final results confirm previously derived symmetry rules and advance new ones.

The basis of the symmetry analysis is the examination, in sequence, of the zero-order, first-order, second-order and third-order terms. Each order must be examined in the light of whether it provides any new symmetry patterns. If it adds a pattern different from patterns of lower order terms by only a totally symmetric representation, then it is considered to provide no new information and can be ignored.

We may best illustrate the above by reference to an example. We choose from the expansion for P_R ; the zero-order term, a first-order term and a second-order term. By examining these not only do we illustrate the symmetry analysis, but in the process, generate a new symmetry conclusion. Taking from equation (4-35), the zero-order term

and the first part of the next term, and substituting from equation (4-26), we have:

$$(4-38) \quad [P_R]_{\text{First Two Terms}} = (K^0 | \mu | J^0) (J^0 | m | K^0) \\ + \sum_{L^0 \neq K^0} F_{LK}^1 (K^0 | \mu | J^0) (J^0 | m | L^0) \\ + \sum_{L^0 \neq K^0} F_{LK}^2 (K^0 | \mu | J^0) (J^0 | m | L^0) \\ + \sum_{L^0 \neq K^0} F_{LK}^3 (K^0 | \mu | J^0) (J^0 | m | L^0)$$

As we are not concerned with third-order terms in this example, we drop the fourth terms in equation (4-38). We now substitute the expressions for F_{LK}^1 and F_{LK}^2 from equation (4-29), including the (previously suppressed) vibrational wave functions.

$$(4-39) \quad [P_R]_{\text{First Two Terms}} = (K^0 | \mu | J^0) (J^0 | m | K^0) (k | j) (j | k) \\ + \sum_{L^0 \neq K^0} \sum_L \frac{1}{E_K^0 - E_L^0} (K^0 | \mu | J^0) (J^0 | m | L^0) (L^0 | V_a | K^0) (k | j) (j | L) (L | k) \\ + \sum_{L^0 \neq K^0} \sum_L \frac{1}{E_K^0 - E_L^0} (K^0 | \mu | J^0) (J^0 | m | L^0) (L^0 | \mathcal{Z}_a | K^0) (k | j) (j | L) (L | Q_a | k) \\ + \sum_{L^0 \neq K^0} \sum_L \frac{1}{E_K^0 - E_L^0} \left\{ \sum_{M^0 \neq K^0} \frac{1}{E_K^0 - E_M^0} \{ (K^0 | \mu | J^0) (J^0 | m | L^0) (L^0 | V_a | M^0) (M^0 | V_b | K^0) (k | j) (j | L) (L | k) \right. \\ + \sum_{\lambda} (K^0 | \mu | J^0) (J^0 | m | L^0) (L^0 | V_a | M^0) (M^0 | \mathcal{Z}_a | K^0) (k | j) (j | L) (L | Q_a | k) \\ + \sum_{\lambda} (K^0 | \mu | J^0) (J^0 | m | L^0) (L^0 | \mathcal{Z}_a | M^0) (M^0 | V_b | K^0) (k | j) (j | L) (L | Q_a | k) \\ \left. + \sum_{\lambda, \delta} (K^0 | \mu | J^0) (J^0 | m | L^0) (L^0 | \mathcal{Z}_a | M^0) (M^0 | \mathcal{Z}_b | K^0) (k | j) (j | L) (L | Q_a Q_b | k) \right\}$$

$$\begin{aligned}
& - \left[\frac{1}{E_k^0 - E_l^0} \left\{ (K^0 | \mu | J^0) (J^0 | m | L^0) (L^0 | v_a | K^0) (K^0 | v_b | K^0) (k | j) (j | l) (l | k) \right. \right. \\
& \quad + \sum_{\lambda} (K^0 | \mu | J^0) (J^0 | m | L^0) (L^0 | v_a | K^0) (K^0 | \lambda_a | K^0) (k | j) (j | l) (l | k) (k | \lambda_a | k) \\
& \quad + \sum_{\lambda} (K^0 | \mu | J^0) (J^0 | m | L^0) (L^0 | \lambda_a | K^0) (K^0 | v_b | K^0) (k | j) (j | l) (l | \lambda_a | k) \\
& \quad \left. \left. + \sum_{\lambda, s} (K^0 | \mu | J^0) (J^0 | m | L^0) (L^0 | \lambda_a | K^0) (K^0 | \lambda_b | K^0) (k | j) (j | l) (l | \lambda_a | k) (\lambda_b | s | k) \right\} \right]
\end{aligned}$$

The zero-order term of equation (4-39) will be zero for groups other than the pure rotation groups. Only for these groups can one have non-zero, zero-order natural optical activity. The first order substitutional contribution adds a new symmetry pattern (for groups other than the pure rotation groups) as, according to Conclusion 4, part of the substitutional perturbation must transform as the pseudoscalar representation. From Conclusion 8, we see that (for other than the pure rotation groups), the first-order vibrational contribution is zero.

We now turn to the second-order terms, of which eight are given in equation (4-39). Examining the first of these, a purely substitutional contribution, we see that from the third and fourth electronic matrix elements result the direct product relations

$$\Gamma_M = \Gamma_L \otimes \Gamma_{v_a}$$

$$\Gamma_M = \Gamma_K \otimes \Gamma_{v_b}$$

Combining these, we have:

$$\Gamma_{v_a} \otimes \Gamma_{v_b} = \Gamma_L \otimes \Gamma_K$$

Combining this equation with equation (4-19), we have:

$$\Gamma_{v_a} \otimes \Gamma_{v_b} = \Gamma_s$$

Thus, there can be a second-order term only if there are two existing substitutional symmetry patterns whose direct product is the pseudoscalar representation. This is a new symmetry conclusion.

Conclusion 10. There is second-order substitutional contribution to natural optical activity only if the direct product of two existing substitutional symmetry patterns transforms as the pseudoscalar. As this does not necessarily mean that there must be a single existing symmetry pattern transforming as the pseudoscalar, therefore there can be a second-order substitutional contribution to natural optical activity when both the zero-order and first-order contributions are zero.

The fifth second-order term also is a purely substitutional contribution. However, Conclusion 10 holds only partially, as a part of the substitutional symmetry pattern must transform as the pseudoscalar representation, in order that this term be non-zero.

Application of the sum rule, equation (4-21) to the second of the eight second-order terms -- a mixed substitutional-vibrational contribution -- enables us to show that the two equations

$$\Gamma_f = \Gamma_k$$

$$\Gamma_f = \Gamma_k \otimes \Gamma_{Q_k}$$

must hold. These two equations, in turn, demonstrate that Γ_{Q_k} is the totally symmetric representation. An examination of the electronic matrix elements, in the light of Conclusion 10, reveals that this second-order term will make a non-zero contribution only if the substitutional

symmetry pattern contains a part transforming as the pseudoscalar. However, more germane to the present discussion is that, upon setting $\Gamma_{\alpha\alpha} = \Gamma_0$ we see that this second-order term is simply a correction on the first-order term, in that it yields no new symmetry pattern. Therefore, we eliminate this term from consideration. These arguments can be shown to apply also to the third, sixth, and seventh-order terms, and they also can be disregarded.

The fourth and eighth second-order terms are purely vibrational contributions. Examining the vibrational matrix elements of the fourth term, we see that though Q_{α} and Q_{β} need not be totally symmetric, they must be of the same symmetry. This means that $\Gamma_{\alpha\alpha} = \Gamma_{\beta\beta}$ and the consequence is that $\Gamma_L = \Gamma_K$. Thus, we see that this purely vibrational contribution can be non-zero only when the zero-order term is non-zero, i.e. for pure rotation groups. The fourth term, and also the eighth term, are simple corrections and introduce no new symmetry patterns to natural optical activity. However, this is not the case for absorption where second-order, purely vibrational terms are the primary contribution to vibronic structuring. We thus have our eleventh conclusion.

Conclusion 11. Other than for the pure rotation groups, there is no second-order purely vibrational contribution to natural optical activity.

Before we leave this discussion, it is well to point out that purely vibrational or mixed vibrational-substitutional contributions introduce no new symmetry patterns in natural optical activity. This is the reason that we expand the natural rotational strength to third-order. At this level, we find that there is a vibrational contribution of importance and in third order, we can begin to discuss the vibronic structuring of natural optical activity for other than pure rotation

groups. The nature of such third-order contributions will be discussed in part C of this Chapter.

Having performed the long and tedious, but necessary, preliminary symmetry simplifications, we list in Table VIII the non-trivial contributions to the oscillator strength and to the natural and magnetically-induced rotational strengths. Although not important to evaluation of symmetry patterns, we also list the pertinent energy difference denominators in the table. However, we do suppress the vibrational wave functions. The pattern of tabling these terms is important to the operation of the computer program and is discussed in section 3.

One will note that there has been an enormous simplification of the various expansions. However, as we shall see in the next section, the symmetry calculations for even these sets of terms are intractable without a computer program.

3. Symmetry Pattern Determination for the Absorption, the Natural Optical Activity, and the Magnetically-Induced Optical Activity of Molecules Belonging to the Point Group C_{4v} : a Computer Analysis.

Non-planar heme and various transition metal complexes belong to the point group C_{4v} . As this point group contains one degenerate representation, a computer program is necessary for the higher order symmetry analysis of the various optical phenomena. This need results from two complications: (i) the existence of symmetry underspecification and (ii) an increase of the number of possible symmetry patterns due to the presence of a degenerate representation.

The first complexity, symmetry underspecification, is observed upon inspection of the second- and third- order terms of the oscillator and rotational strengths listed in Table VIII. Many of these higher order terms are underspecified in that not enough symmetry

*ABSORPTION AND NATURAL OPTICAL ACTIVITY

<u>Term Number</u>	<u>Energy Denominators</u>	<u>Form of Term</u>	<u>Number of Symmetry Terms</u>
		$(K^0 O_1 J^0)(J^0 O_2 K^0)$ $\mu \quad m$	
1	$(E_K^0 - E_L^0)$	$(L^0 O_1 J^0)(J^0 O_2 K^0)(K^0 O_3 L^0)$ $m \quad \mu \quad V_a$	1
2	$(E_J^0 - E_L^0)$	$V_a \quad \mu \quad m$	1
3	$(E_K^0 - E_L^0)(E_K^0 - E_M^0)$	$(L^0 O_1 J^0)(J^0 O_2 K^0)(K^0 O_3 M^0)(M^0 O_4 L^0)$ $m \quad \mu \quad V_a \quad V_b$	N
4	$(E_J^0 - E_L^0)(E_J^0 - E_M^0)$	$V_a \quad \mu \quad m \quad V_b$	N
5	$(E_J^0 - E_L^0)(E_K^0 - E_M^0)$	$V_a \quad \mu \quad V_b \quad m$	N
6	$(E_J^0 - E_L^0)(E_K^0 - E_M^0)$	$(L^0 O_1 J^0)(J^0 O_2 M^0)(M^0 O_3 K^0)(K^0 O_4 L^0)$ $\left\{ \begin{array}{llll} V_a & \mu & V_b & m \\ \mathcal{H}_L & \mu & \mathcal{H}_S & m \end{array} \right\}$	1
7	$(E_J^0 - E_L^0)(E_J^0 - E_M^0)$	$\left\{ \begin{array}{llll} V_a & V_b & \mu & m \\ \mathcal{H}_L & \mathcal{H}_S & \mu & m \end{array} \right\}$	1
8	$(E_K^0 - E_L^0)(E_K^0 - E_M^0)$	$\left\{ \begin{array}{llll} m & \mu & V_a & V_b \\ m & \mu & \mathcal{H}_L & \mathcal{H}_S \end{array} \right\}$	1
9	$(E_K^0 - E_L^0)(E_K^0 - E_M^0)(E_K^0 - E_N^0)$	$(L^0 O_1 J^0)(J^0 O_2 K^0)(K^0 O_3 M^0)(M^0 O_4 N^0)(N^0 O_5 L^0)$ $m \quad \mu \quad V_a \quad V_b \quad V_c$	N ²
10	$(E_J^0 - E_L^0)(E_J^0 - E_M^0)(E_J^0 - E_N^0)$	$V_a \quad \mu \quad m \quad V_b \quad V_c$	N ²
11	$(E_J^0 - E_L^0)(E_K^0 - E_M^0)(E_J^0 - E_N^0)$	$\left\{ \begin{array}{lllll} V_a & \mu & V_b & m & V_c \\ \mathcal{H}_L & \mu & \mathcal{H}_S & m & V_a \end{array} \right\}$	N ²
12	$(E_J^0 - E_L^0)(E_K^0 - E_M^0)(E_K^0 - E_N^0)$	$\left\{ \begin{array}{lllll} V_a & \mu & V_b & V_c & m \\ \mathcal{H}_L & \mu & \mathcal{H}_S & V_a & m \end{array} \right\}$	N ²

TABLE VIII

Term Listing

*ABSORPTION AND NATURAL OPTICAL ACTIVITY (cont.)

Term Number	Energy Denominators	Form of Term	Number of Symmetry Terms
		$(L^0 C_1 J^0)(J^0 O_2 M^0)(M^0 O_3 K^0)(K^0 O_4 N^0)(N^0 O_5 L^0)$	
13	$(E_J^0 - E_L^0)(E_K^0 - E_M^0)(E_J^0 - E_N^0)$	$\left\{ \begin{array}{ccccc} V_a & \mu & V_b & m & V_c \\ \mathcal{H}_r & \mu & \mathcal{H}_s & m & V_a \\ V_a & \mu & \mathcal{H}_r & m & \mathcal{H}_s \end{array} \right\}$	N
14	$(E_J^0 - E_L^0)(E_J^0 - E_M^0)(E_J^0 - E_N^0)$	$\left\{ \begin{array}{ccccc} V_a & V_b & \mu & m & V_c \\ \mathcal{H}_r & \mathcal{H}_s & \mu & m & V_a \\ V_a & \mathcal{H}_r & \mu & m & \mathcal{H}_s \end{array} \right\}$	N
15	$(E_K^0 - E_L^0)(E_K^0 - E_M^0)(E_K^0 - E_N^0)$	$\left\{ \begin{array}{ccccc} m & \mu & V_a & V_b & V_c \\ m & \mu & \mathcal{H}_r & \mathcal{H}_s & V_a \\ m & \mu & \mathcal{H}_r & V_a & \mathcal{H}_s \end{array} \right\}$	N
16	$(E_K^0 - E_L^0)(E_J^0 - E_M^0)(E_K^0 - E_N^0)$	$\left\{ \begin{array}{ccccc} m & V_a & \mu & V_b & V_c \\ m & \mathcal{H}_r & \mu & \mathcal{H}_s & V_a \\ m & \mathcal{H}_r & \mu & V_a & \mathcal{H}_s \end{array} \right\}$	N
17	$(E_J^0 - E_L^0)(E_K^0 - E_M^0)(E_K^0 - E_N^0)$	$\left\{ \begin{array}{ccccc} V_a & \mu & V_b & V_c & m \\ V_a & \mu & \mathcal{H}_r & \mathcal{H}_s & m \\ \mathcal{H}_r & \mu & \mathcal{H}_s & V_a & m \\ \mathcal{H}_r & \mu & \mathcal{H}_s & \mathcal{H}_t & m \end{array} \right\}$	N
18	$(E_J^0 - E_L^0)(E_J^0 - E_M^0)(E_K^0 - E_N^0)$	$\left\{ \begin{array}{ccccc} V_a & V_b & \mu & V_c & m \\ V_a & \mathcal{H}_r & \mu & \mathcal{H}_s & m \\ \mathcal{H}_r & \mathcal{H}_s & \mu & V_a & m \\ \mathcal{H}_r & \mathcal{H}_s & \mu & \mathcal{H}_t & m \end{array} \right\}$	N

*For Absorption, replace all m by μ . For Natural Optical Activity there are additional components where μ and m are interchanged.

TABLE VIII (cont.)

MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM

Term Number	Energy Denominators	Form of Term	Number of Symmetry Terms
1		$(N^0 O_1 K^0)(K^0 O_2 J^0)(J^0 O_3 N^0)$ $\mu \quad \mu \quad m$	1
2	$(E_N^0 - E_L^0)$	$(N^0 O_1 K^0)(K^0 O_2 J^0)(J^0 O_3 L^0)(L^0 O_4 N^0)$ $\mu \quad \mu \quad V_a \quad m$	1
3	$(E_J^0 - E_L^0)$	$(N^0 O_1 K^0)(K^0 O_2 J^0)(J^0 O_3 L^0)(L^0 O_4 N^0)$ $\mu \quad \mu \quad m \quad V_a$	1
4	$(E_J^0 - E_L^0)$	$(N^0 O_1 K^0)(K^0 O_2 L^0)(L^0 O_3 J^0)(J^0 O_4 N^0)$ $\mu \quad \mu \quad V_a \quad m$	1
5	$(E_K^0 - E_L^0)$	$(N^0 O_1 K^0)(K^0 O_2 L^0)(L^0 O_3 J^0)(J^0 O_4 N^0)$ $\mu \quad V_a \quad \mu \quad m$	1
6	$(E_K^0 - E_L^0)$	$(N^0 O_1 L^0)(L^0 O_2 K^0)(K^0 O_3 J^0)(J^0 O_4 N^0)$ $\mu \quad V_a \quad \mu \quad m$	1
7	$(E_N^0 - E_L^0)$	$(N^0 O_1 L^0)(L^0 O_2 K^0)(K^0 O_3 J^0)(J^0 O_4 N^0)$ $V_a \quad \mu \quad \mu \quad m$	1
8	$(E_K^0 - E_L^0)(E_N^0 - E_M^0)$	$(N^0 O_1 L^0)(L^0 O_2 K^0)(K^0 O_3 J^0)(J^0 O_4 M^0)(M^0 O_5 N^0)$ $\left\{ \begin{array}{l} \mu \\ \mu \end{array} \right. \quad \left\{ \begin{array}{l} V_a \\ \mathcal{H}_s \end{array} \right. \quad \left\{ \begin{array}{l} \mu \\ \mu \end{array} \right. \quad \left\{ \begin{array}{l} m \\ m \end{array} \right. \quad \left\{ \begin{array}{l} V_b \\ \mathcal{H}_s \end{array} \right. \}$	1
9	$(E_N^0 - E_L^0)(E_N^0 - E_M^0)$	$(N^0 O_1 L^0)(L^0 O_2 K^0)(K^0 O_3 J^0)(J^0 O_4 M^0)(M^0 O_5 N^0)$ $\left\{ \begin{array}{l} V_a \\ \mathcal{H}_s \end{array} \right. \quad \left\{ \begin{array}{l} \mu \\ \mu \end{array} \right. \quad \left\{ \begin{array}{l} \mu \\ \mu \end{array} \right. \quad \left\{ \begin{array}{l} m \\ m \end{array} \right. \quad \left\{ \begin{array}{l} V_b \\ \mathcal{H}_s \end{array} \right. \}$	1
10	$(E_L^0 - E_L^0)(E_J^0 - E_M^0)$	$(N^0 O_1 L^0)(L^0 O_2 K^0)(K^0 O_3 J^0)(J^0 O_4 M^0)(M^0 O_5 N^0)$ $\left\{ \begin{array}{l} V_a \\ \mathcal{H}_s \end{array} \right. \quad \left\{ \begin{array}{l} \mu \\ \mu \end{array} \right. \quad \left\{ \begin{array}{l} \mu \\ \mu \end{array} \right. \quad \left\{ \begin{array}{l} V_b \\ \mathcal{H}_s \end{array} \right. \quad \left\{ \begin{array}{l} m \\ m \end{array} \right. \}$	1
11	$(E_K^0 - E_L^0)(E_J^0 - E_M^0)$	$(N^0 O_1 L^0)(L^0 O_2 K^0)(K^0 O_3 J^0)(J^0 O_4 M^0)(M^0 O_5 N^0)$ $\left\{ \begin{array}{l} \mu \\ \mu \end{array} \right. \quad \left\{ \begin{array}{l} V_a \\ \mathcal{H}_s \end{array} \right. \quad \left\{ \begin{array}{l} \mu \\ \mu \end{array} \right. \quad \left\{ \begin{array}{l} V_b \\ \mathcal{H}_s \end{array} \right. \quad \left\{ \begin{array}{l} m \\ m \end{array} \right. \}$	1
12	$(E_J^0 - E_L^0)(E_J^0 - E_M^0)$	$(N^0 O_1 K^0)(K^0 O_2 J^0)(J^0 O_3 L^0)(L^0 O_4 M^0)(M^0 O_5 N^0)$ $\mu \quad \mu \quad V_a \quad V_b \quad m$	N
13	$(E_N^0 - E_L^0)(E_N^0 - E_M^0)$	$(N^0 O_1 K^0)(K^0 O_2 J^0)(J^0 O_3 L^0)(L^0 O_4 M^0)(M^0 O_5 N^0)$ $\mu \quad \mu \quad m \quad V_a \quad V_b$	N
14	$(E_J^0 - E_L^0)(E_N^0 - E_M^0)$	$(N^0 O_1 K^0)(K^0 O_2 J^0)(J^0 O_3 L^0)(L^0 O_4 M^0)(M^0 O_5 N^0)$ $\mu \quad \mu \quad V_a \quad m \quad V_b$	N

TABLE VIII (cont.)

MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM (cont.)

Term Number	Energy Denominators	Form of Term	Number of Symmetry Terms
15	$(E_J^0 - E_L^0)(E_J^0 - E_H^0)$	$(N^0 O_1 K^0)(K^0 O_2 M^0)(M^0 O_3 L^0)(L^0 O_4 J^0)(J^0 O_5 N^0)$ $\mu \quad \mu \quad V_a \quad V_b \quad m$	N
16	$(E_J^0 - E_L^0)(E_K^0 - E_H^0)$	$\mu \quad V_a \quad \mu \quad V_b \quad m$	N
17	$(E_K^0 - E_L^0)(E_K^0 - E_H^0)$	$\mu \quad V_a \quad V_b \quad \mu \quad m$	N
18	$(E_N^0 - E_L^0)(E_K^0 - E_H^0)$	$(N^0 O_1 L^0)(L^0 O_2 M^0)(M^0 O_3 K^0)(K^0 O_4 J^0)(J^0 O_5 N^0)$ $V_a \quad \mu \quad V_b \quad \mu \quad m$	N
19	$(E_N^0 - E_L^0)(E_N^0 - E_H^0)$	$V_a \quad V_b \quad \mu \quad \mu \quad m$	N
20	$(E_K^0 - E_L^0)(E_K^0 - E_H^0)$	$\mu \quad V_a \quad V_b \quad \mu \quad m$	N
21	$(E_K^0 - E_L^0)(E_K^0 - E_H^0)$	$(N^0 O_1 L^0)(L^0 O_2 K^0)(K^0 O_3 M^0)(M^0 O_4 J^0)(J^0 O_5 N^0)$ $\left\{ \begin{array}{l} \mu \quad V_a \quad V_b \quad \mu \quad m \\ \mu \quad \mathcal{H}_r \quad \mathcal{H}_s \quad \mu \quad m \end{array} \right\}$	1
22	$(E_N^0 - E_L^0)(E_K^0 - E_H^0)$	$\left\{ \begin{array}{l} V_a \quad \mu \quad V_b \quad \mu \quad m \\ \mathcal{H}_r \quad \mu \quad \mathcal{H}_s \quad \mu \quad m \end{array} \right\}$	1
23	$(E_N^0 - E_L^0)(E_J^0 - E_H^0)$	$\left\{ \begin{array}{l} V_a \quad \mu \quad \mu \quad V_b \quad m \\ \mathcal{H}_r \quad \mu \quad \mu \quad \mathcal{H}_s \quad m \end{array} \right\}$	1
24	$(E_K^0 - E_L^0)(E_J^0 - E_H^0)$	$\left\{ \begin{array}{l} \mu \quad V_a \quad \mu \quad V_b \quad m \\ \mu \quad \mathcal{H}_r \quad \mu \quad \mathcal{H}_s \quad m \end{array} \right\}$	1
25	$(E_K^0 - E_L^0)(E_J^0 - E_H^0)$	$(N^0 O_1 K^0)(K^0 O_2 L^0)(L^0 O_3 J^0)(J^0 O_4 M^0)(M^0 O_5 N^0)$ $\left\{ \begin{array}{l} \mu \quad V_a \quad \mu \quad V_b \quad m \\ \mu \quad \mathcal{H}_r \quad \mu \quad \mathcal{H}_s \quad m \end{array} \right\}$	1
26	$(E_J^0 - E_L^0)(E_J^0 - E_H^0)$	$\left\{ \begin{array}{l} \mu \quad \mu \quad V_a \quad V_b \quad m \\ \mu \quad \mu \quad \mathcal{H}_r \quad \mathcal{H}_s \quad m \end{array} \right\}$	1
27	$(E_J^0 - E_L^0)(E_N^0 - E_H^0)$	$\left\{ \begin{array}{l} \mu \quad \mu \quad V_a \quad m \quad V_b \\ \mu \quad \mu \quad \mathcal{H}_r \quad m \quad \mathcal{H}_s \end{array} \right\}$	1
28	$(E_K^0 - E_L^0)(E_N^0 - E_H^0)$	$\left\{ \begin{array}{l} \mu \quad V_a \quad \mu \quad m \quad V_b \\ \mu \quad \mathcal{H}_r \quad \mu \quad m \quad \mathcal{H}_s \end{array} \right\}$	1

TABLE VIII (cont.)

**MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A" AND "C" TERMS

Term Number	Energy Denominators	Form of Term	Number of Symmetry Terms
1		$(J^0 O_1 K^0)(K^0 O_2 J^0)(J^0 O_3 J^0)$	1
2	$(E_J^0 - E_L^0)$	$(J^0 O_1 K^0)(K^0 O_2 J^0)(J^0 O_3 L^0)(L^0 O_4 J^0)$	1
3	$(E_J^0 - E_L^0)$	$(J^0 O_1 K^0)(K^0 O_2 L^0)(L^0 O_3 J^0)(J^0 O_4 J^0)$	1
4	$(E_K^0 - E_L^0)$	$(J^0 O_1 K^0)(K^0 O_2 J^0)(J^0 O_3 L^0)(L^0 O_4 M^0)(M^0 O_5 J^0)$	1
5	$(E_J^0 - E_L^0)(E_J^0 - E_M^0)$	$(J^0 O_1 K^0)(K^0 O_2 M^0)(M^0 O_3 L^0)(L^0 O_4 J^0)(J^0 O_5 J^0)$	N
6	$(E_J^0 - E_L^0)(E_J^0 - E_M^0)$	$(J^0 O_1 K^0)(K^0 O_2 M^0)(M^0 O_3 L^0)(L^0 O_4 J^0)(J^0 O_5 J^0)$	N
7	$(E_J^0 - E_L^0)(E_J^0 - E_M^0)$	$(J^0 O_1 K^0)(K^0 O_2 M^0)(M^0 O_3 L^0)(L^0 O_4 J^0)(J^0 O_5 J^0)$	N
8	$(E_J^0 - E_L^0)(E_K^0 - E_M^0)$	$(J^0 O_1 K^0)(K^0 O_2 M^0)(M^0 O_3 L^0)(L^0 O_4 J^0)(J^0 O_5 J^0)$	N
9	$(E_K^0 - E_L^0)(E_K^0 - E_M^0)$	$(J^0 O_1 K^0)(K^0 O_2 M^0)(M^0 O_3 L^0)(L^0 O_4 J^0)(J^0 O_5 J^0)$	N
10	$(E_K^0 - E_L^0)(E_K^0 - E_M^0)$	$(J^0 O_1 M^0)(M^0 O_2 K^0)(K^0 O_3 L^0)(L^0 O_4 J^0)(J^0 O_5 J^0)$	1
11	$(E_K^0 - E_L^0)(E_J^0 - E_M^0)$	$(J^0 O_1 M^0)(M^0 O_2 K^0)(K^0 O_3 L^0)(L^0 O_4 J^0)(J^0 O_5 J^0)$	1
12	$(E_J^0 - E_L^0)(E_J^0 - E_M^0)$	$(J^0 O_1 M^0)(M^0 O_2 K^0)(K^0 O_3 L^0)(L^0 O_4 J^0)(J^0 O_5 J^0)$	1
13	$(E_J^0 - E_L^0)(E_J^0 - E_M^0)$	$(J^0 O_1 K^0)(K^0 O_2 M^0)(M^0 O_3 J^0)(J^0 O_4 L^0)(L^0 O_5 J^0)$	1
14	$(E_J^0 - E_L^0)(E_K^0 - E_M^0)$	$(J^0 O_1 K^0)(K^0 O_2 M^0)(M^0 O_3 J^0)(J^0 O_4 L^0)(L^0 O_5 J^0)$	1

** To obtain the excited state permanent magnetic moment terms of the "A" term, we replace the second sets of in each term by the sets and, in terms 2,5 and 6, replace the by , in terms 13 and 14, replace the first by .

TABLE VIII (cont.)

information is given to determine the representations of all the unknown wave functions and operators. As a prime example of underspecification, consider term 9 of the natural optical activity.

$$(L^0 | m | J^0)(J^0 | \mu | K^0)(K^0 | V_a | M^0)(M^0 | V_b | N^0)(N^0 | V_c | L^0)$$

We know the symmetry of $|J^0\rangle$, $|K^0\rangle$, m and μ . They are generally denoted as Γ_J , Γ_K , Γ_m and Γ_μ respectively. Using the standard methods, we may immediately evaluate the symmetry of $|L^0\rangle$:

$$\Gamma_L = \Gamma_m \otimes \Gamma_J$$

However, this is as far as we may go without providing any supplementary information. We therefore, supply the symmetry of one of the remaining unknown operators or wave functions. If there are N representations in the point group of the molecule, then there are N possible supplementary symmetries, and therefore, N possible variations on the original term, henceforth denoted as the parent term. Each of these variations will be referred to as a primary symmetry term.

Let us supply the symmetry of the unknown substitutional perturbation V_a . If the representation is denoted as Γ_{V_a} , we may then write for the symmetry representation of $|M^0\rangle$:

$$\Gamma_M = \Gamma_K \otimes \Gamma_{V_a}$$

However, we are again stymied and must supply a symmetry. Again, there are N possible supplementary symmetries, and therefore, N possible variations on each of the N primary symmetry terms. This results in a total of N^2 secondary symmetry terms, none of which are underspecified.

In the rest of this chapter, we will find it unnecessary to

distinguish between primary and secondary symmetry terms. We therefore, label them all as symmetry terms and a particular parent term is said to give rise to one, N , or N^2 symmetry terms, depending on the existence and degree of underspecification. However, we do make a distinction between undetermined and determined symmetry terms, as we shall make clear in the following paragraphs.

We now assume that for each of the underspecified parent terms, we have supplied the N or N^2 supplementary symmetry representations. The degree of underspecification -- 1, N or N^2 -- can be obtained for any term of the three optical phenomena by reference to Table VIII. We then have a large array (for absorption, $5 + 9N + 4N^2$) of undetermined symmetry terms. The adjective "undetermined" is used to emphasize that for each symmetry term, there are still wave functions and/or operators with unknown symmetry representations. However, unlike the parent terms, these undetermined symmetry terms are completely specified, in the sense that direct multiplication will completely determine these unknown symmetries. For non-degenerate representations direct multiplication yields one determined symmetry term from each undetermined symmetry term, i.e. the case described above. From now on, we shall refer to the undetermined symmetry terms simply as symmetry terms, and to the determined symmetry terms as group product terms.

We now come to the second complication. While for point groups containing only non-degenerate representations, there is one group product term for each symmetry term (as shown above), for groups containing degenerate representations, there can be many group product terms for each symmetry term, particularly for those symmetry terms resulting from the higher-order parent terms.

The source of this many-to-one correspondence is readily understood. As described above, if one has a matrix element in which the representations of two of its three parts are known, the third part can be determined by direct multiplication. If one or both of the known representations are non-degenerate, then for the third part, there results one unique representation, and thus, only one possible way for that matrix element to be totally symmetric (Footnote 11). If all matrix elements of a symmetry term are of such a nature, then there will be only one group product term for the symmetry term. However, if the two known parts of the matrix element belong to doubly-degenerate representations (Footnote 12), then there are three possible results, depending upon the types of doubly-degenerate representations involved: (i) there are four ways for the matrix element to be totally symmetric, corresponding to four non-degenerate representations that result from the direct product multiplication of the two doubly-degenerate representations, (ii) there are three ways for the matrix element to be totally symmetric, corresponding to two non-degenerate representations, and one doubly-degenerate representation that result from direct product multiplication, and (iii) there are two ways for the matrix element to be totally symmetric, corresponding to two doubly-degenerate representations that result from direct product multiplication. For any one of these three cases, there is more than one way for the matrix element to be totally symmetric and, therefore, more than one group product term associated with the symmetry term containing this matrix element.

We saw previously that although absorption has only eighteen parent terms, it has $(5 + 9N + 4N)$ symmetry terms, where N is the order of the point group involved. We now see that there are even more terms to consider due to the many-to-one correspondence of the group product terms to the symmetry terms. Fortunately, many of these group product terms are zero, reducing to a more reasonable level the number of

symmetry patterns that must be considered. We must now show how the number of group product terms can be reduced to only those that contribute.

The key to the group product term reduction is that for each doubly-degenerate representation, there are two members that cannot be physically distinguished, except by the lowering of the symmetry of the system. Consideration of all possible member combinations can be shown to lead to decomposition of each group product term into a sum of what shall be denoted as member product terms. For certain group product terms, these member product terms will sum to zero, and for these cases, the group product terms are zero.

The evaluation of the member product terms begins with the determination of a family of member elements for each matrix element of a group product term. If the matrix element has one non-degenerate representation and two doubly-degenerate representations, the family consists of four (2×2) member elements. If it has three doubly-degenerate representations, the family consists of eight ($2 \times 2 \times 2$) member elements (Footnote 13). The value of any one member element of a family is given by the product of two quantities: an integral common to all member elements of the family, and a constant, the coupling coefficient, which is unique to the member element under consideration. Now there are as many member product terms as there are legitimate permutations over all the families of member elements; a legitimate permutation being one where the ket member of the member element of the N^{th} family matches the bra member of the member element of the $N + 1$ family; and the bra member of the member element of the N^{th} family matches the ket member of the member element of the $N - 1$ family (Footnote 14). Each of these member products has a value which is given by

the product of two products. The first of these is the total product of the integrals associated with the various families and is the same regardless of the member product considered. The second product is the total product of all the coupling coefficients associated with the various families and can vary from one member product to another, due to the variation of coupling coefficients within the individual families (Footnote 15). If all the values of the member products from a particular group product term are zero, or alternately, if they all sum to zero, then that group product term is zero. If, however, the sum is not equal to zero, then that group product term makes a contribution and yields a symmetry pattern of vibration and/or substitution.

This method of group product reduction can be further clarified by reference to an example. We choose C_{4v} as our point group, as this is the group for which we shall do the more complete analysis. Table IX presents the group multiplication table for C_{4v} while Table X presents the coupling coefficients pertinent to our example. The former are available from most books on group theory while the latter can be obtained from Koster et al (90). We specifically examine the first parent term for the xy component of natural optical activity. From Table VIII and equation (4-33), this term is given by:

$$(4-40) \quad \begin{aligned} & (L^0 | m_x | J^0) (J^0 | \mu_x | K^0) (K^0 | V_a | L^0) \\ & + (L^0 | m_y | J^0) (J^0 | \mu_y | K^0) (K^0 | V_a | L^0) \end{aligned}$$

If we examine the transition from the totally symmetric ground state (representation A) to the doubly-degenerate excited state (representation E), then we have:

TABLE IX

Group Multiplication Table for C_{4v}

1	2	3	4	5			
A_1	A_2	B_1	B_2	E			
Γ_1	Γ_2	Γ_3	Γ_4	Γ_5			
1	2	3	4	5	Γ_1	A_1	1
	1	4	3	5	Γ_2	A_2	2
		1	2	5	Γ_3	B_1	3
			1	5	Γ_4	B_2	4
				1+2 +3+4	Γ_5	E	5

TABLE X

Important Coupling Coefficients
for Illustrative Example

	$\mu_{sx} L_{sx}$	$\mu_{sx} L_{sy}$	$\mu_{sy} L_{sx}$	$\mu_{sy} L_{sy}$
J_1	$1/\sqrt{2}$	0	0	$1/\sqrt{2}$

	$m_{sx} L_{sx}$	$m_{sx} L_{sy}$	$m_{sy} L_{sx}$	$m_{sy} L_{sy}$
J_1	0	$1/\sqrt{2}$	$-1/\sqrt{2}$	0

	$V_1 K_{sx}$	$V_2 K_{sx}$	$V_3 K_{sx}$	$V_4 K_{sx}$	$V_1 K_{sy}$	$V_2 K_{sy}$	$V_3 K_{sy}$	$V_4 K_{sy}$
L_{sx}	1	0	1	0	0	1	0	1
L_{sy}	0	-1	0	1	1	0	-1	0

	$\mu_{sx} J_1$	$\mu_{sy} J_1$
K_{sx}	1	0
K_{sy}	0	1

$$(4-41) \quad \begin{aligned} \Gamma_J &= A_1 = J_1 \\ \Gamma_K &= E = K_5 \end{aligned}$$

where, in accordance with the notation in Table IX, we use numbered subscripts to designate the irreducible representations to which the operators and wave functions belong.

We also know that the x and y components of the electric and magnetic moments belong to the doubly-degenerate representation E , and specifically they transform as the members of that representation. Thus, equation (4-40) indicates the only acceptable member permutations for the electric and magnetic moments, the limit of acceptability being set by the rules of scalar multiplication of vectors. We write the symmetries of the x and y members as:

$$(4-42) \quad \begin{aligned} \Gamma_{\mu_x} &= E = \mu_{5x} \\ \Gamma_{\mu_y} &= E = \mu_{5y} \\ \Gamma_{m_x} &= E = m_{5x} \\ \Gamma_{m_y} &= E = m_{5y} \end{aligned}$$

We let Γ_L and Γ_{V_a} be the unknown symmetry representations of the wave function $|L^0\rangle$ and the substitutional perturbation V_a . We then substitute equations (4-41) and (4-42) into expression (4-40) and obtain the symmetry expression for the parent term.

$$(4-43) \quad \begin{aligned} &(\Gamma_L | m_{5x} | J_1)(J_1 | \mu_{5x} | K_5)(K_5 | \Gamma_{V_a} | \Gamma_L) \\ &+ (\Gamma_L | m_{5y} | J_1)(J_1 | \mu_{5y} | K_5)(K_5 | \Gamma_{V_a} | \Gamma_L) \end{aligned}$$

Using the group multiplication rules of Table IX, we have four group product terms resulting from the parent term symmetry expression:

$$\begin{aligned}
& (L_5 | m_{sx} | J_1) (J_1 | \mu_{sx} | K_5) (K_5 | V_1 | L_5) \\
& + (L_5 | m_{sy} | J_1) (J_1 | \mu_{sy} | K_5) (K_5 | V_1 | L_5) \\
(4-44) \quad & (L_5 | m_{sx} | J_1) (J_1 | \mu_{sx} | K_5) (K_5 | V_2 | L_5) \\
& + (L_5 | m_{sy} | J_1) (J_1 | \mu_{sy} | K_5) (K_5 | V_2 | L_5) \\
& (L_5 | m_{sx} | J_1) (J_1 | \mu_{sx} | K_5) (K_5 | V_3 | L_5) \\
& + (L_5 | m_{sy} | J_1) (J_1 | \mu_{sy} | K_5) (K_5 | V_3 | L_5) \\
& (L_5 | m_{sx} | J_1) (J_1 | \mu_{sx} | K_5) (K_5 | V_4 | L_5) \\
& + (L_5 | m_{sy} | J_1) (J_1 | \mu_{sy} | K_5) (K_5 | V_4 | L_5)
\end{aligned}$$

We must now examine each of these group product terms to see which ones are non-zero. We first form all possible member product terms. The first step in this task has already been taken in (4-44) where the acceptable member permutations for the magnetic and electric moments are listed. By now forming all legitimate permutations of the members of the degenerate wave functions L_5 and K_5 , we obtain the final listing of member product terms. These are presented in Table XI, along with the important coupling coefficients for each member element, the latter having been extracted from Table X. In the interests of economy, we have made Table XI serve several purposes (Footnote 16). Thus to the right of each member product term, we list eight member products. Four of these member products result from the four group

					Natural Optical Activity	Absorption
$(L_{sx} m_{sx} J_i) (J_i \mu_{sx} K_{sx}) (K_{sx} V L_{sx})$						
0 ($1/\sqrt{2}$)	1	1	0	V_1	0	$1/\sqrt{2}$
		0	1	V_2	0	0
		1	0	V_3	0	$1/\sqrt{2}$
		0	1	V_4	0	0
$(L_{sy} m_{sx} J_i) (J_i \mu_{sx} K_{sx}) (K_{sx} V L_{sy})$						
$1/\sqrt{2}$ (0)	1	0	1	V_1	0	0
		1	0	V_2	$-1/\sqrt{2}$	0
		0	1	V_3	0	0
		1	0	V_4	$1/\sqrt{2}$	0
$(L_{sx} m_{sx} J_i) (J_i \mu_{sx} K_{sy}) (K_{sy} V L_{sx})$						
0 ($1/\sqrt{2}$)	0	0	1	V_1	0	0
		1	0	V_2	0	0
		0	1	V_3	0	0
		1	0	V_4	0	0
$(L_{sy} m_{sx} J_i) (J_i \mu_{sx} K_{sy}) (K_{sy} V L_{sy})$						
$1/\sqrt{2}$ (0)	0	0	1	V_1	0	0
		1	0	V_2	0	0
		0	-1	V_3	0	0
		1	0	V_4	0	0
$(L_{sx} m_{sy} J_i) (J_i \mu_{sy} K_{sx}) (K_{sx} V L_{sx})$						
$-1/\sqrt{2}$ (0)	0	0	1	V_1	0	0
		1	0	V_2	0	0
		0	1	V_3	0	0
		1	0	V_4	0	0
$(L_{sy} m_{sy} J_i) (J_i \mu_{sy} K_{sx}) (K_{sx} V L_{sy})$						
0 ($1/\sqrt{2}$)	0	0	-1	V_1	0	0
		1	0	V_2	0	0
		0	1	V_3	0	0
		1	0	V_4	0	0
$(L_{sx} m_{sy} J_i) (J_i \mu_{sy} K_{sy}) (K_{sy} V L_{sx})$						
$-1/\sqrt{2}$ (0)	1	0	1	V_1	0	0
		1	0	V_2	$-1/\sqrt{2}$	0
		0	1	V_3	0	0
		1	0	V_4	$-1/\sqrt{2}$	0
$(L_{sy} m_{sy} J_i) (J_i \mu_{sy} K_{sy}) (K_{sy} V L_{sy})$						
0 ($1/\sqrt{2}$)	1	1	0	V_1	0	$1/\sqrt{2}$
		0	1	V_2	0	0
		-1	0	V_3	0	$-1/\sqrt{2}$
		0	1	V_4	0	0

TABLE XI

Coupling Coefficients and Member Products for
Various Perturbations on Absorption
and Natural Optical Activity

product terms of natural optical activity, corresponding to the four possible symmetries for the substitutional perturbation. The other four result from the corresponding group product terms of absorption. From these results, we may determine which of the group product terms of natural optical activity are non-zero and which of the group product terms of absorption are non-zero.

Inspection of the results in Table XI demonstrate that for natural optical activity, only the member products corresponding to the V_2 and V_4 perturbations of the second and seventh member product terms are non-zero, and can therefore contribute. Furthermore, upon addition, the two non-zero V_4 member products cancel and one is left with only $V_2 = \Gamma_2 = A_2$ -- the pseudoscalar representation -- as a contributing substitutional symmetry pattern. Similar reasoning reveals that only the totally symmetric representation, $V_1 = \Gamma_1 = A_1$ contributes to absorption. Both of these results are consistent with previous, more general arguments.

From the above illustration of the evaluation of one of the least complex parent terms, we see that the complications arising from higher order terms make the calculation of symmetry patterns prohibitive other than by computer. Therefore, a computer program to determine the symmetry patterns has been written. The structure of this program, which is rather complex, can be best understood by study of the flow chart of Figure 8, with reference to the prior discussion of this section. In Figure 8, the functions of the main program and of the subroutines, and their interrelationship, are depicted. The solid paths indicate progression through the program while the dashed paths indicate flow of information. Subroutines are designated by the preface SUB- , e.g. the subroutine TERPER is designated in Figure 8

Computer Program Flow Chart

by the block labeled SUB-TERPER.

Three of these subroutines need description at this point, as their functions have not been adequately described in the previous discussion. First, the subroutine TERPER has the primary function of term generation. Inspection of Table VIII shows that each term can be obtained from the one preceeding it by simple interchange of wave functions and/or operators. This interchange or permutation is performed by TERPER. Secondly, the subroutines SYMANA and TRANS are used in conjunction with section 8000 of the main program to reorder the output data. It is tabulated according to: (i) whether the borrowing is by the ground state (a case not previously treated by other authors) or by the excited state, and (ii) what type of perturbation -- vibration or substitution -- initiates the borrowing.

The blocks labeled 1000 to 9000 represents sections of the main program. The listing for the program, which goes under the name of SYMDET, is given in Appendix XI.

Having developed the theoretical background for the problem and a computer program to perform the symmetry analysis, we proceed in section 4 of this part to present the symmetry patterns for the point group C_{4v} .

4. Vibrational and Substitutional Symmetry Patterns for Absorption Natural Optical Activity, and Magnetically-Induced Optical Activity for the Point Group C_{4v} .

In Tables XII and XIII, we present some of the results that are obtained by the computer solution of the possible symmetry patterns for the optical phenomena of absorption, natural optical activity, and magnetically-induced optical activity (Footnote 17). Table XII presents the zero-order contributions to the optical phenomena. These

TABLE XII
Absorption and
Magnetically-induced Optical Activity
Zero-order Contributions

TYPE OF OPTICAL PHENOMENA TYPE OF STATES	"B" TERM NON-ZERO COMPONENTS AND THE MIXING WAVE FUNCTIONS	"A" AND "C" TERMS NON-ZERO COMPONENTS	ABSORPTION NON-ZERO COMPONENTS
BOTH GROUND AND EXCITED STATES NON-DEGENERATE $\Gamma_J = \Gamma_K$	yzx 5	-----	z
Others	-----	-----	-----
EITHER GROUND OR EXCITED STATE DEGENERATE	Borrowing by Degenerate State xyz $\Gamma_{\text{NON-DEG}}$ zxy 5	xyz	xy
	Borrowing by Non-degenerate State xyz 5 zxy $\Gamma_{\text{DEG}} \otimes \Gamma_{\text{NON-DEG}}$		
BOTH GROUND AND EXCITED STATES DEGENERATE	yzx 1,2,3,4	-----	z

TYPE OF OPTICAL PHENOMENA		ABSORPTION	MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A" AND "C" TERMS	MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERMS	NATURAL OPTICAL ACTIVITY
BOTH GROUND AND EXCITED STATES NON-DEGENERATE	Vibrations	xy 55 z $(\Gamma_2 \otimes \Gamma_k)(\Gamma_2 \otimes \Gamma_k) = 11$	None up to Second-order	xyz 55 zyx 55 yzx 11,22,33,44,55	xy 55 z $(\Gamma_2 \otimes \Gamma_k \otimes 2)(\Gamma_2 \otimes \Gamma_k \otimes 2) = 22$ z $(\Gamma_2 \otimes \Gamma_k)(\Gamma_2 \otimes \Gamma_k) = 11$
		xy 55 z $(\Gamma_2 \otimes \Gamma_k)(\Gamma_2 \otimes \Gamma_k)$	None up to Second-order	xyz 55 zxy 55 yzx $(\Gamma_2 \otimes \Gamma_k)(\Gamma_2 \otimes \Gamma_k)$	xy 55 z $(\Gamma_2 \otimes \Gamma_k \otimes 2)(\Gamma_2 \otimes \Gamma_k \otimes 2)$ z $(\Gamma_2 \otimes \Gamma_k)(\Gamma_2 \otimes \Gamma_k)$
	Substitutions	xy 55 z 1,11,22,33,44,55	zxy 55	xyz 55 zxy 55 yzx 1,11,22,33,44,55	xy 552 z 2,21,43
		xy 55 z $(\Gamma_2 \otimes \Gamma_k)(\Gamma_2 \otimes \Gamma_k) = 22$	None up to Second-order	xyz 55 zxy 55 yzx $(\Gamma_2 \otimes \Gamma_k)(\Gamma_2 \otimes \Gamma_k) = 22$	xy 552 z 2,21,43
		xy 55 z $(\Gamma_2 \otimes \Gamma_k)(\Gamma_2 \otimes \Gamma_k)$	None up to Second-order	xyz 55 zxy 55 yzx $(\Gamma_2 \otimes \Gamma_k)(\Gamma_2 \otimes \Gamma_k)$	xy 552 z 43
	Vibrations	xy 11,22,33,44 z 55	xyz 11,22,33,44	xyz 11,22,33,44,55 zxy 11,22,33,44,55 yzx 55	xy 11,22,33,44 z 55
	Substitutions	xy 1,11,22,33,44,55 z 55	xyz 1,11,22,33,44,55 yzx 55	xyz 1,11,22,33,44,55 zxy 1,11,22,33,44,55 yzx 55	xy 2,21,43 z 552
BOTH GROUND AND EXCITED STATES DEGENERATE	Vibrations	xy 11,22,33,44 z 55	xyz 55 zxy 55	xyz 55 zxy 55 yzx 11,22,33,44,55	xy 55 z 11,22,33,44
	Substitutions	xy 1,11,22,33,44,55 z 55	xyz 55 zxy 55	xyz 55 zxy 55 yzx 1,11,22,33,44,55	xy 552 z 2,21,43

TABLE XIII

Higher-order Contributions to Absorption,
Magnetically-induced Optical Activity and Natural Optical Activity

are obtained by substituting the harmonic wave function approximations for the adiabatic wave functions in equation (4-31), (this is identical to assuming zero perturbations in equations (4-35), (4-36), and (4-37)), and then performing a symmetry analysis. It is to be noted that, since a molecule belonging to the point group C_{4v} is not inherently asymmetric, there is no zero-order natural optical activity. Table XIII presents the perturbation symmetry patterns which result in first-order and/or second-order contributions to all three of the optical phenomena. If we make the natural comparison of symmetry patterns for the xyz and zxy components of magnetically-induced optical activity with those for the xy components of absorption and natural optical activity, and the comparison of the patterns of the yzx components with the z components, we note from these tables that there is a much closer correlation between magnetically-induced optical activity and absorption than there is between magnetically-induced optical activity and natural optical activity (Footnote 18). This is consistent with our previous discussions in Chapters 1 and 2, which indicated that magnetically-induced optical activity arises from a static magnetic field perturbation of absorption, gives information regarding the electronic properties of the molecule, and like absorption, is independent of the variations of the electromagnetic fields over the dimensions of the molecule. On the other hand, natural optical activity results from a small electromagnetic field perturbation which is independent of absorption, gives information regarding the stereochemistry of the molecule, and unlike absorption, is dependent on the variations of the electromagnetic fields over the dimensions of the molecule. We thus emphasize the conclusions that magnetically-induced optical activity is more comparable to absorption than to natural optical activity and that experiments using magnetically-

induced optical activity should not be expected to yield information of the same nature as do those using natural optical activity.

Now turning to specific results, we see that inspection of Table XII leads to conclusion 12.

Conclusion 12. For the existence of a zero-order "B" term of magnetically-induced optical activity, the state borrowing and the state borrowed from must be connected by a magnetic dipole operator, i.e. the direct product of the symmetry representations of these states must contain a component of $\vec{m}$.

This confirms the conclusion of McCaffery and Schatz (6a). However, when degenerate states are involved, Conclusion 12 is a necessary but not sufficient condition, as can be seen from inspection of the symmetries of the mixing wave functions. For example, where there is one degenerate state, say the excited state, and that degenerate state borrows from some other state, Conclusion 12 says that the mixing state may have any non-degenerate representation. However, Table XII shows that only states with the same non-degenerate representation as the ground state can be mixing states. To obtain this information, detailed calculation was necessary.

Table XIII is obtained from the data presented in the C_{4v} data sheets included in Appendix XII. These sheets in turn were developed from the raw data resulting from the computer program output. Besides the previously described similarity between magnetically-induced optical activity and absorption, Table XIII confirms Conclusion 10 for C_{4v} , a point group containing a degenerate representation. Thus for all point groups, with or without degenerate representations, it appears that even if no part of the substitutional symmetry pattern

transforms as the pseudoscalar representation, all that is needed is to have two parts of the symmetry pattern, whose representations have a direct product that transforms as the pseudoscalar, thus resulting in a second-order contribution to natural optical activity. In fact, for the point group C_{4v} , it should be noted that, for transitions where both ground and excited states are non-degenerate, certain combinations of ground and excited symmetries have no first-order substitutional contribution, regardless of the existing substitutional symmetry pattern. These combinations are given by the direct product rules

$$\Gamma_J \otimes \Gamma_K = 3$$

$$\Gamma_J \otimes \Gamma_K = 4$$

where, as previously explained, 3 is the representation B_1 and 4 is the representation B_2 . For these cases, the substitutional symmetry pattern needed to produce a second-order contribution to natural optical activity is 43, i.e. there must be a part of the pattern that transforms as B_2 and part that transforms as B_1 .

We also note from Table XIII that for vibrationally allowed transitions between non-degenerate states, for both absorption and natural optical activity, we have for the xy component, the symmetry pattern 55, i.e. two vibrations of symmetry E , and for the z component, the pattern $(\Gamma_J \otimes \Gamma_K)(\Gamma_J \otimes \Gamma_K)$, i.e. two vibrations of symmetry given by the direct product of the ground and excited state representations. However, there is for natural optical activity an additional vibration which contributes. This is given by the symmetry pattern $(\Gamma_J \otimes \Gamma_K \otimes \Gamma_S)(\Gamma_J \otimes \Gamma_K \otimes \Gamma_S)$ where Γ_S is the pseudoscalar representation. The possibility that this may be a general rule for all point groups warrants further investigation.

Another interesting fact is that, for both ground and

excited states non-degenerate, there is no second-order vibrational contribution to the "A" term of magnetically-induced optical activity. It would be necessary to extend the perturbation expansion to higher orders to observe a vibrationally allowed "A" term between non-degenerate states, and it is to be expected that degenerate vibrations would be needed.

We close this chapter with two observations. First, other symmetry conclusions for C_{4v} could likely be generated by further study of Table XIII and the C_{4v} data sheets of Appendix XII. In particular, attention should be drawn to the wave function patterns in the data sheets. Should general rules be found to apply to them, this could be most helpful in determining which wave functions are most effective in the higher order contributions to the optical phenomena. Secondly, we would like to establish general rules, not only for the point group C_{4v} , but for all groups. There are two possible methods of implementing this, either by running a computer analysis for all groups and comparing the output patterns, or by doing a more general theoretical analysis. Now that the former is possible, and now that we have a general idea of what the techniques and results would be for other groups, we may be able to build on this foundation and obtain the latter, a more general theoretical treatment of symmetry perturbations.

FOOTNOTES

1. An excellent introduction to the application to chemical systems of the symmetry rules of group theory is the book by Cotton (83). For a more advanced approach, the reader is referred to Tinkham (84) and to other more general treatments of group theory (85), (86), and (87).

2. It must be noted that while each $\langle f_n |$ is a function of the n^{th} normal coordinate Q_n in the ground state, each $\langle k_n |$ is a function of that normal coordinate in the excited state. Only in the case where the excited state geometry is identical to the ground state geometry and where the respective potential surfaces are identical, is it justifiable to consider the ground state Q_n identical with the excited state Q_n . In this chapter, we shall always use the ground state Q_n for simplicity. However, recognizing the above, we must be cautious in interpreting such matrix elements as $\langle f | Q_n | k \rangle$ when the ground state geometry differs from the excited state geometry.

3. The term, "component", is really a misnomer as it has no relation to the common usage as a vector component. However, here and later in the derivation, it is convenient to denote the X part of the dot product as the X component.

4. In the detailed calculations to follow, the perturbation equations for the oscillator and rotational strengths are taken to second and third-order as was previously stated. However, for the sake of simplicity in

our illustration, we limit ourselves to first-order perturbation theory. All quantities presented without proof in the illustration are derived in detail in the calculations of part C of this chapter.

5. The Hamiltonian $\mathcal{H}'$ can be expanded in a Taylor series of the normal coordinates. Considering only the first two terms of that expansion:

$$\begin{aligned}\mathcal{H}' &= (\mathcal{H}')_0 + \sum_r \left(\frac{\partial \mathcal{H}'}{\partial Q_r} \right)_0 Q_r \\ &= (\mathcal{H}')_0 + \sum_r \mathcal{H}_r Q_r\end{aligned}$$

where we have arbitrarily set the equilibrium value of Q_r at zero. This does not detract from the generality of the arguments presented here. As $\mathcal{H}'$ is totally symmetric, so must be each term in the summation. Therefore, the symmetry of $\mathcal{H}_r$ is the same as that of Q_r .

6. Readers not familiar with the basic rules and terminology of group theory should refer to the work of Cotton (83) and/or Tinkham (84).
7. This is not strictly true for molecules belonging to point groups that contain degenerate representations, i.e. molecules with a three-fold or higher axis of symmetry. The necessary modifications to the analysis will be developed in part C of this chapter. However, for the present, we will ignore this problem.
8. See Footnote 6.
9. See Footnote 5.

10. In equation (4-32), (4-33), and (4-34) the vectors $\vec{m}$ and $\vec{\mu}$ and their components are in reality matrix elements, their form depending on whether we are dealing with P_A , P_B , or P_C . However, indication that they are matrix elements is not necessary to the understanding of the component concept, and we suppress all such notation.
11. It is true that one can have a matrix element uniquely determined even when it contains degenerate representations. However, it is also true that for point groups containing degenerate representations, it is unlikely that all matrix elements of a given symmetry will be uniquely determined, as it is probable that the evaluation of at least one of these matrix elements will involve the direct product of two degenerate representations.
12. In this dissertation, we do not consider triply-degenerate representations. The treatment of these representations would be similar to the doubly-degenerate type but a larger array of group product terms would result.
13. If the members of the n^{TH} doubly-degenerate representation are designated as (x_n, y_n) and the m^{TH} non-degenerate representation as z_m , then the member elements stemming from matrix elements with two doubly-degenerate representations go as $x_1 x_2 z_3$, $x_1 y_2 z_3$, $y_1 x_2 z_3$, $y_1 y_2 z_3$ and the member elements stemming from matrix elements with three doubly-degenerate representations go as $x_1 x_2 x_3$, $x_1 y_2 x_3$, $y_1 x_2 x_3$, $y_1 y_2 x_3$, $x_1 x_2 y_3$, $x_1 y_2 y_3$, $y_1 x_2 y_3$, $y_1 y_2 y_3$.

14. For the typical matrix element $(J^\circ | \mu | K^\circ)$, the wave function $|K^\circ\rangle$ is the ket wave function and the wave function $\langle J^\circ|$ is the bra wave function (see Dirac (89)). Similarly, ket members and the bra members can be defined for member elements.
15. These coupling coefficients, defined and tabled for the various point groups by Koster et al (90) are analogous to the Clebsch-Gordon coefficients and are the coefficients of the linear combinations of member products which transform as specified irreducible representations. This is the more common interpretation, and although the member products could be discussed from this viewpoint, we have used in this dissertation a somewhat different approach for the sake of clarity.
16. First of all, the eight member product terms can apply to any of the four group product terms of expression (4-44), simply by replacing V by V_1, V_2, V_3 or V_4 , and choosing as coupling coefficient for the last member element in each member product term, the appropriate one of the four listed. Here the order goes from top to bottom, the top coupling coefficient corresponding to V_1 , the bottom to V_4 . Secondly, the set of member product terms in Table XI can be made to apply to absorption instead of natural optical activity, simply by replacing m_x by μ_x , m_y by μ_y and by choosing for the first member element of each member product term the coupling coefficient in parenthesis.
17. It should be noted that in these two tables as well as in Appendices XI and XII, we designate irreducible representations by number. For C_{4v} ,

the designation is as in Table IX, i.e. $1 = \Gamma_1 = A_1$, $2 = \Gamma_2 = A_2$, $3 = \Gamma_3 = B_1$, $4 = \Gamma_4 = B_2$, and $5 = \Gamma_5 = E$. When a symmetry pattern is given by the number 12 or 21, this means that part of the symmetry pattern must transform as A_1 , the totally symmetric representation, and part must transform as A_2 , the pseudoscalar representation. Similarly, 55 would mean that both parts must transform as the doubly-degenerate representation E .

18. The exception to this appears for the case where both ground and excited states are degenerate. Here, especially for vibrational perturbations, there is a closer relation between magnetically-induced optical activity and natural optical activity.

CONCLUSIONS AND RECOMMENDATIONS

In this dissertation we have developed the general theory of natural and magnetically-induced optical activity, provided the theoretical foundation for extending this theory to complex systems, and finally, analyzed one such system -- a vibrating, substituted chromophore. Hopefully, we have provided a more physical feeling for both types of optical activity and have clarified some of the more confusing aspects of previous derivations.

The most important lesson to be gained from the study of the preceding analysis, is that natural and magnetically-induced optical activity are more different than alike. Natural optical activity arises from an asymmetric perturbation which bears a fixed geometrical relationship to the chromophore, no matter how wildly the molecule tumbles. On the other hand, magnetically-induced optical activity results from an asymmetric perturbation, the static magnetic field, which is external to the whole molecule and bears a changing geometrical relationship to the tumbling chromophore. Thus, the two types of optical activity give complementary rather than comparable information. Natural optical activity reveals subtleties regarding the molecular stereochemistry while magnetically-induced optical activity measures quantities pertinent to the electronic structure of the molecule.

This dicotomy of natural and magnetically-induced optical activity is emphasized throughout this dissertation. In Chapter 2, we pointed out that magnetically-induced optical activity was more closely related to absorption than to natural optical activity, and

in Chapter 4, we demonstrated that this relationship extends to the vibrational and substitutional structuring of these optical phenomena.

We also reached some specific conclusions regarding vibrational and substitutional structuring in both types of optical activity, and developed for one particular point group -- C_{4v} -- the detailed symmetry patterns needed for higher order vibrational and substitutional contributions. One particularly interesting conclusion was that there can be a second-order substitutional contribution to natural optical activity under conditions where there can be no first-order contributions.

Finally, we turn to Table III of Chapter 1 to note where the work we have done fits into the overall theoretical framework of optical activity. As can be seen, the work of this dissertation supplements the previous investigations into optical activity and for the first time, the vibrational and substitutional structuring of magnetically-induced optical activity is treated in depth. There is, of course, much more to be done. In particular, the areas involving vibrational and substitutional structuring on the optical activity of polymers have hardly been touched. Also, much more remains to be done on magnetically-induced optical activity than on natural optical activity.

In conclusion, we have attempted to prepare a theoretical textbook of optical activity, a manuscript that an individual new to the field, could not only read and understand, but to which he could refer for all the mathematics without continually encountering "it can be shown". In addition, we have provided the springboard for workers in the field to attempt extensions of the theory, and as an example, we have treated one such extension. It is hoped that this

dissertation will thus prove valuable to neophyte and expert alike, and will be helpful in stimulating investigation into new applications of both natural and magnetically-induced optical activity.

Appendix I

Review of Pertinent Quantum-Mechanical Principles

A molecular system is completely described, in the quantum mechanical sense, by specification of the wave functions. Thus, the statics and dynamics of the electrons and nuclei are determinable from the electronic and nuclear wave functions. These wave functions are solutions of the Schrodinger equation. For example, for the electrons, the wave functions ψ_{E_i} form a complete orthonormal set and satisfy the equation

$$(I-1) \quad \mathcal{H}_E \psi_{E_i} = E_i \psi_{E_i}$$

where $\mathcal{H}_E$ is the electronic Hamiltonian and is given by the sum of the kinetic energy operator $T_E = -\frac{\hbar^2}{2m} \nabla^2$ and the potential energy operator V_E . E_i is the electronic energy of the state ψ_{E_i} .

The orthonormality of the wave functions is specified by:

$$(I-2) \quad \int \psi_{E_i}^* \psi_{E_j} dx = \delta_{ij}$$

the integration being over all electronic space. This relation is more concisely expressed in the Dirac bra-ket notation. Thus:

$$(I-3) \quad (\psi_{E_i} | \psi_{E_j}) = (i | j) = \delta_{ij}$$

Similarly, if we multiply equation (I-1) by $\psi_{E_j}^*$ and integrate over all electronic space, we have the resulting

$$\begin{aligned}
 (\psi_{E_j} | \mathcal{H}_E | \psi_{E_i}) &= (j | \mathcal{H}_E | i) \\
 &= E_i (j | i) = E_i \delta_{ij}
 \end{aligned}$$

$$(I-4) \quad \therefore E_i = (i | \mathcal{H}_E | i)$$

The integral $(i | \mathcal{H}_E | i)$ is termed the expectation value of the operator $\mathcal{H}_E$, i.e. the expectation value of the Hamiltonian is identical with the energy of the state ψ_{E_i} .

We may also define the expectation value of an arbitrary operator $\hat{O}$ on the state ψ_{E_i} as $(i | \hat{O} | i)$. If this operator has a definite value in this state, then this value will be identical with the expectation value. Also, as the operator represents a measurement, the expectation value represents the value of this measurement. Transition values of the operator $\hat{O}$ can also be defined. Thus we have $O_{ii} = (i | \hat{O} | i)$ for the expectation value

$$O_{ij} = (i | \hat{O} | j) \text{ for the transition value}$$

Consider now an arbitrary state ψ_a . As the ψ_i (we have dropped the E notation in the subscript) form a complete orthonormal set, the set ψ_a can be expanded in the ψ_i

$$(I-5) \quad \psi_a = \sum_i (\psi_i | \psi_a) \psi_i = \sum_i c_{ia} \psi_i$$

That equation (I-5) is valid is easily seen by multiplying by ψ_j and integrating over all electronic space.

$$\therefore (\psi_j | \psi_a) = \sum_i (\psi_j | \psi_i) (\psi_i | \psi_a) = \sum_i (\psi_i | \psi_a) \delta_{ij} = (\psi_j | \psi_a)$$

With these preliminaries, consider the problem of determining the N eigenstates of a particular system specified by the equation

$$(I-6) \quad \mathcal{H}' \psi_a^1 = E_a^1 \psi_a^1$$

We assume that we know the N eigenstates of a simpler, solvable problem

$$(I-7) \quad \mathcal{H}^0 \psi_a^0 = E_a^0 \psi_a^0$$

We may expand the first-order eigenstates in terms of the N zero-order eigenstates according to equation (I-5)

$$(I-8) \quad \psi_a^1 = \sum_b^N (\psi_b^0 | \psi_a^1) \psi_b^0$$

Substituting equation (I-8) into (I-6)

$$\mathcal{H}' \psi_a^1 = \sum_b^N \mathcal{H}' \psi_b^0 (\psi_b^0 | \psi_a^1) = E_a^1 \psi_a^1 = E_a^1 \sum_b^N (\psi_b^0 | \psi_a^1) \psi_b^0$$

Multiply by ψ_c^0 and integrate over all space, we have:

$$\sum_b^N (\psi_c^0 | \mathcal{H}' | \psi_b^0) (\psi_b^0 | \psi_a^1)$$

remembering $(\psi_c^0 | \psi_b^0) = \delta_{bc}$, we have:

$$(I-9) \quad \sum_b^N (\psi_c^0 | \mathcal{H}' | \psi_b^0) (\psi_b^0 | \psi_a^1) = E_a^1 (\psi_c^0 | \psi_a^1)$$

There are N of these equations, one for each of the N ψ_c^0 . These N linearly independent equations can be written in matrix form

$$(I-10) \quad \begin{bmatrix} (\psi_1^0 | \mathcal{H}' - E_a^1 | \psi_1^0) & (\psi_1^0 | \mathcal{H}' - E_a^1 | \psi_2^0) & \cdots & (\psi_1^0 | \mathcal{H}' - E_a^1 | \psi_N^0) \\ (\psi_2^0 | \mathcal{H}' - E_a^1 | \psi_1^0) & (\psi_2^0 | \mathcal{H}' - E_a^1 | \psi_2^0) & \cdots & (\psi_2^0 | \mathcal{H}' - E_a^1 | \psi_N^0) \\ \vdots & \vdots & \ddots & \vdots \\ (\psi_N^0 | \mathcal{H}' - E_a^1 | \psi_1^0) & (\psi_N^0 | \mathcal{H}' - E_a^1 | \psi_2^0) & \cdots & (\psi_N^0 | \mathcal{H}' - E_a^1 | \psi_N^0) \end{bmatrix} \begin{bmatrix} (\psi_1^0 | \psi_a^1) \\ (\psi_2^0 | \psi_a^1) \\ \vdots \\ (\psi_N^0 | \psi_a^1) \end{bmatrix} = 0$$

This $N \times N$ matrix is termed the representation of the Hamiltonian in the ψ_a^0 basis. We may write equation (I-10) in the more concise form

$$(I-11) \quad \begin{bmatrix} H'_{11} - E_a^1 & H'_{12} & \cdots & H'_{1N} \\ H'_{21} & H'_{22} - E_a^1 & \cdots & H'_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{N1} & H'_{N2} & \cdots & H'_{NN} - E_a^1 \end{bmatrix} \begin{bmatrix} C_{1a} \\ C_{2a} \\ \vdots \\ C_{Na} \end{bmatrix} = 0$$

where

$$C_{ja} = (\psi_j^0 | \psi_a^1)$$

Only for the condition

$$(I-12) \quad \begin{bmatrix} H'_{11} - E_a^1 & H'_{12} & \cdots & H'_{1N} \\ H'_{21} & H'_{22} - E_a^1 & \cdots & H'_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{N1} & H'_{N2} & \cdots & H'_{NN} - E_a^1 \end{bmatrix} = \begin{bmatrix} H'_{11} - E_a^1 & H'_{12} & \cdots & H'_{1N} \\ H'_{21} & H'_{22} - E_a^1 & \cdots & H'_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{N1} & H'_{N2} & \cdots & H'_{NN} - E_a^1 \end{bmatrix} = 0$$

will the set of equations specified by (I-11) have non-trivial solutions for the coefficients C_{ja} (i.e. solutions other than $C_{ja} = 0$). This is a well known property of sets of linearly independent equations.

The equation (I-12) is termed the secular equation, and it is true that if the representation matrix of the Hamiltonian is diagonal, then the initially assumed functions $\psi_1^0, \psi_2^0, \cdots$ are also the correct first-order wave functions. This is easily seen.

The matrix equations (I-11) become

$$(I-13) \quad \begin{bmatrix} H'_{11} - E_a^1 & 0 & \cdots & 0 \\ 0 & H'_{22} - E_a^1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & H'_{NN} - E_a^1 \end{bmatrix} \begin{bmatrix} C_{1a} \\ C_{2a} \\ \vdots \\ C_{Na} \end{bmatrix} = 0$$

This yields N equations of the type

$$(H'_{kk} - E_a^1) C_{ka} = 0$$

$$\therefore H'_{kk} - E_a^1 = 0$$

$$(\psi_k^0 | \mathcal{H}' | \psi_k^0) = E_a^1$$

This will be true if $\mathcal{H}' \psi_k^0 = E_a^1 \psi_k^0$ and thus the ψ_k^0 are also the eigenfunctions of $\mathcal{H}'$, that is, the desired first-order functions.

Assume we may find a matrix S

$$S = \begin{bmatrix} S_{11} & S_{12} & \cdots & S_{1N} \\ S_{21} & S_{22} & \cdots & S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N1} & S_{N2} & \cdots & S_{NN} \end{bmatrix}$$

which is unitary and diagonalizes the representation of the Hamiltonian which we shall term H .

Thus

$$SS^{-1} = I$$

$$SHS^{-1}SC = 0$$

$$\text{where } C = \begin{bmatrix} C_{1a} \\ C_{2a} \\ \vdots \\ C_{Na} \end{bmatrix}$$

and SHS^{-1} is a diagonal matrix of the form of (VIII-5). Then SC is of the form

$$(I-14) \quad SC = \begin{bmatrix} S_{11} & S_{12} & \dots & S_{1N} \\ S_{21} & S_{22} & \dots & S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N1} & S_{N2} & \dots & S_{NN} \end{bmatrix} \begin{bmatrix} C_{1a} \\ C_{2a} \\ \vdots \\ C_{Na} \end{bmatrix} = \begin{bmatrix} S_{11}C_{1a} + S_{12}C_{2a} + \dots + S_{1N}C_{Na} \\ S_{21}C_{1a} + S_{22}C_{2a} + \dots + S_{2N}C_{Na} \\ \vdots \\ S_{N1}C_{1a} + S_{N2}C_{2a} + \dots + S_{NN}C_{Na} \end{bmatrix}$$

from equation (I-8), it is easily seen that the C_{ka} are the representatives of the ψ_a^1 in the zero-order basis functions,

$$\text{i.e. } C_{ka} = (\psi_k^0 / \psi_a^1) \quad \text{for } k=1, N$$

As the matrix SHS^{-1} is diagonal, the elements of the column matrix SC are the representatives of the correct first-order functions ψ_a^1 in the correct first-order functions ψ_a^1 .

$$\begin{aligned} (\psi_i^1 / \psi_a^1) &= S_{11}C_{1a} + S_{12}C_{2a} + \dots + S_{1N}C_{Na} \\ &= S_{11}(\psi_1^0 / \psi_a^1) + S_{12}(\psi_2^0 / \psi_a^1) + \dots + S_{1N}(\psi_N^0 / \psi_a^1) \end{aligned}$$

$$\therefore (\psi_i^1 / \psi_a^1) = (S_{11}\psi_1^0 + S_{12}\psi_2^0 + \dots + S_{1N}\psi_N^0 / \psi_a^1)$$

$$\therefore \psi_i^1 = S_{11}\psi_1^0 + S_{12}\psi_2^0 + \dots + S_{1N}\psi_N^0$$

and in general

$$(I-15) \quad \psi_k^1 = S_{k1}\psi_1^0 + S_{k2}\psi_2^0 + \dots + S_{kN}\psi_N^0$$

Thus if we can determine the elements of the matrix S that diagonalizes, via a similarity transform, the matrix H , then we have determined the linear combinations of the zero-order basis functions which form the correct first-order eigenfunctions.

With these preliminaries, we now examine the conditions under which diagonalization of H leads to the standard perturbation expansions of the first-order wave functions in the zero-order basis set. For simplicity and clarity, we shall illustrate the conditions with 2×2 matrices. Use of higher orders would only confuse matters. Let the matrix S be given by

$$S = \begin{bmatrix} a & b \\ c & d \end{bmatrix}$$

$$S^{-1} = \begin{bmatrix} a & c \\ b & d \end{bmatrix}$$

$$\text{as } ad - bc = 1$$

$$SS^{-1} = \begin{bmatrix} a^2 + b^2 & ac + bd \\ ac + bd & c^2 + d^2 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad \text{as } S \text{ is unitary}$$

We thus have three equations

$$(I-16) \quad a^2 + b^2 = 1$$

$$(I-17) \quad c^2 + d^2 = 1$$

$$(I-18) \quad ac + bd = 0$$

For ease in calculation, let the matrix H be represented by:

$$H = \begin{bmatrix} l & m \\ n & p \end{bmatrix}$$

We can easily show

$$\begin{aligned}
 SHS^{-1} &= \begin{bmatrix} la^2 + (m+n)ba + pb^2 & lac + mad + nbc + pbd \\ lac + mbc + nad + pbd & lc^2 + (m+n)dc + pd^2 \end{bmatrix} \\
 &= \begin{bmatrix} x & 0 \\ 0 & y \end{bmatrix}
 \end{aligned}$$

$$\therefore lac + mbc + nad + pbd = lac + mad + nbc + pbd = 0$$

$$\therefore mbc + nad = mad + nbc$$

$$m(bc - ad) = n(bc - ad)$$

$$\therefore m = n$$

we now have a fourth equation

$$(I-19) \quad lac + m(bc + ad) + pbd = 0$$

combining equations (I-16), (I-17), (I-18), (I-19) and solving for a, b, c, d, we find:

$$b = c = \frac{1}{2} \left\{ 1 + \sqrt{\frac{1}{1+k^2}} \right\}^{1/2}$$

(I-20a)

$$a = d = \frac{1}{2} \left\{ 1 - \sqrt{\frac{1}{1+k^2}} \right\}^{1/2}$$

or

$$(I-20b) \quad b = c = \frac{1}{2} \left\{ 1 - \sqrt{\frac{1}{1+K^2}} \right\}^{1/2}$$

$$K = \frac{2m}{l-p}$$

$$a = d = \frac{1}{2} \left\{ 1 + \sqrt{\frac{1}{1+K^2}} \right\}^{1/2}$$

if K is small, i.e. $2m \ll l-p$

then $\sqrt{\frac{1}{1+K^2}} = (1+K^2)^{-1/2} \cong 1 - \frac{K^2}{2}$

$$\left\{ 1 + \sqrt{\frac{1}{1+K^2}} \right\}^{1/2} \cong \left\{ 2 - \frac{K^2}{2} \right\}^{1/2} \cong \sqrt{2} \left[1 - \frac{K^2}{8} \right] \cong \sqrt{2}$$

$$\left\{ 1 - \sqrt{\frac{1}{1+K^2}} \right\}^{1/2} \cong \left\{ \frac{K^2}{2} \right\}^{1/2} = \frac{K}{\sqrt{2}}$$

we use the second set (I-20b), (we could just as easily have used the first set)

$$b = c \cong \frac{K}{2\sqrt{2}}$$

$$a = d \cong \frac{\sqrt{2}}{2} = \frac{1}{\sqrt{2}}$$

$$S = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{K}{2\sqrt{2}} \\ \frac{K}{2\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & \frac{K}{2} \\ \frac{K}{2} & 1 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & \frac{m}{l-p} \\ \frac{m}{l-p} & 1 \end{bmatrix}$$

Thus we find, according to equation (I-15)

$$\psi_1^1 = \frac{1}{r_2} \left[\psi_1^0 + \frac{m}{l-p} \psi_2^0 \right]$$

$$\psi_2^1 = \frac{1}{r_2} \left[\psi_2^0 + \frac{m}{l-p} \psi_1^0 \right]$$

but $m = H'_{12} - H'_{21} = (\psi_1^0 | \mathcal{H}' | \psi_2^0)$

$$l-p = H'_{11} - E_a^1 - H'_{22} + E_a^1 = H'_{11} - H'_{22} = E_1 - E_2$$

$$\psi_1^1 = \frac{1}{r_2} \left[\psi_1^0 + \frac{(\psi_1^0 | \mathcal{H}' | \psi_2^0)}{E_1 - E_2} \psi_2^0 \right]$$

$$\psi_2^1 = \frac{1}{r_2} \left[\psi_2^0 + \frac{(\psi_2^0 | \mathcal{H}' | \psi_1^0)}{E_1 - E_2} \psi_1^0 \right]$$

thus for the condition

$$H'_{12} = (\psi_1^0 | \mathcal{H}' | \psi_2^0) \ll E_1 - E_2$$

perturbation theory is equivalent to matrix diagonalization.

Appendix II

Relative Magnitude of Perturbations

There are six important perturbations:

- $\mathcal{H}_S^1$ - first-order substitutional perturbation
- $\mathcal{H}_V^1$ - first-order vibrational perturbation
- $\mathcal{H}_I^1$ - first-order chromophore-chromophore interaction perturbation
- $\mathcal{H}_M^2$ - second-order static magnetic field perturbation
- $\mathcal{H}_O^3$ - third-order electromagnetic field perturbation
- $\mathcal{H}_O^4$ - fourth-order electromagnetic field perturbation

It is the intention of this appendix to evaluate the relative magnitudes of five of these six perturbations. We do not evaluate the magnitude of $\mathcal{H}_I^1$, as this is better left to an analysis of weak and strong coupling. However, among the other five perturbations, we will demonstrate that the orders assigned -- i.e. first-order through fourth-order -- are realistic. Here a first-order perturbation is stronger than a second-order, a second-order stronger than a third-order, etc.

We initially show that

$$(II-1) \quad \mathcal{H}_M^2 > \mathcal{H}_O^3 > \mathcal{H}_O^4$$

Then we demonstrate that

$$(II-2) \quad \mathcal{H}_S^1 \approx \mathcal{H}_V^1 > \mathcal{H}_M^2$$

and therefore arrive at the hierarchy

$$(II-3) \quad \mathcal{H}_S^1 \approx \mathcal{H}_V^1 > \mathcal{H}_M^2 > \mathcal{H}_O^3 > \mathcal{H}_O^4$$

There are several ways to calculate the electric and magnetic

field intensities. They all rely on determining the energy flux. For a monochromatic wave, the time-average power per unit area is given by the value of the Poynting vector

$$S = \frac{c}{2} (\epsilon_0 E^2 + \mu_0 H^2)$$

$$\bar{S} = \frac{c}{4} (\epsilon_0 E_0^2 + \mu_0 H_0^2)$$

where E_0 and H_0 are the peak amplitudes

$$\bar{S} = \frac{c}{2} \epsilon_0 E_0^2 = \frac{c}{2} \mu_0 H_0^2$$

where $\bar{S}$ is in watts/meter², $c = 3 \times 10^8 \frac{\text{meters}}{\text{sec.}}$

$$\mu_0 = 4\pi \times 10^{-7} \frac{\text{henrys}}{\text{meter}} \quad \epsilon_0 = 8.854 \times 10^{-12} \text{ farads/meter}$$

E_0 in volts/meter, H_0 in amperes/meter

Actually, $\bar{S}$ is a function of ω and we must integrate over all of the frequencies to obtain the measured quantity $\bar{S}$.

$$\bar{S} = \frac{1}{2\pi} \int \bar{S}(\omega) d\omega = \frac{c\epsilon_0}{4\pi} \int E_0^2(\omega) d\omega = \frac{c\mu_0}{4\pi} \int H_0^2(\omega) d\omega$$

We are interested in the average value of $E_0(\omega)$, averaged over all frequency

$$\overline{E_0(\omega)} = \frac{\int P(\omega) E_0(\omega) d\omega}{\int P(\omega) d\omega}$$

$$\overline{H_0(\omega)} = \frac{\int P(\omega) H_0(\omega) d\omega}{\int P(\omega) d\omega}$$

$P(\omega)$ is the distribution of intensity over the frequency range of interest. For narrow bands, we can consider that $P(\omega)$ is constant over the band. Thus, we have:

$$\overline{E_o(\omega)} \cong \frac{1}{\Delta\omega} \int E_o(\omega) d\omega$$

$$\overline{H_o(\omega)} \cong \frac{1}{\Delta\omega} \int H_o(\omega) d\omega$$

If we assume that

$$\int E_o(\omega) d\omega = \left[\Delta\omega \int H_o^2(\omega) d\omega \right]^{1/2}$$

$$\int H_o(\omega) d\omega = \left[\Delta\omega \int E_o^2(\omega) d\omega \right]^{1/2}$$

then

$$\int E_o^2(\omega) d\omega = \Delta\omega (\overline{E_o(\omega)})^2$$

$$\int H_o^2(\omega) d\omega = \Delta\omega (\overline{H_o(\omega)})^2$$

This, of course, is not true. However, there are so many other uncertainties that we will make this approximation. It will give a larger value for $\overline{E_o(\omega)}$ and $\overline{H_o(\omega)}$ than is actually the case.

$$\overline{S} = \frac{c\epsilon_o}{4\pi} \Delta\omega (\overline{E_o(\omega)})^2 = \frac{c\mu_o}{4\pi} \Delta\omega (\overline{H_o(\omega)})^2$$

$$\overline{E_o(\omega)} = \left[\frac{4\pi \overline{S}}{c\epsilon_o \Delta\omega} \right]^{1/2}$$

$$= \left[\frac{2}{c\epsilon_o} \right]^{1/2} \left[\frac{2\pi \overline{S}}{\Delta\omega} \right]^{1/2}$$

$$\overline{H_o(\omega)} = \left[\frac{4\pi \overline{S}}{c\mu_o \Delta\omega} \right]$$

$$= \left[\frac{2}{c\mu_o} \right]^{1/2} \left[\frac{2\pi \overline{S}}{\Delta\omega} \right]^{1/2}$$

Thus, if we know $\Delta\omega$, $\bar{S}$ we can determine $\overline{E_o(\omega)}$, $\overline{H_o(\omega)}$

$$\overline{E_o(\omega)} = 27.4 \left[\frac{2\pi\bar{S}}{\Delta\omega} \right]^{1/2}$$

$$\overline{H_o(\omega)} = 0.0728 \left[\frac{2\pi\bar{S}}{\Delta\omega} \right]^{1/2}$$

The problem is to determine $\bar{S}/\Delta\omega$. This can be done in several ways:

1. Use of measured values by P.M. tube
2. Calculated values from blackbody curves
3. Calculated values from other data (# of photons)

We have:

$$\frac{2\pi\bar{S}}{\Delta\omega} = \frac{1}{\Delta\omega} \int \overline{S(\omega)} d\omega$$

where

$$\overline{S(\omega)} = \frac{N\hbar\omega}{a}$$

N is # photons/sec.

a is the area of illumination

Thus

$$\frac{2\pi\bar{S}}{\Delta\omega} = \frac{1}{\Delta\omega} \int_{\omega_o - \frac{\Delta\omega}{2}}^{\omega_o + \frac{\Delta\omega}{2}} \frac{N\hbar\omega}{a} d\omega = \frac{N\hbar}{a\Delta\omega} \int_{\omega_o - \frac{\Delta\omega}{2}}^{\omega_o + \frac{\Delta\omega}{2}} \omega d\omega$$

ω_o is the center frequency, $\Delta\omega$ is the bandwidth

$$\begin{aligned} \frac{2\pi\bar{S}}{\Delta\omega} &= \frac{N\hbar}{2a\Delta\omega} \omega^2 \Big|_{\omega_o - \frac{\Delta\omega}{2}}^{\omega_o + \frac{\Delta\omega}{2}} \\ &= \frac{N\hbar}{2a\Delta\omega} \left[\omega_o^2 + \omega_o\Delta\omega + \frac{\Delta\omega^2}{4} - \omega_o^2 + \omega_o\Delta\omega - \frac{\Delta\omega^2}{4} \right] \\ &= \frac{N\hbar}{2a\Delta\omega} (2\omega_o\Delta\omega) = \frac{N\hbar\omega_o}{a} = \frac{N\hbar c}{a\lambda_o} \end{aligned}$$

We measure 1.5×10^{10} photons/sec. @ 3000 Å. In the visible we will have a higher intensity so this forms a lower limit. The area illuminated is 1 cm^2 .

$$\frac{2\pi \bar{S}}{\Delta\omega} = \frac{(1.5 \times 10^{10})(6.625 \times 10^{-34})(3 \times 10^8)}{(3 \times 10^7)(10^{-2})(10^{-2})} \cong 10^{-4} \text{ watts/meter}^2$$

We can now calculate $\overline{H_o(\omega)}$

$$\overline{H_o(\omega)} \cong (0.073)(10^{-4})^{1/2} = 7.3 \times 10^{-4} \text{ amperes/meter}$$

$$\begin{aligned} \overline{B_o(\omega)} &= \mu_o \overline{H_o(\omega)} \cong (4\pi)(10^{-7})(7.3 \times 10^{-4}) = 9.15 \times 10^{-10} \text{ webers/meter}^2 \\ &= 9.15 \times 10^{-6} \text{ gauss} \end{aligned}$$

Thus we see that the magnetic field strengths of the electromagnetic fields contribute perturbations much smaller than those of the static magnetic field, which is about 5000 gauss. The electric field strength of the electromagnetic field is

$$\overline{E_o(\omega)} = 377 \overline{H_o(\omega)} \cong 0.275 \text{ volts/meter}$$

The perturbations are of the order

$$\begin{aligned} \mathcal{H}_M^2 &= -\vec{m} \cdot \vec{H}' \\ \mathcal{H}_o^3 &= \vec{\mu} \cdot \vec{E}_o(\omega) \\ \mathcal{H}_o^4 &= -\vec{m} \cdot \vec{H}_o(\omega) \end{aligned}$$

as $\frac{H'}{\overline{H_o(\omega)}} \approx 5 \times 10^8$

thus $\frac{\mathcal{H}_M^2}{\mathcal{H}_o^4} \cong 5 \times 10^8$

since

$$\vec{E}_o(\omega) \approx 377 \vec{H}_o(\omega)$$

and

$$\vec{\mu} \approx 377 \vec{m}$$

$$\frac{\mathcal{H}_0^3}{\mathcal{H}_0^4} \cong 1.4 \times 10^5$$

$$\therefore \frac{\mathcal{H}_1^2}{\mathcal{H}_0^3} \cong 3.5 \times 10^3$$

$$\therefore \mathcal{H}_M^2 \cong 3.5 \times 10^3 \mathcal{H}_0^3 \cong 5 \times 10^8 \mathcal{H}_0^4$$

Consider now, greater intensities. From Rikmenspoel (12), we see that we can go up (in the visible) to about 10^{-6} watts or 10^{-2} watts/meter for $\frac{2\pi \bar{S}}{\Lambda \omega}$

This increases $\overline{H_0(\omega)}$ and $\overline{E_0(\omega)}$ only by a factor of 10.

If the power increased to 10^{-4} watts (a very liberal estimate) or 1 watt/meter², this would increase $\overline{H_0(\omega)}$ and $\overline{E_0(\omega)}$ by another factor of 10. This would result in

$$\mathcal{H}_M^2 \cong 35 \mathcal{H}_0^3 \cong 5 \times 10^6 \mathcal{H}_0^4$$

Thus, even in this case, the hierarchy given by equation (II-3) is valid.

To verify equation (II-2), we need consider three perturbations.

1. Magnetic field (static)
2. Electric potential field (static)
3. Vibrational perturbation.

We must determine the energies of these perturbations. From page 16 of Stephen's thesis (23), we have as the perturbing Hamiltonian due to the magnetic field

$$\mathcal{H}_M^2 = \sum_i -\frac{e_i}{2m_i c} [(\vec{r}_i \times \vec{p}_i) + 2\vec{s}_i] \cdot \vec{H}'$$

H' is the static magnetic field

e_i is the i^{th} electron

$\vec{L}_i \times \vec{p}_i$ is the i^{th} orbital angular momentum

$\vec{S}_i$ is the i^{th} spin angular momentum

m_i is the i^{th} electron mass

The static electric field perturbation is simply a Coulombs' law perturbation

$$\mathcal{H}_s^1 = \sum_i \sum_{j \neq i} \frac{z_j e_j e_i}{|r_{ij}|}$$

$z_j e_j$ is the charge of the j^{th} perturbation

e_i is the i^{th} electron

r_{ij} is the distance between the i^{th} electron and the j^{th} perturbing group

The vibrational perturbation is basically a Coulomb's law perturbation. From Albrecht's paper (53), we find:

$$\mathcal{H}_v^1 = \sum_a \frac{\partial}{\partial Q_a} \left[\sum_i \sum_{j \neq i} \frac{z_j e_j e_i}{|r_{ij}|} \right] Q_a$$

$z_j e_j$ is the charge of the displaced atom

e_i is the i^{th} electron

r_{ij} is the distance between the i^{th} electron and the j^{th} displaced atom

Q_a is the amplitude of the a^{th} normal mode

From Albrecht's paper, Table IV, we see that the vibrational perturbation energies in benzene and benzene derivatives range from .3 to .03 eV. A more realistic figure would be about .1 eV.

Now let us look at the static field perturbation. The strongest situation would be an ionized group directly attached to the chromophore. Here we have $z = 1$, $|r_{ij}| \sim 3 \text{ \AA} = r$

The energy is of the order of

$$\frac{Ze^2}{r} \approx \frac{(4.8)^2 (10^{-20})}{3 \times 10^{-8}} \text{ ergs}$$

$$= 7.68 \times 10^{-12} \text{ ergs}$$

$$1.6 \times 10^{-12} \text{ ergs} = 1 \text{ eV}$$

$\therefore$ the energy is $\sim 4.8 \text{ eV}$

This, of course, is quite unrealistic. In general Z is not 1 even for an ion, due to shielding by other electrons. A more realistic value might be $Z \approx .1$ or less. This would bring the perturbation energy down to the same range as that due to vibrations. Thus we conclude that vibrational and static field perturbations can be of the same order of magnitude. For our derivations, we shall assume that they are the same.

Now to consider the magnetic perturbation energy. This is

$$\frac{e}{2mc} \vec{l} \cdot \vec{H}$$

where $\vec{l}$ is the angular momentum.

For an electron, we measure angular momentum in units of $\hbar$. We can therefore get an idea of the magnitude of the energy by replacing the above by

$$\frac{e\hbar H'}{2mc}$$

$$e = 4.8 \times 10^{-10} \text{ e.s.u.}$$

$$H' \approx 5000 \text{ gauss.}$$

$$\hbar = \frac{1}{2\pi} (6.625 \times 10^{-27}) \text{ erg-sec}$$

$$m = 9.11 \times 10^{-28} \text{ grams}$$

$$c = 3 \times 10^8 \text{ meters/second}$$

$$\begin{aligned}
 \therefore \frac{e\hbar H'}{2mc} &= \frac{(4.8)(10^{-10})(6.625)(10^{-27})(5)(10^3)}{(2)(2)(3.14)(9.11)(10^{-28})(3)(10^{10})} \\
 &= \frac{(1.2)(6.625)(5)}{(3.14)(9.11)(3)} \frac{(10^{-10})(10^{-27})(10^3)}{(10^{-28})(10^{10})} \\
 &= 0.47 \times 10^{-16} \text{ ergs}
 \end{aligned}$$

This is a reasonable value since the Zeeman splitting (a direct measure of the perturbation energy) is of the order

$$\begin{aligned}
 \mu_B H' & 0.927 \times 10^{-20} \text{ ergs/gauss} \\
 \mu_B = \frac{e\hbar}{2mc} & \text{Bohr magneton}
 \end{aligned}$$

thus this is $2.6 \times 10^{-5} \text{ eV}$

Thus, the ratio of the perturbations is

$$\frac{V}{\mu_B H'} \approx \frac{10^{-1} \text{ eV}}{2.5 \times 10^{-5} \text{ eV}} = 4 \times 10^3$$

and we, therefore, have shown the validity of equation (II-2).

Appendix III

Expansion of Vector Potential about Origin Fixed in Molecule

The vector potential due to the electromagnetic wave is given by equation (2-2).

$$(III-1) \quad \vec{A}_{Li} = \frac{1}{2} \left[\vec{\tilde{A}}_{Lo} e^{-i\frac{\omega n}{c}(\hat{k} \cdot \vec{r}_i)} + \vec{\tilde{A}}_{Lo}^* e^{i\frac{\omega n}{c}(\hat{k} \cdot \vec{r}_i)} \right]$$

where $\vec{r}_i$ are the vectors from the origin fixed in the molecule to the various parts of the molecule. $\vec{A}_{Lo} = \frac{1}{2} (\vec{\tilde{A}}_{Lo} + \vec{\tilde{A}}_{Lo}^*)$ is the vector potential at this origin.

For most molecules (even giant macromolecules can be broken down into smaller chromophoric groups), we find that:

$$(III-2) \quad \hat{k} \cdot \vec{r}_i \ll \frac{c}{\omega n} = \frac{\lambda}{2\pi}$$

Thus we can approximate the exponentials by $e^x \cong 1 + x$

$$(III-3) \quad \therefore \vec{A}_{Li} \cong \frac{1}{2} \left[(\vec{\tilde{A}}_{Lo} + \vec{\tilde{A}}_{Lo}^*) - \frac{i\omega n}{2c} (\vec{\tilde{A}}_{Lo} - \vec{\tilde{A}}_{Lo}^*)(\hat{k} \cdot \vec{r}_i) \right]$$

This can also be written:

$$(III-4) \quad \vec{A}_{Li} = \frac{1}{2} [\vec{\tilde{A}}_{Lo} + \vec{\tilde{A}}_{Lo}^*] - \frac{i\omega n}{4c} [\vec{\tilde{A}}_{Lo} - \vec{\tilde{A}}_{Lo}^*](\hat{k} \cdot \vec{r}_i) - \frac{i\omega n}{4c} [\vec{\tilde{A}}_{Lo} - \vec{\tilde{A}}_{Lo}^*](\hat{k} \cdot \vec{r}_i)$$

Using the common method of expanding a triple cross-product, we have:

$$(III-5) \quad (\hat{k} \times \vec{\tilde{A}}_{Lo}) \times \vec{r}_i = \vec{\tilde{A}}_{Lo} (\hat{k} \cdot \vec{r}_i) - (\vec{\tilde{A}}_{Lo} \cdot \vec{r}_i) \hat{k}$$

$$\text{thus } \vec{\tilde{A}}_{Lo} (\hat{k} \cdot \vec{r}_i) = (\hat{k} \times \vec{\tilde{A}}_{Lo}) \times \vec{r}_i + (\vec{\tilde{A}}_{Lo} \cdot \vec{r}_i) \hat{k}$$

substituting into the expression for $\vec{A}_{Li}$

$$(III-6) \quad \vec{A}_{Li} = \frac{1}{2} [\vec{\tilde{A}}_{Lo} + \vec{\tilde{A}}_{Lo}^*] - \frac{i\omega n}{4c} [(\hat{k} \times \vec{\tilde{A}}_{Lo}) - (\hat{k} \times \vec{\tilde{A}}_{Lo}^*)] \times \vec{r}_i \\ - \frac{i\omega n}{4c} \{[(\vec{\tilde{A}}_{Lo} \cdot \vec{r}_i) \hat{k} + \vec{\tilde{A}}_{Lo} (\hat{k} \cdot \vec{r}_i)] - [(\vec{\tilde{A}}_{Lo}^* \cdot \vec{r}_i) \hat{k} + \vec{\tilde{A}}_{Lo}^* (\hat{k} \cdot \vec{r}_i)]\}$$

the last of the three terms can be shown(23) to lead to the interaction of the electric quadrupole with the electric field gradient and make a negligible contribution to

We know that:

$$(III-7) \quad \nabla \times \vec{A}_{Li} = \frac{1}{2} [(\nabla \times \vec{\tilde{A}}_{Li}) + (\nabla \times \vec{\tilde{A}}_{Li}^*)] \\ = - \frac{i\omega n}{2c} [(\hat{k} \times \vec{\tilde{A}}_{Li}) - (\hat{k} \times \vec{\tilde{A}}_{Li}^*)]$$

$$\therefore (\nabla \times \vec{A}_{Li})_o = (\nabla \times \vec{A}_{Li})_{\vec{r}_i=0} \\ = - \frac{i\omega n}{c} [(\hat{k} \times \vec{\tilde{A}}_{Lo}) - (\hat{k} \times \vec{\tilde{A}}_{Lo}^*)]$$

Substituting this equation for $(\nabla \times \vec{A}_{Li})_o$ and the equation for $\vec{A}_{Lo}$ into the equation for $\vec{A}_{Li}$, we have:

$$(III-8) \quad \vec{A}_{Li} \cong \vec{A}_{Lo} + \frac{1}{2} (\nabla \times \vec{A}_{Li})_o \times \vec{r}_i$$

Appendix IV

Derivation of $[C_{ab}^*(t)e^{i\omega_{ba}t} \vec{O}_{ba} + C_{ab}(t)e^{-i\omega_{ba}t} \vec{O}_{ab}]$

We want to evaluate the expression

$$C_{ab}^*(t)e^{i\omega_{ba}t} \vec{O}_{ba} + C_{ab}(t)e^{-i\omega_{ba}t} \vec{O}_{ab}$$

We must first evaluate $C_{ab}(t)$ from equations (2-70) and (2-20).

$$(2-70) \quad C_{ab}(t) = \frac{1}{i\hbar} \int_0^t \langle \psi_b^2(t) | \mathcal{H}_0^3 + \mathcal{H}_0^4 | \psi_a^2(t) \rangle dt$$

$$(2-20) \quad \mathcal{H}_0^3 = -\frac{1}{c} (\sum_i e \dot{\vec{r}}_i) \cdot \vec{A}_{L0}$$

$$\mathcal{H}_0^4 = -\vec{m} \cdot (\nabla \times \vec{A}_{Li})_0$$

Substituting (2-20) into (2-70)

$$C_{ab}(t) = -\frac{1}{i\hbar} \int_0^t \langle \psi_b^2(t) | (\sum_i e \dot{\vec{r}}_i) \cdot \vec{A}_{L0} | \psi_a^2(t) \rangle dt \\ - \frac{1}{i\hbar} \int_0^t \langle \psi_b^2(t) | \vec{m} \cdot (\nabla \times \vec{A}_{Li})_0 | \psi_a^2(t) \rangle dt$$

substituting $\dot{\vec{r}}_i = \frac{i}{\hbar} (\mathcal{H} \vec{r}_i - \vec{r}_i \mathcal{H})$

and recognizing that $\mathcal{H} | \psi_a^2(t) \rangle = \hbar \omega_a | \psi_a^2(t) \rangle$
 $\langle \psi_b^2(t) | \mathcal{H} = \langle \psi_b^2(t) | \hbar \omega_b$
 $\omega_{ba} = \omega_b - \omega_a$

we have:

$$C_{ab}(t) = -\frac{1}{i\hbar} \int_0^t \frac{i\omega_{ba}}{c} \langle \psi_b^2(t) | \sum_i e\vec{r}_i \cdot \vec{A}_{L0} | \psi_a^2(t) \rangle dt$$

$$- \frac{1}{i\hbar} \int_0^t \langle \psi_b^2(t) | \vec{m} \cdot (\nabla \times \vec{A}_{L0}) | \psi_a^2(t) \rangle dt$$

Substituting in

$$\sum_i e\vec{r}_i = \vec{\mu}$$

$$\langle \psi_b^2(t) | = \langle \psi_b^2 | e^{i\omega_b t}$$

$$| \psi_a^2(t) \rangle = e^{-i\omega_a t} | \psi_a^2 \rangle$$

interchanging the integrals over space and time

$$C_{ab}(t) = -\frac{1}{i\hbar} \left\{ \langle \psi_b^2 | \frac{i\omega_{ba}}{c} \vec{\mu} \cdot \int_0^t \vec{A}_{L0} e^{i\omega_{ba}t} dt | \psi_a^2 \rangle \right.$$

$$\left. + \langle \psi_b^2 | \vec{m} \cdot \int_0^t (\nabla \times \vec{A}_{L0})_0 e^{i\omega_{ba}t} dt | \psi_a^2 \rangle \right\}$$

we thus have two integrals to evaluate

$$\int_0^t \vec{A}_{L0} e^{i\omega_{ba}t} dt = \frac{\vec{A}_{L0}^0}{2} \int_0^t e^{i(\omega + \omega_{ba})t} dt + \frac{\vec{A}_{L0}^{0*}}{2} \int_0^t e^{-i(\omega - \omega_{ba})t} dt$$

$$= \frac{i}{2} \left\{ \vec{A}_{L0}^0 \left[\frac{1 - e^{i(\omega + \omega_{ba})t}}{\omega + \omega_{ba}} \right] - \vec{A}_{L0}^{0*} \left[\frac{1 - e^{-i(\omega - \omega_{ba})t}}{\omega - \omega_{ba}} \right] \right\}$$

$$= \frac{i}{2} \left\{ \vec{A}_{L0}^0 e^{i\omega t} \left[\frac{e^{-i\omega t} - e^{i\omega_{ba}t}}{\omega + \omega_{ba}} \right] - \vec{A}_{L0}^{0*} e^{-i\omega t} \left[\frac{e^{i\omega t} - e^{i\omega_{ba}t}}{\omega - \omega_{ba}} \right] \right\}$$

$$= \frac{i}{2} \left\{ \vec{A}_{L0}^0 \left[\frac{e^{-i\omega t} - e^{i\omega_{ba}t}}{\omega + \omega_{ba}} \right] - \vec{A}_{L0}^{0*} \left[\frac{e^{i\omega t} - e^{i\omega_{ba}t}}{\omega - \omega_{ba}} \right] \right\}$$

similarly:

$$\begin{aligned} \int_0^t (\nabla \times \vec{A}_{Li})_0 e^{i\omega_{bat}} dt &= \frac{(\nabla \times \vec{A}_{Li})_0}{2} \int_0^t e^{i(\omega + \omega_{ba})t} dt + \frac{(\nabla \times \vec{A}_{Li})_0^*}{2} \int_0^t e^{-i(\omega - \omega_{ba})t} dt \\ &= \frac{i}{2} \left\{ (\nabla \times \vec{A}_{Li})_0 \left[\frac{e^{-i\omega t} - e^{i\omega_{bat}}}{\omega + \omega_{ba}} \right] - (\nabla \times \vec{A}_{Li})_0^* \left[\frac{e^{i\omega t} - e^{i\omega_{bat}}}{\omega - \omega_{ba}} \right] \right\} \end{aligned}$$

multiplying $C_{ab}(t)$ by $e^{-i\omega_{bat}}$ and substituting in the above expressions for the integrals, we have:

$$\begin{aligned} e^{-i\omega_{bat}} C_{ab}(t) &= \frac{1}{2\hbar} e^{-i\omega_{bat}} \left\{ (\psi_b^2 | \frac{i\omega_{ba}}{c} \vec{\mu} \cdot [\vec{A}_{Lo} \left(\frac{e^{-i\omega t} - e^{i\omega_{bat}}}{\omega + \omega_{ba}} \right) - \vec{A}_{Lo}^* \left(\frac{e^{i\omega t} - e^{i\omega_{bat}}}{\omega - \omega_{ba}} \right)] | \psi_a^2) \right. \\ &\quad \left. + (\psi_b^2 | \vec{m} \cdot [(\nabla \times \vec{A}_{Li})_0 \left(\frac{e^{-i\omega t} - e^{i\omega_{bat}}}{\omega + \omega_{ba}} \right) - (\nabla \times \vec{A}_{Li})_0^* \left(\frac{e^{i\omega t} - e^{i\omega_{bat}}}{\omega - \omega_{ba}} \right)] | \psi_a^2) \right\} \\ &= \frac{1}{2\hbar} \left\{ (\psi_b^2 | \frac{i\omega_{ba}}{c} \vec{\mu} \cdot [\vec{A}_{Lo} \left(\frac{1 - e^{-i(\omega + \omega_{ba})t}}{\omega + \omega_{ba}} \right) - \vec{A}_{Lo}^* \left(\frac{1 - e^{i(\omega - \omega_{ba})t}}{\omega - \omega_{ba}} \right)] | \psi_a^2) \right. \\ &\quad \left. + (\psi_b^2 | \vec{m} \cdot [(\nabla \times \vec{A}_{Li})_0 \left(\frac{1 - e^{-i(\omega + \omega_{ba})t}}{\omega + \omega_{ba}} \right) - (\nabla \times \vec{A}_{Li})_0^* \left(\frac{1 - e^{i(\omega - \omega_{ba})t}}{\omega - \omega_{ba}} \right)] | \psi_a^2) \right\} \end{aligned}$$

If we retain the exponential terms $e^{-i(\omega + \omega_{ba})t}$ and $e^{i(\omega - \omega_{ba})t}$ these will lead to CD and MCD. Stephens (23) does this in his thesis. However, it makes subsequent expansions unwieldy and difficult to follow. It also necessitates the use of a complex tensor notation. Therefore, in the interests of clarity, we shall drop these exponentials and will instead obtain the equations for CD and MCD from those for ORD and MORD via the Kronig-Kramers transforms. The terms remaining after dropping the exponentials are those terms that lead to ORD and MORD. Thus we approximate:

$$\begin{aligned}
e^{-i\omega_{ba}t} C_{ab}(t) &= \frac{i\omega_{ba}}{2\hbar c} \left\{ (\psi_b^2 | \vec{\mu} \cdot [\vec{A}_{Lo} \left(\frac{1}{\omega + \omega_{ba}} \right) - \vec{A}_{Lo}^* \left(\frac{1}{\omega - \omega_{ba}} \right)] | \psi_a^2) \right\} \\
&\quad + \frac{1}{2\hbar} \left\{ (\psi_b^2 | \vec{m} \cdot [(\vec{\nabla} \times \vec{A}_{Li})_o \left(\frac{1}{\omega + \omega_{ba}} \right) - (\vec{\nabla} \times \vec{A}_{Li})_o^* \left(\frac{1}{\omega - \omega_{ba}} \right)] | \psi_a^2) \right\} \\
&= \frac{i\omega_{ba}}{2\hbar c} \left(\frac{1}{\omega + \omega_{ba}} \right) \vec{A}_{Lo} \cdot (\psi_b^2 | \vec{\mu} | \psi_a^2) - \frac{i\omega_{ba}}{2\hbar c} \left(\frac{1}{\omega - \omega_{ba}} \right) \vec{A}_{Lo}^* \cdot (\psi_b^2 | \vec{\mu} | \psi_a^2) \\
&\quad + \frac{1}{2\hbar} \left(\frac{1}{\omega + \omega_{ba}} \right) (\vec{\nabla} \times \vec{A}_{Li})_o \cdot (\psi_b^2 | \vec{m} | \psi_a^2) - \frac{1}{2\hbar} \left(\frac{1}{\omega - \omega_{ba}} \right) (\vec{\nabla} \times \vec{A}_{Li})_o^* \cdot (\psi_b^2 | \vec{m} | \psi_a^2) \\
&= \frac{1}{2\hbar} \left\{ \frac{i}{c} \left(\frac{\omega_{ba}}{\omega + \omega_{ba}} \right) (\vec{A}_{Lo} \cdot \vec{\mu}_{ba}) - \frac{i}{c} \left(\frac{\omega_{ba}}{\omega - \omega_{ba}} \right) (\vec{A}_{Lo}^* \cdot \vec{\mu}_{ba}) \right. \\
&\quad \left. + \left(\frac{1}{\omega + \omega_{ba}} \right) ((\vec{\nabla} \times \vec{A}_{Li})_o \cdot \vec{m}_{ba}) - \left(\frac{1}{\omega - \omega_{ba}} \right) ((\vec{\nabla} \times \vec{A}_{Li})_o^* \cdot \vec{m}_{ba}) \right\}
\end{aligned}$$

Reducing to the common denominator $\omega^2 - \omega_{ba}^2$

$$\begin{aligned}
e^{-i\omega_{ba}t} C_{ab}(t) &= \frac{1}{2\hbar(\omega^2 - \omega_{ba}^2)} \left\{ \frac{i}{c} \omega_{ba} [(\omega - \omega_{ba})(\vec{A}_{Lo} \cdot \vec{\mu}_{ba}) - (\omega + \omega_{ba})(\vec{A}_{Lo}^* \cdot \vec{\mu}_{ba})] \right. \\
&\quad \left. + [(\omega - \omega_{ba})((\vec{\nabla} \times \vec{A}_{Li})_o \cdot \vec{m}_{ba}) - (\omega + \omega_{ba})((\vec{\nabla} \times \vec{A}_{Li})_o^* \cdot \vec{m}_{ba})] \right\} \\
&= \frac{1}{2\hbar(\omega^2 - \omega_{ba}^2)} \left\{ \frac{i\omega\omega_{ba}}{c} [(\vec{A}_{Lo} - \vec{A}_{Lo}^*) \cdot \vec{\mu}_{ba}] - \frac{i\omega_{ba}^2}{c} [(\vec{A}_{Lo} + \vec{A}_{Lo}^*) \cdot \vec{\mu}_{ba}] \right. \\
&\quad \left. + \omega [((\vec{\nabla} \times \vec{A}_{Li})_o - (\vec{\nabla} \times \vec{A}_{Li})_o^*) \cdot \vec{m}_{ba}] - \omega_{ba} [((\vec{\nabla} \times \vec{A}_{Li})_o + (\vec{\nabla} \times \vec{A}_{Li})_o^*) \cdot \vec{m}_{ba}] \right\}
\end{aligned}$$

We have the following relations:

$$\vec{E}_{Lo} = -\frac{1}{c} \dot{\vec{A}}_{Lo}$$

$$\vec{H}_{Lo} = \nabla \times \vec{A}_{Lo}$$

substituting in

$$\vec{A}_{L_0} = \frac{1}{2} [\vec{\tilde{A}}_{L_0} e^{i\omega t} + \vec{\tilde{A}}_{L_0}^* e^{-i\omega t}] = \frac{1}{2} [\vec{\tilde{A}}_{L_0} + \vec{\tilde{A}}_{L_0}^*]$$

we have;

$$-c \vec{E}_{L_0} = \frac{i\omega}{2} [\vec{\tilde{A}}_{L_0} e^{i\omega t} - \vec{\tilde{A}}_{L_0}^* e^{-i\omega t}] = \frac{i\omega}{2} [\vec{\tilde{A}}_{L_0} - \vec{\tilde{A}}_{L_0}^*]$$

$$c \vec{E}_{L_0} = \frac{\omega^2}{2} [\vec{\tilde{A}}_{L_0} + \vec{\tilde{A}}_{L_0}^*]$$

$$\vec{H}_{L_0} = \frac{1}{2} [(\nabla \times \vec{\tilde{A}}_{L_0})_0 + (\nabla \times \vec{\tilde{A}}_{L_0})_0^*]$$

$$\vec{H}_{L_0} = \frac{i\omega}{2} [(\nabla \times \vec{\tilde{A}}_{L_0})_0 - (\nabla \times \vec{\tilde{A}}_{L_0})_0^*]$$

thus

$$[\vec{\tilde{A}}_{L_0} - \vec{\tilde{A}}_{L_0}^*] = \frac{i2c}{\omega} \vec{E}_{L_0}$$

$$[\vec{\tilde{A}}_{L_0} + \vec{\tilde{A}}_{L_0}^*] = \frac{2c}{\omega^2} \vec{E}_{L_0}$$

$$[(\nabla \times \vec{\tilde{A}}_{L_0})_0 - (\nabla \times \vec{\tilde{A}}_{L_0})_0^*] = -\frac{2i}{\omega} \vec{H}_{L_0}$$

$$[(\nabla \times \vec{\tilde{A}}_{L_0})_0 + (\nabla \times \vec{\tilde{A}}_{L_0})_0^*] = 2 \vec{H}_{L_0}$$

Substituting these expressions into the expression for $e^{-i\omega_{bat}t} C_{ab}(t)$

we have:

$$e^{-i\omega_{ba}t} C_{ab}(t) = \frac{1}{\hbar(\omega^2 - \omega_{ba}^2)} \left\{ -\omega_{ba} (\vec{E}_{Lo} \cdot \vec{\mu}_{ba}) - i \frac{\omega_{ba}^2}{\omega^2} (\vec{E}_{Lo} \cdot \vec{\mu}_{ba}) \right. \\ \left. - i (\vec{H}_{Lo} \cdot \vec{m}_{ba}) - \omega_{ba} (\vec{H}_{Lo} \cdot \vec{m}_{ba}) \right\}$$

we want $(e^{i\omega_{ba}t} C_{ab}^*(t) \vec{O}_{ba} + e^{-i\omega_{ba}t} C_{ab}(t) \vec{O}_{ab})$. This is the same as $2 \operatorname{Re} \{ e^{-i\omega_{ba}t} C_{ab}(t) \vec{O}_{ab} \}$. Thus:

$$e^{i\omega_{ba}t} C_{ab}^*(t) \vec{O}_{ba} + e^{-i\omega_{ba}t} C_{ab}(t) \vec{O}_{ab} = \frac{2\omega_{ba}}{\hbar(\omega_{ba}^2 - \omega^2)} \operatorname{Re} \{ (\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) \vec{O}_{ab} \} \\ - \frac{2(\omega_{ba}^2/\omega^2)}{\hbar(\omega_{ba}^2 - \omega^2)} \operatorname{Im} \{ (\vec{\mu}_{ba} \cdot \vec{E}_{Lo}) \vec{O}_{ab} \} \\ - \frac{2}{\hbar(\omega_{ba}^2 - \omega^2)} \operatorname{Im} \{ (\vec{m}_{ba} \cdot \vec{H}_{Lo}) \vec{O}_{ab} \} \\ + \frac{2\omega_{ba}}{\hbar(\omega_{ba}^2 - \omega^2)} \operatorname{Re} \{ (\vec{m}_{ba} \cdot \vec{H}_{Lo}) \vec{O}_{ab} \}$$

Appendix V

Spatial Averages Over All Molecular Orientations

We have three types of vector quantities to average over all molecular orientation. There are three forms:

$$\vec{a}; \quad (\vec{a} \cdot \vec{U})\vec{b}; \quad (\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V})\vec{c}$$

where $\vec{a}, \vec{b}, \vec{c}$ are molecule fixed vectors, $\vec{U}, \vec{V}$ are space fixed vectors.

The first average $\overline{\vec{a}}$ is the spatial average of a molecule fixed vector over all molecular orientations. The result is zero and we can show this by demonstrating that the projection of $\vec{a}$ on any space fixed axis is zero on the average. This is an obvious proof.

The second average $\overline{(\vec{a} \cdot \vec{U})\vec{b}}$ is a more complex spatial average. The arguments we use for this average are patterned after Condon (28). We must average for all orientations of $\vec{a}$ and $\vec{b}$ keeping fixed the magnitudes of $\vec{a}$ and $\vec{b}$ and the angle between them. Now $(\vec{a} \cdot \vec{U})\vec{b}$ is a vector in the direction of $\vec{b}$. As $\vec{b}$ takes on all possible directions consistent with a fixed direction of $\vec{a}$, the average value of $(\vec{a} \cdot \vec{U})\vec{b}$ will be the component of this along $\vec{a}$, or

$$(\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{a}_0)\vec{a}_0$$

where $\vec{a}_0$ is a unit vector in the direction of $\vec{a}$. We must now average over all directions of $\vec{a}$. Consider first those directions of $\vec{a}$ making a fixed angle Θ with $\vec{U}$, the space fixed vector.

Here $(\vec{a} \cdot \vec{U}) = |\vec{a}| |\vec{U}| \cos \theta$

$$\begin{aligned} \therefore (\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{a}_0) \vec{a}_0 &= |\vec{a}| |\vec{U}| \cos \theta (\vec{b} \cdot \vec{a}_0) \vec{a}_0 \\ &= |\vec{U}| \cos \theta (\vec{b} \cdot \vec{a}) \vec{a}_0 \end{aligned}$$

If we now average over all positions of $\vec{a}_0$ while maintaining the angle θ between $\vec{a}$ and $\vec{U}$ we substitute for $\vec{a}_0$ the projection on $\vec{U}_0$, the unit vector in the $\vec{U}$ direction.

$$\therefore \vec{a}_0 \rightarrow (\vec{a}_0 \cdot \vec{U}_0) \vec{U}_0 = \vec{U}_0 \cos \theta$$

$$\begin{aligned} \therefore (\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{a}_0) \vec{a}_0 &\longrightarrow |\vec{U}| \cos^2 \theta (\vec{b} \cdot \vec{a}) \vec{U}_0 \\ &= (\vec{b} \cdot \vec{a}) \vec{U} \cos^2 \theta \end{aligned}$$

We now do the final averaging by averaging over all values of θ weighting them per unit solid angle. This is a common procedure and

$$\int_{\Omega} \cos^2 \theta d\Omega = \frac{4}{3} \pi$$

$$\therefore \overline{(\vec{a} \cdot \vec{U}) \vec{b}} = \frac{1}{3} (\vec{a} \cdot \vec{b}) \vec{U}$$

The third average $\overline{(\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V}) \vec{C}}$ can be obtained from the second average with the aid of some vector identities. We first have:

$$(\vec{a} \times \vec{b}) \cdot (\vec{U} \times \vec{V}) = (\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V}) - (\vec{a} \cdot \vec{V})(\vec{b} \cdot \vec{U})$$

multiplying both sides by $\vec{C}$ and averaging

$$\overline{[(\vec{a} \times \vec{b}) \cdot (\vec{U} \times \vec{V})] \vec{c}} = \overline{(\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V}) \vec{c}} - \overline{(\vec{a} \cdot \vec{V})(\vec{b} \cdot \vec{U}) \vec{c}}$$

A moment's thought will convince one that

$$\overline{(\vec{a} \cdot \vec{V})(\vec{b} \cdot \vec{U}) \vec{c}} = - \overline{(\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V}) \vec{c}}$$

To show this we note that if we put

$$\vec{a} = |\vec{a}| \vec{a}_0 = \alpha \vec{a}_0$$

$$\vec{b} = |\vec{b}| \vec{b}_0 = \beta \vec{b}_0$$

$$\vec{c} = |\vec{c}| \vec{c}_0 = \gamma \vec{c}_0$$

then

$$\overline{(\vec{a} \cdot \vec{V})(\vec{b} \cdot \vec{U}) \vec{c}} = \alpha \beta \gamma \overline{(\vec{a}_0 \cdot \vec{V})(\vec{b}_0 \cdot \vec{U}) \vec{c}_0}$$

If we consider rotating the molecule so that $\vec{c}_0$ is now lying along the line where $\vec{a}_0$ lay before, then $\vec{c}_0$ appears related to $\vec{V}$ in the same manner as $\vec{a}_0$ did previously. Similarly, $\vec{a}_0$ is now related to $\vec{U}$ in a manner like $\vec{b}_0$ was previously. And finally $\vec{b}_0$ fills the former role of $\vec{c}_0$. Since the average cannot change, we have:

$$\overline{(\vec{a} \cdot \vec{V})(\vec{b} \cdot \vec{U}) \vec{c}} = \alpha \beta \gamma \overline{(\vec{a}_0 \cdot \vec{V})(\vec{b}_0 \cdot \vec{U}) \vec{c}_0}$$

$$= \alpha \beta \gamma \overline{(\vec{c}_0 \cdot \vec{V})(\vec{a}_0 \cdot \vec{U}) \vec{b}_0}$$

$$= \alpha \beta \gamma \overline{(\vec{b}_0 \cdot \vec{V})(\vec{c}_0 \cdot \vec{U}) \vec{a}_0}$$

The last equality results from another molecular rotation which aligns $\vec{b}_0$ with the former direction of $\vec{a}_0$. Thus $\vec{a}_0, \vec{b}_0, \vec{c}_0$ behave as the triple product $\vec{a}_0 \cdot \vec{b}_0 \times \vec{c}_0$ behaves. Accepting this we have (remembering that

$$(\vec{a}_0 \times \vec{b}_0) \cdot \vec{c}_0 = -(\vec{b}_0 \times \vec{a}_0) \cdot \vec{c}_0.$$

$$\begin{aligned} \overline{(\vec{a} \cdot \vec{V})(\vec{b} \cdot \vec{U})\vec{c}} &= \alpha\beta\gamma \overline{(\vec{a}_0 \cdot \vec{V})(\vec{b}_0 \cdot \vec{U})\vec{c}_0} = -\alpha\beta\gamma \overline{(\vec{b}_0 \cdot \vec{V})(\vec{a}_0 \cdot \vec{U})\vec{c}_0} \\ &= -\overline{(\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V})\vec{c}} \end{aligned}$$

Thus

$$\overline{[(\vec{a} \times \vec{b}) \cdot (\vec{U} \times \vec{V})]\vec{c}} = 2 \overline{(\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V})\vec{c}}$$

$$\therefore \overline{(\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V})\vec{c}} = \frac{1}{2} \overline{[(\vec{a} \times \vec{b}) \cdot (\vec{U} \times \vec{V})]\vec{c}}$$

$$\text{let } \vec{d} = \vec{a} \times \vec{b} \quad \vec{w} = \vec{U} \times \vec{V}$$

$$\overline{(\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V})\vec{c}} = \frac{1}{2} \overline{(\vec{d} \cdot \vec{w})\vec{c}}$$

but from calculation of the second average

$$\overline{(\vec{d} \cdot \vec{w})\vec{c}} = \frac{1}{3} (\vec{d} \cdot \vec{c}) \vec{w}$$

$$\therefore \overline{(\vec{a} \cdot \vec{U})(\vec{b} \cdot \vec{V})\vec{c}} = \frac{1}{6} (\vec{a} \times \vec{b} \cdot \vec{c})(\vec{U} \times \vec{V}) = \frac{1}{6} (\vec{a} \cdot \vec{b} \times \vec{c})(\vec{U} \times \vec{V})$$

Appendix VIKronig-Kramers Transforms As Applied to Molecular Optical Activity

Optical activity is specified by a complex function of frequency, namely:

$$\Phi(z, \omega) = \varphi(z, \omega) - i \Theta(z, \omega)$$

or in terms of partial molecular optical activity

$$[\Phi_{ab}(\omega)] = [\phi_{ab}(\omega)] - i [\Theta_{ab}(\omega)]$$

for natural optical activity and

$$[\Phi_{ab}(\omega)]_M = [\phi_{ab}(\omega)]_M - i [\Theta_{ab}(\omega)]_M$$

for magnetically-induced optical activity. The integral transformations that relate the real and imaginary parts of such functions are known as the Kronig-Kramers transformation. In this appendix, we obtain the equations for the partial molecular optical ellipticity (partial molecular circular dichroism) from the equations for the partial molecular optical rotation by applying the Kronig-Kramers transformations. The transformations are developed for natural optical activity by Moscowitz (29).

$$(VI-1) \quad (a) \quad [\phi_{ab}(\omega)] = \frac{2\omega^2}{\pi} \int_0^\infty \frac{[\Theta_{ab}(\omega')]}{\omega'(\omega'^2 - \omega^2)} d\omega'$$

$$[\Theta_{ab}(\omega)] = - \frac{2\omega^3}{\pi} \int_0^\infty \frac{[\phi_{ab}(\omega')]}{\omega'^2(\omega'^2 - \omega^2)} d\omega'$$

There are comparable relations for the magnetically-induced optical activity.

From part A of Chapter 2, we have equations (2-106) for the partial molecular rotations, both natural and magnetically-induced.

$$(2-106) \quad \begin{aligned} [\phi_{ab}(\omega)] &= - \frac{48N}{\hbar c} f_2(\omega, \omega_{ba}) R_{ab} \\ [\phi_{ab}(\omega)]_M &= - \frac{24NH'}{\hbar c} \left[f_1(\omega, \omega_{ba}) A_{ab} \right. \\ &\quad \left. + f_2(\omega, \omega_{ba}) B_{ab} + \frac{1}{kT} f_2(\omega, \omega_{ba}) C_{ab} \right] \end{aligned}$$

The only frequency dependent parts of either of equations (2-106) are the functions $f_1(\omega, \omega_{ba})$ and $f_2(\omega, \omega_{ba})$. These functions are given by equations (2-101). Therefore, upon substituting (2-106) into equation (VI-1b) and its counterpart for magnetically-induced optical activity, we have:

$$\begin{aligned} [\Theta_{ab}(\omega)] &= \left(\frac{2\omega^3}{\pi} \right) \left(\frac{48N}{\hbar c} R_{ab} \right) \int_0^\infty \frac{f_2(\omega', \omega_{ba})}{\omega'^2(\omega'^2 - \omega^2)} d\omega' \\ [\Theta_{ab}(\omega)]_M &= \left(\frac{2\omega^3}{\pi} \right) \left(\frac{24NH'}{\hbar c} \right) \left[A_{ab} \int_0^\infty \frac{f_1(\omega', \omega_{ba})}{\omega'^2(\omega'^2 - \omega^2)} d\omega' \right. \\ &\quad \left. + B_{ab} \int_0^\infty \frac{f_2(\omega', \omega_{ba})}{\omega'^2(\omega'^2 - \omega^2)} d\omega' \right. \\ &\quad \left. + \frac{1}{kT} C_{ab} \int_0^\infty \frac{f_2(\omega', \omega_{ba})}{\omega'^2(\omega'^2 - \omega^2)} d\omega' \right] \end{aligned}$$

Here we have only two integrals to determine:

$$\int_0^\infty \frac{f_1(\omega', \omega_{ba})}{\omega'^2(\omega'^2 - \omega^2)} d\omega'$$

$$\int_0^\infty \frac{f_2(\omega', \omega_{ba})}{\omega'^2(\omega'^2 - \omega^2)} d\omega'$$

The evaluation of these integrals is complex and tedious and is not done here. For readers interested, Macdonald and Brachman (35) discuss the evaluation of such integrals. We merely present the results for the partial molecular ellipticities.

$$\begin{aligned} (VI-2) \quad [\Theta_{ab}(\omega)] &= - \frac{48N}{\hbar c} f_4(\omega, \omega_{ba}) R_{ab} \\ [\Theta_{ab}(\omega)]_M &= - \frac{24NH'}{\hbar c} \left[f_3(\omega, \omega_{ba}) A_{ab} \right. \\ &\quad \left. + f_4(\omega, \omega_{ba}) B_{ab} + \frac{1}{kT} f_4(\omega, \omega_{ba}) C_{ab} \right] \end{aligned}$$

where

$$(VI-3) \quad f_3(\omega, \omega_{ba}) = \frac{4\omega_{ba}\omega^3(\omega_{ba}^2 - \omega^2)\Gamma_{ba}}{\hbar[(\omega_{ba}^2 - \omega^2)^2 + \omega^2\Gamma_{ba}^2]^2}$$

$$f_4(\omega, \omega_{ba}) = \frac{\omega^3\Gamma_{ba}}{(\omega_{ba}^2 - \omega^2)^2 + \omega^2\Gamma_{ba}^2}$$

Appendix VII

Born-Oppenheimer Approximations

In this appendix, we describe the two most common of the Born-Oppenheimer approximations, the harmonic and the adiabatic, and the modifications of the Born-Oppenheimer approach to treat degenerate and near-degenerate states where the above approximations lose validity. The description here borrows heavily from the work of Longuet-Higgins (42) who presents a simpler, if less elegant treatment of these approximations than do the original authors (43).

We will show that under the harmonic approximation, the suitable zero-order molecular wave function is given by:

$$(VII-1) \quad \psi_a^0(x, q) = \phi_e^0(x, q^0) \chi_{en}^0(q)$$

under the adiabatic approximation by:

$$(VII-2) \quad \psi_a^0(x, q) = \phi_e^0(x, q) \chi_{en}^0(q)$$

and for degenerate and near-degenerate states the above approximations break down and the zero-order molecular wave functions are given by a linear combination of the adiabatic states, i.e.

$$(VII-3) \quad \psi_a^0(x, q) = \sum_{e,n} \phi_e^0(x, q) \chi_{en}^0(q)$$

Here the $\phi_e^0(x, q)$ and $\phi_e^0(x, q^0)$ are the zero-order electronic wave functions and have as arguments x , the electronic coordinate, and q or q^0 , the nuclear coordinate and the equilibrium nuclear coordinate

respectively. These electronic wave functions form complete orthonormal sets as defined by the equations:

$$(VII-4) \quad \int \varphi_e^{\circ*}(x, q) \varphi_{e'}^{\circ}(x, q) dx = \delta_{ee'} \quad \text{for all } q$$

$$\int \varphi_e^{\circ*}(x, q^{\circ}) \varphi_{e'}^{\circ}(x, q^{\circ}) dx = \delta_{ee'}$$

The meaning of the $\chi_{en}^{\circ}(q)$ can be most clearly seen by examination of equation (VII-3). As the $\varphi_e^{\circ}(x, q)$ form a complete orthonormal set, they can be used for the construction of proper molecular eigenstates. This assumption, though never proved (44) is the basis for all studies of molecular dynamics. This is basically what equation (VII-3) is, an expansion of the proper zero-order molecular eigenstate $\psi^{\circ}(x, q)$ in the zero-order electronic wave functions $\varphi_e^{\circ}(x, q)$, with the $\chi_{en}^{\circ}(q)$ filling the role of q dependent expansion coefficients. In the more simple harmonic approximation, the electronic wave functions $\varphi_e^{\circ}(x, q^{\circ})$ are independent of q and the function $\chi_{en}^{\circ}(q)$ will be seen to be identical with the nuclear wave functions that describe the position and movement of the nuclei in the average field of the electrons. However, in general, this identity is not valid and no such simple interpretation can be given to the $\chi_{en}^{\circ}(q)$.

By applying the variational procedure to the most general zero-order molecular wave function (equation VII-3), we may arrive at the equations which determine the $\chi_{en}^{\circ}(q)$. At that point, we will be able to see what assumptions must be made to make valid the adiabatic and the harmonic approximations.

Before we proceed, however, we make one simplification in the zero-order molecular wave functions given by equation (VII-3). We assume that the coefficients $\chi_{en}^{\circ}(q)$ are so chosen that they form an orthonormal

set, i.e. :

$$(VII-5) \quad \int \chi_{en}^{\circ*}(q) \chi_{en'}^{\circ}(q) dq = \delta_{nn'}$$

This is standard procedure and insures that any particular zero-order molecular wave function will contain only one member of the set $\chi_{en}^{\circ}(q)$, $\chi_{en'}^{\circ}(q)$, $\chi_{en''}^{\circ}(q)$, We thus may drop the summation over n in equation (VII-3). Therefore we have:

$$(VII-6) \quad \psi_a^{\circ}(x, q) = \sum_e \phi_e^{\circ}(x, q) \chi_{en}^{\circ}(q)$$

Here we have, of course, assumed only one normal mode q . For other than diatomics, there are more than one normal mode and one must sum (VII-6) over all q_i normal modes. However, this adds little to the derivation and the increased complexity of the mathematics make it an undesirable complication. We shall hereafter use equation (VII-6) as our defining equation for the most general zero-order molecular wave function.

The $\psi_a^{\circ}(x, q)$ are solutions of the wave equation

$$(VII-7) \quad \mathcal{H}^{\circ}(x, q) \psi_a^{\circ}(x, q) = E_a^{\circ} \psi_a^{\circ}(x, q)$$

where E_a° is the energy of the state $\psi_a^{\circ}(x, q)$. $\mathcal{H}^{\circ}(x, q)$ is the zero-order molecular Hamiltonian and is given by:

$$(VII-8) \quad \mathcal{H}^{\circ}(x, q) = \mathcal{H}_E^{\circ}(x, q) + \mathcal{H}_N^{\circ}(q)$$

$$\mathcal{H}_E^{\circ}(x, q) = T_E(x) + V_E(x) + V_{EN}(x, q)$$

where

$$\mathcal{H}_N^{\circ}(q) = T_N(q) + V_N(q)$$

here $T_E(x)$ - electronic kinetic energy operator
 $V_E(x)$ - electronic potential energy operator
 $T_N(q)$ - nuclear kinetic energy operator
 $V_N(q)$ - nuclear potential energy operator
 $V_{EN}(x, q)$ - electron-nuclear potential energy operator

By the variational principle, the choice of $\chi_{en}^{\circ}(q)$ is determined by the condition that for small variations in this function, the resulting change in the expression

$$\iint \psi_a^{\circ*}(x, q) \mathcal{H}^{\circ}(x, q) \psi_a^{\circ}(x, q) dx dq$$

must be E_a° times the change in the integral

$$\iint \psi_a^{\circ*}(x, q) \psi_a^{\circ}(x, q) dx dq$$

In symbols we have:

$$\begin{aligned} \delta \iint \psi_a^{\circ*}(x, q) \mathcal{H}^{\circ}(x, q) \psi_a^{\circ}(x, q) dx dq \\ = E_a^{\circ} \delta \iint \psi_a^{\circ*}(x, q) \psi_a^{\circ}(x, q) dx dq \end{aligned}$$

Substituting in equations (VII-6) and (VII-8) and taking the variation of $\chi_e^{\circ*}(q)$ we have (suppressing the arguments x and q in the wave functions)

$$\begin{aligned} (VII-9) \quad \iint \sum_e \varphi_e^{\circ*} \delta \chi_{en}^{\circ*} [\mathcal{H}_E^{\circ}(x, q) + \mathcal{H}_N^{\circ}(q)] \sum_{e'} \varphi_{e'}^{\circ} \chi_{en'}^{\circ} dx dq \\ = E^{\circ} \iint \sum_{e, e'} \varphi_e^{\circ*} \delta \chi_{en}^{\circ*} \varphi_{e'}^{\circ} \chi_{en'}^{\circ} dx dq \end{aligned}$$

We now rewrite $\mathcal{H}_E^\circ(x, q) + \mathcal{H}_N^\circ(q)$ in a more useful form:

$$\mathcal{H}_E^\circ(x, q) + \mathcal{H}_N^\circ(q) = H^\circ(x, q) + T_N(q)$$

where

$$\begin{aligned} (VII-10) \quad H^\circ(x, q) &= T_E(x) + V_E(x) + V_{EN}(x, q) + V_N(q) \\ &= T_E(x) + V(x, q) \end{aligned}$$

now $T_N(q) = \frac{1}{2M} P_N^2(q)$ where $P_N(q)$ is the nuclear momentum operator $P_N(q) = i\hbar \partial/\partial q$. Thus we have:

$$\begin{aligned} (VII-11) \quad \mathcal{H}_E^\circ(x, q) + \mathcal{H}_N^\circ(q) &= H^\circ(x, q) + T_N(q) \\ &= H^\circ(x, q) + \frac{1}{2M} P_N^2(q) \\ &= H^\circ(x, q) - \frac{\hbar^2}{2M} \frac{\partial^2}{\partial q^2} \end{aligned}$$

Substituting equation (VII-11) into (VII-9), we have:

$$\begin{aligned} (VII-12) \quad \sum_{e, e'} \iint \delta \chi_{en}^{\circ*} \varphi_e^{\circ*} \left[H^\circ(x, q) + \frac{1}{2M} P_N^2(q) \right] \varphi_{e'}^\circ \chi_{e'n'}^\circ dx dq \\ = E^\circ \sum_{e, e'} \iint \delta \chi_{en}^{\circ*} \varphi_e^{\circ*} \varphi_{e'}^\circ \chi_{e'n'}^\circ dx dq \end{aligned}$$

We may simplify this equation. First note that the operator $H^\circ(x, q)$, as it does not contain $P_N(q)$ commutes with $\chi_{e'n'}^\circ(q)$ in the sense that

$$(VII-13) \quad H^\circ(x, q) \{ \varphi_{e'}^\circ \chi_{e'n'}^\circ \} = \{ H^\circ(x, q) \varphi_{e'}^\circ \} \chi_{e'n'}^\circ$$

Second $P_N(q)$ affects both $\varphi_{e'}^\circ$ and $\chi_{e'n'}^\circ$, so that

$$(VII-14) \quad P_N^2(q) \{ \phi_e^\circ \chi_{e'n'}^\circ \} = (P_N^2(q) \phi_e^\circ) \chi_{e'n'}^\circ + 2 (P_N(q) \phi_e^\circ) (P_N(q) \chi_{e'n'}^\circ) + \phi_e^\circ (P_N^2(q) \chi_{e'n'}^\circ)$$

Third, we choose the $\phi_e^\circ(x, q)$ so that they are eigenfunctions of $H^\circ(x, q)$. Thus:

$$(VII-15) \quad H^\circ(x, q) \phi_e^\circ(x, q) = W_e(q) \phi_e^\circ(x, q)$$

Here the eigenvalue $W_e(q)$ is what the total energy would be if the nuclei, placed in the configuration q , merely provided an electrostatic field for the electrons (and repelled one another) but did not themselves move. Thus $W_e(q)$ is the adiabatic energy in that it is the total energy in a system with stationary nuclei, and it is in the same sense that the $\phi_e^\circ(x, q)$ are termed the adiabatic electronic wave functions. Thus referring back to equation (VII-2) we see that the adiabatic approximation sets the zero-order molecular wave function equal to the product of an adiabatic electronic wave function and the, to be determined, function of q , $\chi_{en}^\circ(q)$. Also we see that the expansion equation (VII-6) represents a situation where the adiabatic approximation has broken down and no one adiabatic electronic wave function can represent the total molecular wave function, thus necessitating a linear combination of two or more of the adiabatic wave functions.

Using equations (VII-13), (VII-14), (VII-15) in equation (VII-12), we have:

$$(VII-16) \quad \sum_e \int \delta \chi_{en}^* \sum_{e'} \left\{ \left[\int \phi_e^{\circ*} W_{e'}(q) \phi_{e'}^\circ dx \right] \chi_{e'n'}^\circ + \left[\int \phi_e^{\circ*} T_N(q) \phi_{e'}^\circ dx \right] \chi_{e'n'}^\circ + \frac{1}{M} \left[\int \phi_e^{\circ*} P_N(q) \phi_{e'}^\circ dx \right] P_N(q) \chi_{e'n'}^\circ + \left[\int \phi_e^{\circ*} \phi_{e'}^\circ dx \right] T_N(q) \chi_{e'n'}^\circ \right\} dq = E^\circ \sum_e \int \delta \chi_{en}^* \sum_{e'} \left\{ \left[\int \phi_e^{\circ*} \phi_{e'}^\circ dx \right] \chi_{e'n'}^\circ \right\} dq$$

now from equation (VII-4) $\int \varphi_e^{\circ*} \varphi_{e'}^{\circ} dx = \delta_{ee'}$. Also since $W_e(q)$ is independent of x .

$$(VII-17) \quad \int \varphi_e^{\circ*} W_{e'}(q) \varphi_{e'}^{\circ} dx = W_{e'}(q) \int \varphi_e^{\circ*} \varphi_{e'}^{\circ} dx = W_{e'}(q)$$

Using equations (VII-4) and (VII-17) in (VII-16), we find:

$$\begin{aligned} \sum_e \int \delta \chi_{en}^{\circ*} \left\{ W_e(q) \chi_{en}^{\circ} + T_N(q) \chi_{en}^{\circ} + \sum_{e'} \langle \varphi_e^{\circ} | T_N(q) | \varphi_{e'}^{\circ} \rangle \chi_{e'n}^{\circ} \right. \\ \left. + \sum_{e'} \frac{1}{M} \langle \varphi_e^{\circ} | P_N(q) | \varphi_{e'}^{\circ} \rangle P_N(q) \chi_{e'n}^{\circ} \right\} dq = \sum_e \int \delta \chi_{en}^{\circ*} E^{\circ} \chi_{en}^{\circ} dq \end{aligned}$$

where $\langle \varphi_e^{\circ} | T_N(q) | \varphi_{e'}^{\circ} \rangle$ is Dirac's Bra-Ket notation for the integral $\int \varphi_e^{\circ*} T_N(q) \varphi_{e'}^{\circ} dx$. Equating the coefficients of $\delta \chi_{en}^{\circ*}$ on both sides, we have:

$$\begin{aligned} \left[W_e(q) + T_N(q) + \langle \varphi_e^{\circ} | T_N(q) | \varphi_e^{\circ} \rangle + \frac{1}{M} \langle \varphi_e^{\circ} | P_N(q) | \varphi_e^{\circ} \rangle P_N(q) \right] \chi_{en}^{\circ} \\ + \sum_{e' \neq e} \left[\langle \varphi_e^{\circ} | T_N(q) | \varphi_{e'}^{\circ} \rangle + \frac{1}{M} \langle \varphi_e^{\circ} | P_N(q) | \varphi_{e'}^{\circ} \rangle P_N(q) \right] \chi_{e'n}^{\circ} = E^{\circ} \chi_{en}^{\circ} \end{aligned}$$

noting that we may choose the $\varphi_e^{\circ}(x, q)$ real, we have:

$$\langle \varphi_e^{\circ} | P_N(q) | \varphi_e^{\circ} \rangle = 0$$

Thus we have:

$$\begin{aligned}
 \text{(VII-18)} \quad & \left[W_e(q) + T_N(q) + \langle \varphi_e^0 | T_N(q) | \varphi_e^0 \rangle - E^0 \right] \chi_{en}^0 \\
 & + \sum_{e' \neq e} \left[\langle \varphi_e^0 | T_N(q) | \varphi_{e'}^0 \rangle + \frac{1}{M} \langle \varphi_e^0 | P_N(q) | \varphi_{e'}^0 \rangle P_N(q) \right] \chi_{e'n}^0 = 0
 \end{aligned}$$

The coefficients $\chi_{en}^0(q)$ are determined from this series of coupled equations (there is one equation for each value of the quantum number e , i.e. for each electronic state).

It is readily seen that if the coupling coefficients are zero, equation (VII-18) reduces to the eigen-equation

$$\left[W_e(q) + T_N(q) + \langle \varphi_e^0 | T_N(q) | \varphi_e^0 \rangle \right] \chi_{en}^0 = E^0 \chi_{en}^0$$

With this condition satisfied, it is seen that

$$\text{(VII-2)} \quad \psi_a^0(x, q) = \varphi_e^0(x, q) \chi_{en}^0(q)$$

is an eigenfunction of the Hamiltonian $\mathcal{H}^0(x, q)$ with eigenvalue E^0 . This will be the adiabatic approximation only if the function $\varphi_e^0(x, q)$ is the adiabatic electronic wave function. This will be the case only if the correction term $\langle \varphi_e^0 | T_N(q) | \varphi_e^0 \rangle$ is negligible. If not, this means that the expectation value of the kinetic energy in the electronic state $\varphi_e^0(x, q)$ is non-zero. This of course means that $\varphi_e^0(x, q)$ cannot be an adiabatic state as, by definition, an adiabatic electronic state is one in which the nuclei are assumed stationary, and therefore, the nuclear kinetic energy $T_N(q)$ to be negligible. Thus under the adiabatic approximation, the zero-order molecular wave function is given by equation (VII-2), where the electronic wave functions satisfy equation (VII-15).

$$(VII-15) \quad H^0(x, q) \varphi_e^0(x, q) = W_e(q) \varphi_e^0(x, q)$$

and the coefficients $\chi_{en}(q)$ satisfy the equation

$$(VII-19) \quad [T_N(q) + W_e(q)] \chi_{en}^0(q) = E^0 \chi_{en}^0(q)$$

Before we discuss the simplest of the Born-Oppenheimer approximations, the harmonic approximation, it is worth while to discuss under what conditions the adiabatic approximation will break down. There are two possible sources of breakdown; first a non-zero correction term, and second non-zero coupling coefficients. The existence of the former occurs when nuclear frequencies are comparable to electronic frequencies. Thus, comparatively close-lying electronic states may result in break down of the adiabatic approximation. The existence of non-zero coupling coefficients also results in the adiabatic breakdown. To understand the underlying reason one must reexpress these terms. Referring to equation (VII-18), we see there are two coupling terms, namely

$$\langle \varphi_e^0 | T_N(q) | \varphi_{e'}^0 \rangle = -\frac{\hbar^2}{2M} \langle \varphi_e^0 | \partial^2 / \partial q^2 | \varphi_{e'}^0 \rangle$$

$$\langle \varphi_e^0 | P_N(q) | \varphi_{e'}^0 \rangle = i\hbar \langle \varphi_e^0 | \partial / \partial q | \varphi_{e'}^0 \rangle$$

The first can be expressed in terms of the second via the expression

$$(VII-20) \quad \begin{aligned} \langle \varphi_e^0 | \partial^2 / \partial q^2 | \varphi_{e'}^0 \rangle &= \sum_{e''} \langle \varphi_e^0 | \partial / \partial q | \varphi_{e''}^0 \rangle \langle \varphi_{e''}^0 | \partial / \partial q | \varphi_{e'}^0 \rangle \\ &\quad + \frac{\partial}{\partial q} \langle \varphi_e^0 | \partial / \partial q | \varphi_{e'}^0 \rangle \end{aligned}$$

Using equations (VII-10) and (VII-15), we have:

$$[T_E(x) + V(x, q)] \varphi_e^o(x, q) = W_e(q) \varphi_e^o(x, q)$$

Taking the derivative of both sides with respect to q , multiplying by $\varphi_{e'}^o(x, q)$ and integrating over all electron space, we obtain:

$$(VII-21) \quad \langle \varphi_e^o | \partial / \partial q | \varphi_{e'}^o \rangle = \frac{\langle \varphi_e^o | \frac{\partial V(x, q)}{\partial q} | \varphi_{e'}^o \rangle}{W_{e'}(q) - W_e(q)}$$

substituting into equation (VII-20)

$$(VII-22) \quad \langle \varphi_e^o | \partial^2 / \partial q^2 | \varphi_{e'}^o \rangle = \sum_{e''} \frac{\langle \varphi_e^o | \frac{\partial V(x, q)}{\partial q} | \varphi_{e''}^o \rangle \langle \varphi_{e''}^o | \frac{\partial V(x, q)}{\partial q} | \varphi_{e'}^o \rangle}{(W_{e''}(q) - W_e(q))(W_{e'}(q) - W_{e''}(q))} + \frac{\partial}{\partial q} \frac{\langle \varphi_e^o | \frac{\partial V(x, q)}{\partial q} | \varphi_{e'}^o \rangle}{W_{e'}(q) - W_e(q)}$$

The matrix elements given by equations (VII-21) and (VII-22) and therefore the coupling terms are negligible only under the condition where the energy difference between the vibronic states is large relative to the nuclear matrix elements connecting these states. These conditions along with those for the correction term show that breakdown of the adiabatic approximation occurs for degenerate or near-degenerate vibronic states. Three cases where this occurs are: for a degenerate electronic state (the Jahn-Teller effect and exciton coupling), for a nearly degenerate electronic state (the pseudo Jahn-Teller effect), and for the case of widely separated electronic states giving rise to vibrationally-induced transitions (the Hertzberg-Teller effect).

Finally we consider the harmonic approximation. The condition that must be fulfilled for the harmonic approximation to hold is that there be no electron-nuclear coupling, i.e. there be no part of $V(x, q)$ that is

not separable as $V(x) + V(q)$. If there is no such non-separable potential, both the coupling and correction terms are identically zero, and the Hamiltonian $\mathcal{H}^0(x, q)$ is separable and admits of a separable solution for the molecular wave function. In general, the electronic Hamiltonian, although independent of q in this approximation, is assumed dependent on the equilibrium nuclear position q^0 . Thus we have, modifying equation (VII-8)

$$(VII-23) \quad \mathcal{H}^0(x, q) = \mathcal{H}_E^0(x, q^0) + \mathcal{H}_N^0(q)$$

and using equation (VII-1)

$$(VII-1) \quad \psi_a^0(x, q) = \phi_e^0(x, q^0) \chi_{en}^0(q)$$

Substituting equations (VII-23) and (VII-1) into (VII-7)

$$(VII-24) \quad [\mathcal{H}_E^0(x, q^0) + \mathcal{H}_N^0(q)] \phi_e^0(x, q^0) \chi_{en}^0(q) = E_a^0 \phi_e^0(x, q^0) \chi_{en}^0(q)$$

Analogous to equations (VII-10) and (VII-11), we can rewrite

$$(VII-25) \quad \mathcal{H}_E^0(x, q) + \mathcal{H}_N^0(q) = H^0(x, q^0) + V_N(q) + T_N(q)$$

$$\text{where } H^0(x, q^0) = T_E(x) + V_E(x) + V_{EN}(x, q^0)$$

and we choose $\phi_e^0(x, q^0)$ to be the solution of

$$(VII-26) \quad H^0(x, q^0) \phi_e^0(x, q^0) = W_e^0 \phi_e^0(x, q^0)$$

Substituting equations (VII-25) into (VII-24), using equation (VII-26), we have:

$$[W_e^\circ + V_N(q) + T_N(q)] \phi_e^\circ(x, q^\circ) \chi_{en}^\circ(q) = E_a^\circ \phi_e^\circ(x, q^\circ) \chi_{en}^\circ(q)$$

Multiplying by $\phi_e^{\circ*}(x, q^\circ)$ and integrating over all electronic space, we have:

$$[W_e^\circ + V_N(q) + T_N(q)] \chi_{en}^\circ(q) = E_a^\circ \chi_{en}^\circ(q)$$

or

$$[T_N(q) + V_N(q)] \chi_{en}^\circ(q) = (E_a^\circ - W_e^\circ) \chi_{en}^\circ(q)$$

Here the $\chi_{en}^\circ(q)$ are, for $V_N(q)$ a quadratic function of q , the solutions for a harmonic oscillator. Hence we have the name, harmonic approximation. The $\chi_{en}^\circ(q)$ are seen to be, as predicted earlier, the solutions for the statics and dynamics of the nuclei in the average field of the electrons.

Appendix VIII

Specification of Hamiltonian for General Chemical Systems

A general chemical system can be thought of as a concentration of solute (guest) molecules present in a solvent (host). The system can be in a gaseous, a liquid, or a solid state. A system is completely described, in the quantum mechanical sense, by specifying the total wave functions Ψ_T . These wave functions are determined by the wave equation:

$$(VIII-1) \quad \mathcal{H}_T \Psi_T = E_T \Psi_T$$

where the total system Hamiltonian is given by:

$$(VIII-2) \quad \mathcal{H}_T = \mathcal{H}_G + \mathcal{H}_H + \mathcal{H}_{GH}^s + \mathcal{H}_{GH}^d$$

where

$\mathcal{H}_G$ - Hamiltonian of guest molecules.

$\mathcal{H}_H$ - Hamiltonian of host molecules

$\mathcal{H}_{GH}^s$ - static interaction Hamiltonian between guest and host molecules

$\mathcal{H}_{GH}^d$ - dynamic interaction Hamiltonian between guest and host molecules

We consider that adjacent guest-guest, host-host, and guest-host interactions are mediated through free space, while non-adjacent interactions are mediated through a medium whose dielectric constant is determined by the intervening guest and host molecules. Here it is understood that the interactions are only in pairs, that is we only

treat two-body problems and ignore three-body and higher.

Only if the terms $\mathcal{H}_{GH}^s$ and $\mathcal{H}_{GH}^d$ are negligible, is the wave function Ψ_T separable into guest and host wave functions. Thus we can then write:

$$(VIII-3) \quad \Psi_T = \Psi_G \Psi_H$$

and the Hamiltonian is:

$$(VIII-4) \quad \mathcal{H}_T = \mathcal{H}_G + \mathcal{H}_H$$

Substituting equations (VIII-4) and (VIII-3) into (VIII-1), we have:

$$(VIII-5) \quad \mathcal{H}_T \Psi_T = (\mathcal{H}_G + \mathcal{H}_H) \Psi_G \Psi_H = E_T \Psi_G \Psi_H$$

Now $\mathcal{H}_G$ does not operate on the coordinates of Ψ_H , $\mathcal{H}_H$ does not operate on the coordinates of Ψ_G . Thus equation (VIII-5) becomes:

$$(VIII-6) \quad (\mathcal{H}_G \Psi_G) \Psi_H + \Psi_G (\mathcal{H}_H \Psi_H) = E_T \Psi_G \Psi_H$$

As Ψ_G and Ψ_H are eigenfunctions of $\mathcal{H}_G$ and $\mathcal{H}_H$ respectively, we have:

$$(VIII-7) \quad \mathcal{H}_G \Psi_G = E_G \Psi_G$$

$$(VIII-8) \quad \mathcal{H}_H \Psi_H = E_H \Psi_H$$

Substituting into equation (VIII-6), we have:

$$(VIII-9) \quad E_T = E_G + E_H$$

Thus under the conditions of separability, we can deal with the guest and host molecules separately. As we are, in general, only interested in the chemistry of the solute (guest), this is a desirable situation. We therefore, look for a method whereby the terms $\mathcal{H}_{GH}^s$ and $\mathcal{H}_{GH}^d$ can be ignored or accounted for in such a way that separability is maintained.

We first of all make the assumption that the concentration of guest molecules is small compared to the surrounding host. If this is the case, the terms $\mathcal{H}_{GH}^s$ and $\mathcal{H}_{GH}^d$ are negligible corrections to the Hamiltonian $\mathcal{H}_H$. However, they are important compared to $\mathcal{H}_G$. If we define a new guest-modified-by-host Hamiltonian and wave functions, we have:

$$(VIII-10) \quad \mathcal{H}_{GH} = \mathcal{H}_G + \mathcal{H}_{GH}^s + \mathcal{H}_{GH}^d$$

and

$$(VIII-11) \quad \Psi_T = \Psi_{GH} \Psi_H, \quad E_T = E_{GH} + E_H$$

where

$$(VIII-12) \quad \mathcal{H}_{GH} \Psi_{GH} = E_{GH} \Psi_{GH}$$

This approximation has similarities to the more familiar Born-Oppenheimer approximations for separation of electronic and nuclear motion.

If we can now account for $\mathcal{H}_{GH}^s$ and $\mathcal{H}_{GH}^d$ in such a way that the Hamiltonian $\mathcal{H}_{GH}$ is independent of the host coordinates, then we can replace equation (VIII-12) with equation (VIII-7), where now $\mathcal{H}_G$ is a modified Hamiltonian. First consider $\mathcal{H}_{GH}^s$. This is a static potential energy term and can be lumped in with the potential energy portion of

$\mathcal{H}_G$. The wave functions one determines will thus be the wavefunctions in the static field of the host molecules. As for the dynamic guest-host interaction $\mathcal{H}_{GH}^d$, we can show this to be negligible under two normally valid conditions: first, that the atoms of the host molecules are removed from those of the guest molecules by distances several times greater than Van der Waal's distances; and second, that the electronic absorption bands of the host molecules occur in different spectral regions than those of the guest molecules. Thus if we include $\mathcal{H}_{GH}^s$ in $\mathcal{H}_G$ and ignore $\mathcal{H}_{GH}^d$, we may consider equation (VIII-7) as valid.

$$(VIII-7) \quad \mathcal{H}_G \Psi_G = E_G \Psi_G$$

or dropping the G subscript, as it will be understood that we are discussing only the guest molecules.

$$(VIII-13) \quad \mathcal{H} \Psi = E \Psi$$

We may now break down $\mathcal{H}$, basing the breakdown on the assumption that the particles (electrons and nuclei) in a molecule or set of molecules can be assigned to particular groups. Each particle belongs only to one group, and no transitions (electronic transitions or chemical reactions) remove it from this group. In quantum mechanical language, the group particle wave functions do not overlap each other, there is no particle exchange between groups, and there are no charge transfer transitions. Therefore, we have:

$$(VIII-14) \quad \mathcal{H} = \sum_i \mathcal{H}_i + \sum_i \sum_{j \neq i} V_{ij}, \quad \text{the sums over all groups.}$$

where

$$(VIII-15) \quad \mathcal{H}_i = T_i + V_i = T_{Ei} + T_{Ni} + V_{Ei} + V_{Ni} + V_{EiNi}$$

$$(VIII-16) \quad V_{ij} = V_{EiEj} + V_{EiNj} + V_{EjNi} + V_{NiNj}$$

here

$$T_{Ei} = T_{Ei}(x_i) \quad - \quad \text{electronic kinetic energy of group } i$$

$$T_{Ni} = T_{Ni}(q_i) \quad - \quad \text{nuclear kinetic energy of group } i$$

$$V_{Ei} = V_{Ei}(x_i) \quad - \quad \text{electron-electron potential of group } i$$

$$V_{Ni} = V_{Ni}(q_i) \quad - \quad \text{nuclear-nuclear potential of group } i$$

$$V_{EiNi} = V_{EiNi}(x_i, q_i) \quad - \quad \text{interaction between electrons and nuclei of group } i$$

$$V_{EiEj} = V_{EiEj}(x_i, x_j) \quad - \quad \text{interaction between the electrons in group } i \text{ and those in group } j$$

$$V_{NiNj} = V_{NiNj}(q_i, q_j) \quad - \quad \text{interaction between the nuclei in group } i \text{ and those in group } j$$

$$V_{EiNj} = V_{EiNj}(x_i, q_j) \quad - \quad \text{interaction between the electrons in group } i \text{ and the nuclei in group } j$$

$$V_{EjNi} = V_{EjNi}(x_j, q_i) \quad - \quad \text{interaction between the electrons in group } j \text{ and the nuclei in group } i$$

Here x_i and q_i are the sets of electronic and nuclear coordinates for the group i . As i and j are just dummy variables, we note:

$$\sum_i \sum_{j>i} V_{EiNj} + \sum_i \sum_{j>i} V_{EjNi} = \sum_i \sum_{j \neq i} V_{EiNj}$$

thus

$$(VIII-17) \quad \sum_i \sum_{j>i} V_{EiNj} + \sum_i \sum_{j>i} V_{EjNi} = \sum_i \sum_{j \neq i} V_{EiNj}$$

Substituting (VIII-15), (VIII-16), (VIII-17) into (VIII-14),

we have:

$$\begin{aligned}
 \text{(VIII-18)} \quad \mathcal{H} = & \sum_i \left[T_{Ei} + V_{Ei} + V_{EiN_i} + T_{Ni} + V_{Ni} \right] \\
 & + \sum_i \sum_{j>i} \left[V_{EiE_j} + V_{NiN_j} \right] \\
 & + \sum_i \sum_{j \neq i} V_{EiN_j}
 \end{aligned}$$

We have thus derived the Hamiltonian for the solute molecules of a general physical chemical system. As the eigenfunctions of this Hamiltonian will be the wave functions describing the solute molecules in the static field of the surrounding solvent, it is well to discuss the practicality of using such wave functions before we terminate the appendix. The strongest argument for using such wave functions is an experimental one, i.e. that the qualities of the solute that we measure are usually qualities of the solute in some solvent. Thus wave functions of the above type are usually more apropos than free molecule wave functions. The argument against these more complex wave functions is the greater difficulty of calculation; i.e. it is difficult to determine the exact effect of the static field of the solvent. However, as one must eventually take the solvent effects into account when comparing with experimental measurements, the choice becomes one of when to consider the influence of the solvent. Thus practicality is not sacrificed and the Hamiltonian defined by (VIII-18) has a simpler interpretation.

Appendix IX

Determination of Matrix Elements for Various Hamiltonian Representations

In this appendix, we determine the matrix elements of the representations of the first-order Hamiltonians in the zero-order basis functions for several of the cases listed in Table VI of Chapter 3. We include the harmonic and adiabatic subtypes of the electronic, excitonic, product vibronic, and sum of product vibronic representations. The representations for weak coupling, strong coupling, and the second quantization are not calculated for several reasons. First of all, calculation of these matrix elements is long and complicated. Secondly, diagonalization of the matrix representation of the Hamiltonian in these three cases present such great difficulties that only under the condition that perturbation theory is applicable is the problem tractable. Finally, calculation of these three cases is of no interest to us in our present investigations.

The format of each representation calculation is as follows: First, the zero-order basis functions and the first-order Hamiltonians are listed. Then the pertinent Schroedinger equations are set down. Finally, using the basis functions, Hamiltonian, and Schroedinger equations, the matrix elements of the Hamiltonian representation are evaluated.

A. Electronic - Harmonic

Zero-order basis functions

$$\varphi_e^0(x, q^0)$$

First-order Hamiltonian

$$\mathcal{H}' = T_E(x) + V_E(x) + V_{EN}(x, q)$$

We approximate $V_{EN}(x, q)$ by the first three terms of the expansion about the nuclear equilibrium position q^0 .

$$(IXA-1) \quad V_{EN}(x, q) \cong V_{EN}^0(x, q^0) + (q - q^0) V_{EN}'(x, q^0) + (q - q^0)^2 V_{EN}''(x, q^0)$$

where

$$V_{EN}^0(x, q^0) = V_{EN}(x, q) \big|_{q=q^0}$$

$$V_{EN}'(x, q^0) = \frac{\partial V_{EN}(x, q)}{\partial q} \bigg|_{q=q^0}$$

$$V_{EN}''(x, q^0) = \frac{1}{2} \frac{\partial^2 V_{EN}(x, q)}{\partial q^2} \bigg|_{q=q^0}$$

Thus the first-order Hamiltonian can be approximated by:

$$(IXA-2) \quad \mathcal{H}' \cong T_E(x) + V_E(x) + V_{EN}^0(x, q^0) + (q - q^0) V_{EN}'(x, q^0) + (q - q^0)^2 V_{EN}''(x, q^0)$$

(IXA-3)

Schroedinger Equation

$$[T_E(x) + V_E(x) + V_{EN}^0(x, q^0)] \psi_e^0(x, q^0) = E_e^0(q^0) (\psi_e^0(x, q^0))$$

We may now evaluate the matrix elements of the Hamiltonian representation. We suppress the arguments of wave functions and Hamiltonians in this and succeeding derivations where such suppression is not confusing.

$$(\psi_e^0 | \mathcal{H}' | \psi_e^0) = (\psi_e^0 | T_E + V_E + V_{EN}^0 + (q - q^0) V_{EN}' + (q - q^0)^2 V_{EN}'' | \psi_e^0)$$

Using equation (IXA-3) and the orthonormality of the ψ_e^0 , we have:

$$(IXA-4) \quad (\psi_e^0 | \mathcal{H}' | \psi_e^0) = E_e^0(q^0) \delta_{ee} + (q - q^0) (\psi_e^0 | V_{EN}' | \psi_e^0) + (q - q^0)^2 (\psi_e^0 | V_{EN}'' | \psi_e^0)$$

Equation (IXA-4) yields the following matrix elements.

Diagonal elements

$$(\varphi_e^0 | \mathcal{H}' | \varphi_e^0) = E_e^0(q^0) + (q - q^0)^2 (\varphi_e^0 | V_{EN}'' | \varphi_e^0)$$

Off-diagonal elements

$$(\varphi_e^0 | \mathcal{H}' | \varphi_e^i) = (q - q^0) (\varphi_e^0 | V_{EN}' | \varphi_e^i) + (q - q^0)^2 (\varphi_e^0 | V_{EN}'' | \varphi_e^i)$$

Where in calculating the diagonal elements, we have used the fact that $(\varphi_e^0 | V_{EN}'(x, q^0) | \varphi_e^0) = 0$. The following reasoning justifies this equality. For the above matrix element to be non-zero, $V_{EN}'(x, q^0)$ must be totally symmetric. As the total Hamiltonian must be totally symmetric, this means that if $V_{EN}'(x, q^0)$ is totally symmetric, then we are dealing with a symmetric nuclear coordinate q . However, it is a fact that a totally symmetric vibration will not cause instability, thus necessitating that $V_{EN}'(x, q^0)$ is zero for a totally symmetric coordinate. Thus, $(\varphi_e^0 | V_{EN}'(x, q^0) | \varphi_e^i) = 0$ for all cases. We shall use this result in the three following harmonic representations. It will be referenced there as the stability requirement.

B. Electronic - Adiabatic

(IXB-1) Zero-order basis functions $\varphi_e^0(x, q)$

First-order Hamiltonian $\mathcal{H}' = T_E(x) + V_E(x) + V_{EN}(x, q)$

(IX B-2)

Schroedinger Equation

$$[T_E(x) + V_E(x) + V_{EN}(x, q)] \varphi_e^o(x, q) = E_e^o(q) \varphi_e^o(x, q)$$

We may now evaluate the matrix elements of the Hamiltonian representation.

$$(IX B-3) \quad (\varphi_e^o | \mathcal{H}' | \varphi_e^o) = (\varphi_e^o | T_E + V_E + V_{EN} | \varphi_e^o) = E_e^o(q)$$

This yields the following matrix elements:

Diagonal elements

$$(\varphi_e^o | \mathcal{H}' | \varphi_e^o) = E_e^o(q)$$

Off-diagonal elements

$$(\varphi_e^o | \mathcal{H}' | \varphi_{e'}^o) = 0$$

C. Excitonic - Harmonic

(IX C-1)

Zero-order basis functions

$$\Phi(k, e') = \frac{1}{\sqrt{N}} \sum_i e^{-i\hat{k} \cdot \vec{r}_i} (\varphi_{e'}^{o(i)}(x_i, q_i^o)) \prod_{j \neq i} \varphi_e^{o(j)}(x_j, q_j)$$

First-order Hamiltonian

$$\mathcal{H}' = \sum_i [T_{E_i}(x_i) + V_{E_i}(x_i) + V_{E_i N_i}(x_i, q_i)] + \sum_i \sum_{j \neq i} V_{E_i E_j}(x_i, x_j)$$

Using an expansion of $V_{E_i N_i}(x_i, q_i)$ about q_i^o , as is done in

equation (IX A-1), we have:

$$\begin{aligned}
 \text{(IX C-2)} \quad \mathcal{H}' = & \sum_i^N \left[T_{E_i}(x_i) + V_{E_i}(x_i) + V_{E_i N_i}^0(x_i, q_i^0) \right] \\
 & + \sum_i^N \left[(q_i - q_i^0) V_{E_i N_i}'(x_i, q_i^0) + (q_i - q_i^0)^2 V_{E_i N_i}''(x_i, q_i^0) \right] \\
 & + \sum_i^N \sum_{j>i}^N V_{E_i E_j}(x_i, x_j)
 \end{aligned}$$

(IX C-3) Thus

$$\mathcal{H}' = \mathcal{H}'_1 + \mathcal{H}'_2 + \mathcal{H}'_3$$

where

$$\begin{aligned}
 \text{(IX C-4)} \quad \mathcal{H}'_1 = & \sum_i^N \left[T_{E_i}(x_i) + V_{E_i}(x_i) + V_{E_i N_i}^0(x_i, q_i^0) \right] \\
 \mathcal{H}'_2 = & \sum_i^N \left[(q_i - q_i^0) V_{E_i N_i}'(x_i, q_i^0) + (q_i - q_i^0)^2 V_{E_i N_i}''(x_i, q_i^0) \right] \\
 \mathcal{H}'_3 = & \sum_i^N \sum_{j>i}^N V_{E_i E_j}(x_i, x_j)
 \end{aligned}$$

Schroedinger Equation

$$\begin{aligned}
 \text{(IX C-5)} \quad & \left[T_{E_i}(x_i) + V_{E_i}(x_i) + V_{E_i N_i}^0(x_i, q_i^0) \right] \varphi_e^{o(i)}(x_i, q_i) \\
 & = E_e^{o(i)}(q_i^0) \varphi_e^{o(i)}(x_i, q_i^0)
 \end{aligned}$$

but as all monomers are identical, so are all q_i^0

Thus:

$$\text{(IX C-6)} \quad E_e^{o(i)}(q_i^0) = E_e^o(q^0) \quad \text{for all } i$$

$$\begin{aligned}
 \text{(IX C-7)} \quad & \left[T_{E_i}(x_i) + V_{E_i}(x_i) + V_{E_i N_i}^0(x_i, q_i^0) \right] \varphi_e^{o(i)}(x_i, q_i^0) \\
 & = E_e^o(q^0) \varphi_e^{o(i)}(x_i, q_i^0)
 \end{aligned}$$

We now evaluate the matrix elements, suppressing arguments of wave functions and Hamiltonians where such suppression is not confusing.

$$\begin{aligned}
 \text{(IX C-8)} \quad (\Phi(\hat{k}, e') / \mathcal{H}' / \Phi(\hat{k}', e'')) &= (\Phi(\hat{k}, e') / \mathcal{H}' / \Phi(\hat{k}', e'')) \\
 &+ (\Phi(\hat{k}, e') / \mathcal{H}'_2 / \Phi(\hat{k}', e'')) \\
 &+ (\Phi(\hat{k}, e') / \mathcal{H}'_3 / \Phi(\hat{k}', e''))
 \end{aligned}$$

We now proceed to evaluate the first term in equation (IX C-8). Using the expression for $\mathcal{H}'$ from equation (IX C-4) and equation (IX C-1) for the wave functions, we have:

$$\begin{aligned}
 \text{(IX C-9)} \quad (\Phi(\hat{k}, e') / \mathcal{H}' / \Phi(\hat{k}', e'')) \\
 = \frac{1}{N} \sum_i \sum_j e^{-i(\hat{k} \cdot \vec{r}_i - \hat{k}' \cdot \vec{r}_j)} (\varphi_{e'}^{o(i)} \prod_{m \neq i}^N \varphi_e^{o(m)} / \sum_p [T_{E_p} + V_{E_p} + V_{E_p N_p}^o] \varphi_{e''}^{o(j)} \prod_{n \neq j}^N \varphi_e^{o(n)})
 \end{aligned}$$

Using equation (IX C-7), we have:

$$\begin{aligned}
 \text{(IX C-10)} \quad \sum_p [T_{E_p} + V_{E_p} + V_{E_p N_p}^o] \varphi_{e''}^{o(j)} \prod_{n \neq j}^N \varphi_e^{o(n)} \\
 = [E_{e''}^o(q^o) + (N-1) E_e^o(q^o)] \varphi_{e''}^{o(j)} \prod_{n \neq j}^N \varphi_e^{o(n)}
 \end{aligned}$$

Substituting this into equation (IX C-9) yields:

$$\begin{aligned}
 (\Phi(\hat{k}, e') / \mathcal{H}' / \Phi(\hat{k}', e'')) \\
 = \frac{1}{N} \sum_i \sum_j e^{-i(\hat{k} \cdot \vec{r}_i - \hat{k}' \cdot \vec{r}_j)} [E_{e''}^o(q^o) + (N-1) E_e^o(q^o)] (\varphi_{e'}^{o(i)} \prod_{m \neq i}^N \varphi_e^{o(m)} / \varphi_{e''}^{o(j)} \prod_{n \neq j}^N \varphi_e^{o(n)}) \\
 + \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} [E_{e''}^o(q^o) + (N-1) E_e^o(q^o)] \delta_{e'e''} \\
 + \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i(\hat{k} \cdot \vec{r}_i - \hat{k}' \cdot \vec{r}_j)} [E_{e''}^o(q^o) + (N-1) E_e^o(q^o)] \delta_{e'e} \delta_{e''e}
 \end{aligned}$$

If we ignore terms in the Hamiltonian representation where either e' or e'' are the ground state e , then we can drop the third term. We also set:

$$(IX\ C-11) \quad \frac{1}{N} \sum_i e^{-i(\hat{k}-\hat{k}') \cdot \vec{r}_i} = \delta_{\hat{k}-\hat{k}', 2\pi\vec{b}}$$

where $\vec{b}$ is any sum of primitive translation vectors in the reciprocal lattice. Thus we have:

$$(IX\ C-12) \quad (\Phi(\hat{k}, e') | \mathcal{H}' | \Phi(\hat{k}', e'')) = [E_e^o(q^o) + (N-1) E_e^o(q^o)] \delta_{e'e''} \delta_{\hat{k}-\hat{k}', 2\pi\vec{b}}$$

We now turn to the second term in equation (IX C-8).

Rewriting the expression for $\mathcal{H}'_2$ from equation (IX C-4), we have:

$$(IX\ C-13) \quad \mathcal{H}'_2 = \sum_p^N \mathcal{H}'_{2p}$$

where

$$(IX\ C-14) \quad \mathcal{H}'_{2p} = (q_p - q_p^o) V'_{EpNp} + (q_p - q_p^o)^2 V''_{EpNp}$$

Substituting equation (IX C-13) and the expression for the wave functions, equation (IX C-1), into the second term in equation (IX C-8), we have:

$$\begin{aligned} & (\Phi(\hat{k}, e') | \mathcal{H}'_2 | \Phi(\hat{k}', e'')) \\ &= \frac{1}{N} \sum_i \sum_j^N e^{-i(\hat{k} \cdot \vec{r}_i - \hat{k}' \cdot \vec{r}_j)} (\varphi_{e'}^{o(i)} \prod_{m \neq i}^N \varphi_e^{o(m)} | \sum_p^N \mathcal{H}'_{2p} | \varphi_{e''}^{o(j)} \prod_{n \neq j}^N \varphi_e^{o(n)}) \\ (IX\ C-15) \quad & (\Phi(\hat{k}, e') | \mathcal{H}'_2 | \Phi(\hat{k}', e'')) \\ &= \frac{1}{N} \sum_i^N e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} (\varphi_{e'}^{o(i)} \prod_{m \neq i}^N \varphi_e^{o(m)} | \sum_p^N \mathcal{H}'_{2p} | \varphi_{e''}^{o(i)} \prod_{n \neq i}^N \varphi_e^{o(n)}) \\ &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i(\hat{k} \cdot \vec{r}_i - \hat{k}' \cdot \vec{r}_j)} (\varphi_{e'}^{o(i)} \prod_{m \neq i}^N \varphi_e^{o(m)} | \sum_p^N \mathcal{H}'_{2p} | \varphi_{e''}^{o(j)} \prod_{n \neq j}^N \varphi_e^{o(n)}) \end{aligned}$$

In the first term, we substitute

$$\sum_p \mathcal{A}'_{2p} = \mathcal{A}'_{2i} + \sum_{p \neq i} \mathcal{A}'_{2p}$$

while in the second term, we substitute

$$\sum_p \mathcal{A}'_{2p} = \mathcal{A}'_{2i} + \mathcal{A}'_{2j} + \sum_{\substack{p \neq i \\ p \neq j}} \mathcal{A}'_{2p}$$

Thus we have from equation (IX C-15):

$$\begin{aligned}
 \text{(IX C-16)} \quad & (\Phi(\hat{k}, e') / \mathcal{A}'_2 / \Phi(\hat{k}', e'')) \\
 &= \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} (\varphi_{e'}^{(i)} / \mathcal{A}'_{2i} / \varphi_{e''}^{(i)}) \\
 &+ \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} (\varphi_{e'}^{(i)} / \varphi_{e''}^{(i)}) \left(\prod_m \varphi_e^{(m)} / \sum_{p \neq i} \mathcal{A}'_{2p} / \prod_n \varphi_e^{(n)} \right) \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i(\hat{k} \cdot \vec{r}_i - \hat{k}' \cdot \vec{r}_j)} (\varphi_{e'}^{(i)} / \mathcal{A}'_{2i} / \varphi_e^{(i)}) \delta_{e'e} \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i(\hat{k} \cdot \vec{r}_i - \hat{k}' \cdot \vec{r}_j)} (\varphi_e^{(j)} / \mathcal{A}'_{2j} / \varphi_{e''}^{(j)}) \delta_{e'e} \\
 &+ \frac{1}{N} \sum_i \sum_{\substack{j \neq i \\ p \neq j}} e^{-i(\hat{k} \cdot \vec{r}_i - \hat{k}' \cdot \vec{r}_j)} \sum_{\substack{p \neq i \\ p \neq j}} (\varphi_e^{(p)} / \mathcal{A}'_{2p} / \varphi_e^{(p)}) \delta_{e'e} \delta_{e''e}
 \end{aligned}$$

Again we ignore terms when either e' or e'' must be the ground state e . Thus we drop the last three terms in (IX C-16). Now substituting:

$$\sum_{p \neq i} \mathcal{A}'_{2p} = \sum_p \mathcal{A}'_{2p} - \mathcal{A}'_{2i}$$

into the second term of equation (IX C-16), we have:

$$\begin{aligned}
 \text{(IX C-17)} \quad & (\Phi(\hat{k}, e') / \mathcal{A}'_2 / \Phi(\hat{k}', e'')) \\
 &= \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} [(\varphi_{e'}^{(i)} / \mathcal{A}'_{2i} / \varphi_{e''}^{(i)}) - (\varphi_e^{(i)} / \mathcal{A}'_{2i} / \varphi_e^{(i)})] \\
 &+ \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} \sum_p (\varphi_e^{(p)} / \mathcal{A}'_{2p} / \varphi_e^{(p)}) \delta_{e'e}
 \end{aligned}$$

Using equation (IX C-11), substituting in equation (IX C-14), and using the stability requirement discussed in part A of this appendix, we have:

$$\begin{aligned}
 & (\Phi(\hat{k}, e') | \mathcal{X}_2' | \Phi(\hat{k}', e'')) \\
 \text{(IX C-18)} \quad & = \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{\lambda}_i} (q_i - q_i^0) (\varphi_{e'}^{o(i)} | V_{E_i N_i}' | \varphi_{e''}^{o(i)}) \\
 & + \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{\lambda}_i} (q_i - q_i^0)^2 \left[(\varphi_{e'}^{o(i)} | V_{E_i N_i}'' | \varphi_{e''}^{o(i)}) \right. \\
 & \quad \left. - (\varphi_{e'}^{o(i)} | V_{E_i N_i}'' | \varphi_{e''}^{o(i)}) \delta_{e'e''} \right] \\
 & + \sum_i (q_i - q_i^0)^2 (\varphi_{e'}^{o(i)} | V_{E_i N_i}'' | \varphi_{e''}^{o(i)})
 \end{aligned}$$

We now turn to the third term in equation (IX C-8). Using the expression for $\mathcal{X}_3'$ from equation (IX C-4), we have:

$$\begin{aligned}
 & (\Phi(\hat{k}, e') | \mathcal{X}_3' | \Phi(\hat{k}', e'')) \\
 \text{(IX C-19)} \quad & = \frac{1}{N} \sum_i \sum_j e^{-i(\hat{k} \cdot \vec{\lambda}_i - \hat{k}' \cdot \vec{\lambda}_j)} (\varphi_{e'}^{o(i)} | \prod_{m \neq i} \varphi_{e''}^{o(m)} | \sum_{p \neq j} \sum_{l \neq p} V_{E_p E_l} | \varphi_{e''}^{o(j)} | \prod_{n \neq j} \varphi_{e''}^{o(n)}) \\
 & = \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{\lambda}_i} (\varphi_{e'}^{o(i)} | \prod_{m \neq i} \varphi_{e''}^{o(m)} | \sum_{p \neq i} \sum_{l \neq p} V_{E_p E_l} | \varphi_{e''}^{o(i)} | \prod_{n \neq i} \varphi_{e''}^{o(n)}) \\
 & + \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i(\hat{k} \cdot \vec{\lambda}_i - \hat{k}' \cdot \vec{\lambda}_j)} (\varphi_{e'}^{o(i)} | \prod_{m \neq i} \varphi_{e''}^{o(m)} | \sum_{p \neq j} \sum_{l \neq p} V_{E_p E_l} | \varphi_{e''}^{o(j)} | \prod_{n \neq j} \varphi_{e''}^{o(n)})
 \end{aligned}$$

In the first term of equation (IX C-19), we use the relation

$$\text{(IX C-20)} \quad \sum_{p \neq j} \sum_{l \neq p} V_{E_p E_l} = \sum_{j \neq i} V_{E_i E_j} + \sum_{p \neq i} \sum_{l \neq p, \neq i} V_{E_p E_l}$$

and in the second term of equation (IX C-19), we use

$$\text{(IX C-21)} \quad \sum_{p \neq j} \sum_{l \neq p} V_{E_p E_l} = V_{E_i E_j} + \sum_{\substack{p \neq i \\ \neq j}} V_{E_i E_p} + \sum_{\substack{p \neq i \\ \neq j}} V_{E_j E_p} + \sum_{\substack{p \neq i \\ \neq j}} \sum_{\substack{l \neq p \\ \neq j}} V_{E_p E_l}$$

Thus we have:

$$(IX\ C-22) \quad (\Phi(\hat{k}, e') / \partial \mathcal{L}_3' / \Phi(\hat{k}', e''))$$

$$\begin{aligned} &= \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{\lambda}_i} \sum_{j \neq i}^N (\varphi_{e'}^{o(i)} \varphi_e^{o(j)} / V_{E_i E_j} | \varphi_{e''}^{o(i)} \varphi_e^{o(j)}) \\ &+ \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{\lambda}_i} \left(\prod_m^N \varphi_e^{o(m)} / \sum_{p \neq i}^N \sum_{\substack{q \neq p \\ q \neq i}}^N V_{E_p E_q} | \prod_n^N \varphi_e^{o(n)} \right) \delta_{e' e''} \\ &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i(\hat{k} \cdot \vec{\lambda}_i - \hat{k}' \cdot \vec{\lambda}_j)} (\varphi_{e'}^{o(i)} \varphi_e^{o(j)} / V_{E_i E_j} | \varphi_{e''}^{o(i)} \varphi_e^{o(j)}) \\ &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i(\hat{k} \cdot \vec{\lambda}_i - \hat{k}' \cdot \vec{\lambda}_j)} \sum_{\substack{p \neq i \\ p \neq j}}^N (\varphi_{e'}^{o(i)} \varphi_e^{o(p)} / V_{E_i E_p} | \varphi_{e''}^{o(i)} \varphi_e^{o(p)}) \delta_{ee''} \\ &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i(\hat{k} \cdot \vec{\lambda}_i - \hat{k}' \cdot \vec{\lambda}_j)} \sum_{\substack{p \neq i \\ p \neq j}}^N (\varphi_{e'}^{o(j)} \varphi_e^{o(p)} / V_{E_j E_p} | \varphi_{e''}^{o(j)} \varphi_e^{o(p)}) \delta_{ee'} \\ &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i(\hat{k} \cdot \vec{\lambda}_i - \hat{k}' \cdot \vec{\lambda}_j)} \left(\prod_m^N \varphi_e^{o(m)} / \sum_{\substack{p \neq i \\ p \neq j}}^N \sum_{\substack{q \neq p \\ q \neq i \\ q \neq j}}^N V_{E_p E_q} | \prod_n^N \varphi_e^{o(n)} \right) \delta_{ee'} \delta_{ee''} \end{aligned}$$

Again dropping all terms for which $e = e'$ or $e = e''$ we have

(upon substituting equation (IX C-20) into the second term of equation (IX C-22)):

$$(IX\ C-23) \quad (\Phi(\hat{k}, e') / \partial \mathcal{L}_3' / \Phi(\hat{k}', e'')) = \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{\lambda}_i} \sum_{j \neq i}^N \left[(\varphi_{e'}^{o(i)} \varphi_e^{o(j)} / V_{E_i E_j} | \varphi_{e''}^{o(i)} \varphi_e^{o(j)}) \right. \\ \left. - (\varphi_{e'}^{o(i)} \varphi_e^{o(j)} / V_{E_i E_j} | \varphi_{e''}^{o(i)} \varphi_e^{o(j)}) \delta_{e' e''} \right]$$

$$\begin{aligned} &+ \sum_i \sum_{j > i}^N (\varphi_{e'}^{o(i)} \varphi_e^{o(j)} / V_{E_i E_j} | \varphi_{e''}^{o(i)} \varphi_e^{o(j)}) \delta_{e' e''} \delta_{\hat{k} - \hat{k}', 2\pi \vec{b}} \\ &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i(\hat{k} \cdot \vec{\lambda}_i - \hat{k}' \cdot \vec{\lambda}_j)} (\varphi_{e'}^{o(i)} \varphi_e^{o(j)} / V_{E_i E_j} | \varphi_{e''}^{o(j)} \varphi_e^{o(i)}) \end{aligned}$$

From equations (IX C-12), (IX C-18), and (IX C-25), we have the following matrix elements (using the stability requirement for diagonal elements).

Diagonal Elements

$$\begin{aligned}
 & (\Phi(\hat{k}, e') / \mathcal{H}' / \Phi(\hat{k}', e'')) \\
 &= [E_{e'}^0(q^0) + (N-1) E_e^0(q^0)] \\
 &+ \frac{1}{N} \sum_i (q_i - q_i^0)^2 [(\varphi_{e'}^{(i)} | V_{E_i N_i}'' | \varphi_{e'}^{(i)}) - (\varphi_e^{(i)} | V_{E_i N_i}'' | \varphi_e^{(i)})] \\
 &+ \sum_i (q_i - q_i^0)^2 (\varphi_e^{(i)} | V_{E_i N_i}'' | \varphi_e^{(i)}) \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N [(\varphi_{e'}^{(i)} \varphi_e^{(j)} | V_{E_i E_j} | \varphi_{e'}^{(i)} \varphi_e^{(j)}) - (\varphi_e^{(i)} \varphi_e^{(j)} | V_{E_i E_j} | \varphi_e^{(i)} \varphi_e^{(j)})] \\
 &+ \sum_i \sum_{j > i}^N (\varphi_e^{(i)} \varphi_e^{(j)} | V_{E_i E_j} | \varphi_e^{(i)} \varphi_e^{(j)}) \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i\hat{k}(\hat{x}_i - \hat{x}_j)} (\varphi_{e'}^{(i)} \varphi_e^{(j)} | V_{E_i E_j} | \varphi_e^{(i)} \varphi_e^{(j)})
 \end{aligned}$$

Off-diagonal elements $\hat{k} = \hat{k}', e' \neq e''$

$$\begin{aligned}
 & (\Phi(\hat{k}, e') / \mathcal{H}' / \Phi(\hat{k}', e'')) \\
 &= \frac{1}{N} \sum_i (q_i - q_i^0) (\varphi_{e'}^{(i)} | V_{E_i N_i}' | \varphi_{e''}^{(i)}) \\
 &+ \frac{1}{N} \sum_i (q_i - q_i^0)^2 (\varphi_{e'}^{(i)} | V_{E_i N_i}'' | \varphi_{e''}^{(i)}) \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N (\varphi_{e'}^{(i)} \varphi_e^{(j)} | V_{E_i E_j} | \varphi_{e''}^{(i)} \varphi_e^{(j)}) \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i\hat{k}(\hat{x}_i - \hat{x}_j)} (\varphi_{e'}^{(i)} \varphi_e^{(j)} | V_{E_i E_j} | \varphi_{e''}^{(i)} \varphi_e^{(j)})
 \end{aligned}$$

Off-diagonal Elements $\hat{k} \neq \hat{k}'$, $e' = e''$

$$\begin{aligned}
 & (\Phi(\hat{k}, e') | \mathcal{X}' | \Phi(\hat{k}', e')) \\
 &= \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} (q_i - q_i^0)^2 \left[(\varphi_{e'}^{(i)} | V_{E_i N_i} | \varphi_{e'}^{(i)}) - (\varphi_{e'}^{(i)} | V_{E_i N_i}'' | \varphi_{e'}^{(i)}) \right] \\
 &+ \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} \sum_{j \neq i} \left[(\varphi_{e'}^{(i)} \varphi_e^{(j)} | V_{E_i E_j} | \varphi_{e'}^{(i)} \varphi_e^{(j)}) - (\varphi_{e'}^{(i)} \varphi_e^{(j)} | V_{E_i E_j}'' | \varphi_{e'}^{(i)} \varphi_e^{(j)}) \right] \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i(\hat{k} \cdot \vec{r}_i - \hat{k}' \cdot \vec{r}_j)} (\varphi_{e'}^{(i)} \varphi_e^{(j)} | V_{E_i E_j} | \varphi_{e'}^{(j)} \varphi_e^{(i)})
 \end{aligned}$$

Off-diagonal Elements $\hat{k} \neq \hat{k}'$, $e' \neq e''$

$$\begin{aligned}
 & (\Phi(\hat{k}, e') | \mathcal{X}' | \Phi(\hat{k}', e'')) \\
 &= \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} (q_i - q_i^0) (\varphi_{e'}^{(i)} | V_{E_i N_i}' | \varphi_{e''}^{(i)}) \\
 &+ \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} (q_i - q_i^0) (\varphi_{e'}^{(i)} | V_{E_i N_i}'' | \varphi_{e''}^{(i)}) \\
 &+ \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} \sum_{j \neq i} (\varphi_{e'}^{(i)} \varphi_{e''}^{(j)} | V_{E_i E_j} | \varphi_{e''}^{(i)} \varphi_e^{(j)}) \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i} e^{-i(\hat{k} \cdot \vec{r}_i - \hat{k}' \cdot \vec{r}_j)} (\varphi_{e'}^{(i)} \varphi_{e''}^{(j)} | V_{E_i E_j} | \varphi_{e''}^{(j)} \varphi_e^{(i)})
 \end{aligned}$$

D. Excitonic - Adiabatic

Zero-order basis functions

(IX D-1)

$$\Phi(\hat{k}, e') = \frac{1}{\sqrt{N}} \sum_i e^{-i\hat{k} \cdot \vec{r}_i} \varphi_{e'}^{(i)}(x_i, q_i) \prod_{j \neq i} \varphi_e^{(j)}(x_j, q_j)$$

First-order Hamiltonian

$$(IX D-2) \quad \mathcal{H}' = \sum_i^N \left[T_{E_i}(x_i) + V_{E_i}(x_i) + V_{E_i N_i}(x_i, q_i) \right] \\ + \sum_i^N \sum_{j>i}^N V_{E_i E_j}(x_i, x_j)$$

$$(IX D-3) \quad \text{Let:} \\ \mathcal{H}' = \mathcal{H}'_1 + \mathcal{H}'_2$$

$$(IX D-4) \quad \text{where:} \\ \mathcal{H}'_1 = \sum_i^N \left[T_{E_i}(x_i) + V_{E_i}(x_i) + V_{E_i N_i}(x_i, q_i) \right] \\ \mathcal{H}'_2 = \sum_i^N \sum_{j>i}^N V_{E_i E_j}(x_i, x_j)$$

Schroedinger Equations

$$(IX D-5) \quad \left[T_{E_i}(x_i) + V_{E_i}(x_i) + V_{E_i N_i}(x_i, q_i) \right] \varphi_e^{o(i)}(x_i, q_i) = E_e^o(q_i) \varphi_e^{o(i)}(x_i, q_i)$$

whereas all monomers are identical

$$E_e^{o(i)}(q_i) = E_e^o(q_i) \quad \text{for all } i$$

We may now evaluate the matrix elements, suppressing arguments wherever we can, as before. Using equation (IX D-3) for $\mathcal{H}'$ we have:

$$(IX D-6) \quad (\Phi(\hat{k}, e') | \mathcal{H}' | \Phi(\hat{k}', e'')) = (\Phi(\hat{k}, e') | \mathcal{H}'_1 | \Phi(\hat{k}', e'')) \\ + (\Phi(\hat{k}, e') | \mathcal{H}'_2 | \Phi(\hat{k}', e''))$$

Evaluating the first term of equation (IX D-6), we get the parallel of equation (IX C-12).

$$(IX D-7) \quad (\Phi(\hat{k}, e') | \mathcal{H}'_1 | \Phi(\hat{k}', e'')) \\ = \frac{1}{N} \sum_i^N e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} \left[E_{e''}^o(q_i) + \sum_{j \neq i}^N E_e^o(q_j) \right] \delta_{ee''}$$

Evaluating the second term of equation (IX D-6), we obtain equation (IX C-23), only here the $\varphi_e^{o(i)}$ are $\varphi_e^{o(i)}(x_i, q_i)$. From

equation (IX D-7) and (IX C-23), we may write the matrix elements.

Diagonal elements

$$\begin{aligned}
 & (\Phi(\hat{k}, e') | \mathcal{H}' | \Phi(\hat{k}, e')) \\
 &= \frac{1}{N} \sum_i \left[E_e^o(q_i) + \sum_{j \neq i}^N E_e^o(q_j) \right] \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N \left[(\varphi_e^{o(i)} \varphi_e^{o(j)} | V_{E_i E_j} | \varphi_e^{o(i)} \varphi_e^{o(j)}) - (\varphi_e^{o(i)} \varphi_e^{o(j)} | V_{E_i E_j} | \varphi_e^{o(i)} \varphi_e^{o(j)}) \right] \\
 &+ \sum_i \sum_{j > i}^N (\varphi_e^{o(i)} \varphi_e^{o(j)} | V_{E_i E_j} | \varphi_e^{o(i)} \varphi_e^{o(j)}) \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i\hat{k}(\hat{r}_i - \hat{r}_j)} (\varphi_e^{o(i)} \varphi_e^{o(j)} | V_{E_i E_j} | \varphi_e^{o(j)} \varphi_e^{o(i)})
 \end{aligned}$$

Off-diagonal elements $\hat{k} = \hat{k}', e' \neq e''$

$$\begin{aligned}
 & (\Phi(\hat{k}, e') | \mathcal{H}' | \Phi(\hat{k}, e'')) \\
 &= \frac{1}{N} \sum_i \sum_{j \neq i}^N (\varphi_e^{o(i)} \varphi_e^{o(j)} | V_{E_i E_j} | \varphi_{e''}^{o(i)} \varphi_{e''}^{o(j)}) \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i\hat{k}(\hat{r}_i - \hat{r}_j)} (\varphi_e^{o(i)} \varphi_e^{o(j)} | V_{E_i E_j} | \varphi_{e''}^{o(j)} \varphi_{e''}^{o(i)})
 \end{aligned}$$

Off-diagonal elements $\hat{k} \neq \hat{k}', e' = e''$

$$\begin{aligned}
 & (\Phi(\hat{k}, e') | \mathcal{H}' | \Phi(\hat{k}', e')) \\
 &= \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \hat{r}_i} \sum_{j \neq i}^N \left[(\varphi_e^{o(i)} \varphi_e^{o(j)} | V_{E_i E_j} | \varphi_e^{o(i)} \varphi_e^{o(j)}) - (\varphi_e^{o(i)} \varphi_e^{o(j)} | V_{E_i E_j} | \varphi_e^{o(i)} \varphi_e^{o(j)}) \right] \\
 &+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i(\hat{k} \cdot \hat{r}_i - \hat{k}' \cdot \hat{r}_j)} (\varphi_e^{o(i)} \varphi_e^{o(j)} | V_{E_i E_j} | \varphi_e^{o(j)} \varphi_e^{o(i)})
 \end{aligned}$$

Off-diagonal elements $\hat{k} \neq \hat{k}'$, $e' \neq e''$

$$(\Phi(\hat{k}, e') | \mathcal{H}' | \Phi(\hat{k}', e''))$$

$$= \frac{1}{N} \sum_i e^{-i(\hat{k} - \hat{k}') \cdot \vec{r}_i} \sum_{j \neq i}^N (\varphi_{e'}^{(i)} \varphi_{e''}^{(j)} | V_{E_i E_j} | \varphi_{e''}^{(i)} \varphi_{e'}^{(j)})$$

$$+ \frac{1}{N} \sum_i \sum_{j \neq i}^N e^{-i(\hat{k} \cdot \vec{r}_i - \hat{k}' \cdot \vec{r}_j)} (\varphi_{e'}^{(i)} \varphi_{e''}^{(j)} | V_{E_i E_j} | \varphi_{e''}^{(j)} \varphi_{e'}^{(i)})$$

E. Vibronic Product - Harmonic

Zero-order basis functions

(IX E-1)

$$\Phi_{en}(x, q) = \varphi_e^0(x, q^0) \chi_{en}^0(q)$$

First-order Hamiltonian

$$\mathcal{H}' = T_E(x) + V_E(x) + V_{EN}(x, q) + V_N(q) + T_N(q)$$

Again we expand $V_{EN}(x, q)$ as in equation (IX A-1). Thus the first-order Hamiltonian can be approximated as:

$$\mathcal{H}' = T_E(x) + V_E(x) + V_{EN}^0(x, q^0)$$

(IX E-2)

$$+ (q - q^0) V_{EN}'(x, q^0) + (q - q^0)^2 V_{EN}''(x, q^0) + V_N(q) + T_N(q)$$

Schroedinger Equations

(IX E-3)

$$[T_E(x) + V_E(x) + V_{EN}^0(x, q^0)] \varphi_e^0(x, q^0) = W_e^0(q^0) \varphi_e^0(x, q^0)$$

(IX E-4)

$$[T_N(q) + V_N(q) + W_e^0(q^0)] \chi_{en}^0(q) = E_{en}^0 \chi_{en}^0(q)$$

We may now evaluate the matrix elements of the Hamiltonian representation.

$$(\Phi_{en} | \mathcal{H}' | \Phi_{e'n'})$$

$$= (\varphi_e^0 \chi_{en}^0 | T_E + V_E + V_{EN} | \varphi_{e'}^0 \chi_{e'n'}^0)$$

$$+ (\varphi_e^0 \chi_{en}^0 | (q - q^0) V_{EN}' + (q - q^0)^2 V_{EN}'' | \varphi_{e'}^0 \chi_{e'n'}^0)$$

$$+ (\varphi_e^0 \chi_{en}^0 | T_N + V_N | \varphi_{e'}^0 \chi_{e'n'}^0)$$

Using the Schroedinger equation (IX E-3), we have:

$$(\Phi_{en} | \mathcal{H}' | \Phi_{e'n'})$$

$$= (\varphi_e^0 \chi_{en}^0 | T_N + V_N + W_{e'}^0 | \varphi_{e'}^0 \chi_{e'n'}^0)$$

$$+ (\varphi_e^0 \chi_{en}^0 | (q - q^0) V_{EN}' + (q - q^0)^2 V_{EN}'' | \varphi_{e'}^0 \chi_{e'n'}^0)$$

Using the Schroedinger equation (IX E-4), we have:

$$(\Phi_{en} | \mathcal{H}' | \Phi_{e'n'}) = E_{e'n'}^0 \delta_{ee'} \delta_{nn'}$$

$$+ (\varphi_e^0 | V_{EN}'(x, q^0) | \varphi_{e'}^0) (\chi_{en}^0 | (q - q^0) | \chi_{e'n'}^0)$$

$$+ (\varphi_e^0 | V_{EN}''(x, q^0) | \varphi_{e'}^0) (\chi_{en}^0 | (q - q^0)^2 | \chi_{e'n'}^0)$$

remembering the stability requirement and recognizing that $(\chi_{en}^0 | q | \chi_{en}^0) = q^0$ we have for the matrix elements

Diagonal elements

$$(\Phi_{en} | \mathcal{H}' | \Phi_{en}) = E_{en}^0$$

$$+ (\varphi_e^0 | V_{EN}''(x, q^0) | \varphi_e^0) (\chi_{en}^0 | (q - q^0)^2 | \chi_{en}^0)$$

Off-diagonal elements $e = e'$, $n \neq n'$

$$(\Phi_{en} | \mathcal{H}' | \Phi_{en'}) = (\varphi_e^0 | V_{EN}''(x, q^0) | \varphi_e^0) (\chi_{en}^0 | (q - q^0)^2 | \chi_{en'}^0)$$

Off-diagonal elements $e \neq e'$, all n, n'

$$\begin{aligned} (\Phi_{en} | \mathcal{H}' | \Phi_{en'}) &= (\varphi_e^0 | V_{EN}'(x, q^0) | \varphi_{e'}^0) (\chi_{en}^0 | (q - q^0) | \chi_{e'n'}^0) \\ &\quad + (\varphi_e^0 | V_{EN}''(x, q^0) | \varphi_{e'}^0) (\chi_{en}^0 | (q - q^0)^2 | \chi_{e'n'}^0) \end{aligned}$$

F. Vibronic Product - Adiabatic

Zero-order basis functions

$$(IX F-1) \quad \Phi_{en}(x, q) = \varphi_e^0(x, q) \chi_{en}^0(q)$$

First-order Hamiltonian

$$(IX F-2) \quad \mathcal{H}' = T_E(x) + V_E(x) + V_{EN}(x, q) + V_N(q) + T_N(q)$$

Schroedinger equations

(IX F-3)

$$[T_E(x) + V_E(x) + V_{EN}(x, q)] \varphi_e^0(x, q) = W_e^0(q) \varphi_e^0(x, q)$$

(IX F-4)

$$[T_N(q) + V_N(q) + W_e^0(q)] \chi_{en}^0(q) = E_{en}^0 \chi_{en}^0(q)$$

We may now evaluate the matrix elements of the Hamiltonian representation.

$$\begin{aligned} (\Phi_{en} | \mathcal{H}' | \Phi_{en'}) &= (\varphi_e^0 \chi_{en}^0 | T_E + V_E + V_{EN} | \varphi_{e'}^0 \chi_{e'n'}^0) \\ &\quad + (\varphi_e^0 \chi_{en}^0 | T_N + V_N | \varphi_{e'}^0 \chi_{e'n'}^0) \end{aligned}$$

Using the Schrodinger equation (IX F-3), we have:

$$(IX F-5) \quad (\Phi_{en} | \mathcal{H}' | \Phi_{e'n'}) = (\varphi_e^0 \chi_{en}^0 | T_N | \varphi_{e'}^0 \chi_{e'n'}^0) \\ + (\varphi_e^0 \chi_{en}^0 | V_N + W_{e'}^0 | \varphi_{e'}^0 \chi_{e'n'}^0)$$

$$\text{now } T_N(q) = \frac{1}{2M} P_N^2(q)$$

Thus

$$(IX F-6) \quad T_N(q) | \varphi_e^0 \chi_{en}^0 \rangle = \{ T_N | \varphi_e^0 \rangle \} | \chi_{en}^0 \rangle + \frac{1}{2M} \{ P_N | \varphi_e^0 \rangle \} \{ P_N | \chi_{en}^0 \rangle \} \\ + | \varphi_e^0 \rangle T_N | \chi_{en}^0 \rangle$$

Thus we have:

$$(IX F-7) \quad (\varphi_e \chi_{en}^0 | T_N | \varphi_{e'}^0 \chi_{e'n'}^0) = (\chi_{en}^0 | (\varphi_e^0 | T_N | \varphi_{e'}^0) | \chi_{e'n'}^0) \\ + (\chi_{en}^0 | T_N | \chi_{e'n'}^0) \delta_{ee'} \\ + \frac{1}{2M} (\chi_{en}^0 | (\varphi_e^0 | P_N | \varphi_{e'}^0) P_N | \chi_{e'n'}^0)$$

Substituting equation (IX F-7) into equation (IX F-5), we have:

$$(IX F-8) \quad (\Phi_{en} | \mathcal{H}' | \Phi_{e'n'}) = (\chi_{en}^0 | T_N + V_N + W_{e'}^0 | \chi_{e'n'}^0) \delta_{ee'} \\ + (\chi_{en}^0 | [(\varphi_e^0 | T_N | \varphi_{e'}^0) + \frac{1}{2M} (\varphi_e^0 | P_N | \varphi_{e'}^0) P_N] | \chi_{e'n'}^0)$$

noting that the $(\varphi_e^0 | \chi_{en}^0)$ can be chosen so that $(\varphi_e^0 | P_N | \varphi_{e'}^0) = 1 - \delta_{ee'}$,
we have the following, using the Schrodinger equation (IX F-4):

$$(IX F-9) \quad (\Phi_{en} | \mathcal{H}' | \Phi_{e'n'}) = E_{en}^0 \delta_{ee'} \delta_{nn'} \\ + (\chi_{en}^0 | \{ (\varphi_e^0 | T_N | \varphi_{e'}^0) \} | \chi_{e'n'}^0) \\ + \frac{1}{2M} (\chi_{en}^0 | \{ (\varphi_e^0 | P_N | \varphi_{e'}^0) P_N \} | \chi_{e'n'}^0) (1 - \delta_{ee'})$$

We thus have for the various elements:

Diagonal

$$(\Phi_{en} | \mathcal{H}' | \Phi_{e'n'}) = E_{en}^0 + (\chi_{en}^0 | \{(\varphi_e^0 | T_N | \varphi_e^0)\} | \chi_{en}^0)$$

Off-diagonal $e = e', n \neq n'$

$$(\Phi_{en} | \mathcal{H}' | \Phi_{en'}) = (\chi_{en}^0 | \{(\varphi_e^0 | T_N | \varphi_e^0)\} | \chi_{en'})$$

Off-diagonal $e \neq e', \text{ all } n, n'$

$$(\Phi_{en} | \mathcal{H}' | \Phi_{e'n'}) = (\chi_{en}^0 | \{(\varphi_e^0 | T_N | \varphi_{e'}^0)\} | \chi_{e'n'}) + \frac{1}{2M} (\chi_{en}^0 | \{(\varphi_e^0 | P_N | \varphi_{e'}^0) P_N\} | \chi_{e'n'})$$

G. Vibronic Sum of Products - HarmonicZero-order basis functions

$$(IX\ G-1) \quad \Phi_{en}^K = \frac{1}{\sqrt{K}} \sum_i^K \varphi_e^{o(i)}(x_i, q^0) \chi_{en}^{o(i)}(q_i)$$

First order Hamiltonian

$$\mathcal{H}' = T_E(x) + V_E(x) + V_{EN}(x, q) + T_N(q) + V_N(q)$$

again we approximate

$$(IX\ G-2) \quad \mathcal{H}' = T_E(x) + V_E(x) + V_{EN}^0(x, q^0) + (q - q^0) V_{EN}'(x, q^0) + (q - q^0)^2 V_{EN}''(x, q^0) + T_N(q) + V_N(q)$$

Schroedinger Equations

$$(IX\ G-3) \quad [T_E(x) + V_E(x) + V_{EN}^0(x, q^0)] \varphi_e^{o(i)}(x, q^0) = W_e^{o(i)}(q^0) \varphi_e^{o(i)}(x, q^0)$$

$$(IX\ G-4) \quad [T_N(q) + V_N(q) + W_e^{o(i)}(q^o)] \chi_{en}^{o(i)}(q) = E_{en}^{o(i)} \chi_{en}^{o(i)}(q)$$

We may now evaluate the matrix elements of the Hamiltonian representation.

$$(IX\ G-5) \quad (\Phi_{en}^K | \mathcal{H}' | \Phi_{e'n'}^{K'})$$

$$= \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} \chi_{en}^{o(i)} | T_E + V_E + V_{EN}' | \varphi_{e'}^{o(j)} \chi_{e'n'}^{o(j)})$$

$$+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} \chi_{en}^{o(i)} | (q - q^o) V_{EN}' | \varphi_{e'}^{o(j)} \chi_{e'n'}^{o(j)})$$

$$+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} \chi_{en}^{o(i)} | (q - q^o)^2 V_{EN}'' | \varphi_{e'}^{o(j)} \chi_{e'n'}^{o(j)})$$

$$+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} \chi_{en}^{o(i)} | T_N + V_N | \varphi_{e'}^{o(j)} \chi_{e'n'}^{o(j)})$$

Using the Schroedinger equation (IX G-3) and the orthogonality of the electronic wave functions.

$$(IX\ G-6) \quad (\Phi_{en}^K | \mathcal{H}' | \Phi_{e'n'}^{K'})$$

$$= \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\chi_{en}^{o(i)} | T_N + V_N + W_e^{o(j)} | \chi_{e'n'}^{o(j)}) \delta_{ee'}$$

$$+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} | V_{EN}' | \varphi_{e'}^{o(j)}) (\chi_{en}^{o(i)} | (q - q^o) | \chi_{e'n'}^{o(j)})$$

$$+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} | V_{EN}'' | \varphi_{e'}^{o(j)}) (\chi_{en}^{o(i)} | (q - q^o)^2 | \chi_{e'n'}^{o(j)})$$

Using the Schrodinger equation (IX G-4), we have:

$$\begin{aligned}
 (\Phi_{en}^K | \mathcal{H}' | \Phi_{e'n'}^{K'}) &= \frac{1}{K} \sum_i^K E_{e'n'}^{o(i)} \delta_{KK'} \delta_{ee'} \delta_{nn'} \\
 &+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} | V_{EN}' | \varphi_{e'}^{o(j)}) (\chi_{en}^{o(i)} | (q - q^0) | \chi_{e'n'}^{o(j)}) \\
 &+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} | V_{EN}'' | \varphi_{e'}^{o(j)}) (\chi_{en}^{o(i)} | (q - q^0)^2 | \chi_{e'n'}^{o(j)})
 \end{aligned}$$

We can now write the matrix elements:

Diagonal

$$\begin{aligned}
 (\Phi_{en}^K | \mathcal{H}' | \Phi_{en}^K) &= \frac{1}{K} \sum_i^K E_{en}^{o(i)} \\
 &+ \frac{1}{K} \sum_i^K \sum_j^K (\varphi_e^{o(i)} | V_{EN}' | \varphi_e^{o(j)}) (\chi_{en}^{o(i)} | (q - q^0) | \chi_{en}^{o(j)}) \\
 &+ \frac{1}{K} \sum_i^K \sum_j^K (\varphi_e^{o(i)} | V_{EN}'' | \varphi_e^{o(j)}) (\chi_{en}^{o(i)} | (q - q^0)^2 | \chi_{en}^{o(j)})
 \end{aligned}$$

Off-diagonal $e = e'$ ($\therefore K = K'$), $n \neq n'$

$$\begin{aligned}
 (\Phi_{en}^K | \mathcal{H}' | \Phi_{en'}^K) &= \frac{1}{K} \sum_i^K \sum_j^K (\varphi_e^{o(i)} | V_{EN}' | \varphi_e^{o(j)}) (\chi_{en}^{o(i)} | (q - q^0) | \chi_{en'}^{o(j)}) \\
 &+ \frac{1}{K} \sum_i^K \sum_j^K (\varphi_e^{o(i)} | V_{EN}'' | \varphi_e^{o(j)}) (\chi_{en}^{o(i)} | (q - q^0)^2 | \chi_{en'}^{o(j)})
 \end{aligned}$$

Off-diagonal $e \neq e'$, all K, K', n, n'

$$\begin{aligned}
 (\Phi_{en}^K | \mathcal{H}' | \Phi_{e'n'}^{K'}) &= \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} | V_{EN}' | \varphi_{e'}^{o(j)}) (\chi_{en}^{o(i)} | (q - q^0) | \chi_{e'n'}^{o(j)}) \\
 &+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} | V_{EN}'' | \varphi_{e'}^{o(j)}) (\chi_{en}^{o(i)} | (q - q^0)^2 | \chi_{e'n'}^{o(j)})
 \end{aligned}$$

Normally the vibrational wave functions are chosen via a variational procedure such that the matrix elements between $\varphi_e^{o(j)} \chi_{en}^{o(j)}$ and $\varphi_e^{o(i)} \chi_{en}^{o(i)}$ are zero. This fact, along with the conditions $(\varphi_e^{o(i)} | V_{EN}' | \varphi_e^{o(i)}) = 0$, $(\chi_{en}^{o(i)} | (q - q^0) | \chi_{en}^{o(i)}) = 0$ yield the following matrix elements.

Diagonal

$$(\Phi_{en}^K | \mathcal{H}' | \Phi_{en}^K) = \frac{1}{K} \sum_i^K E_{en}^{o(i)} + \frac{1}{K} \sum_i^K (\varphi_e^{o(i)} | V_{EN}'' | \varphi_e^{o(i)}) (\chi_{en}^{o(i)} | (q - q^0)^2 | \chi_{en}^{o(i)})$$

Off-diagonal $e = e'$ ($\therefore k = k'$), $n \neq n'$

$$(\Phi_{en}^K | \mathcal{H}' | \Phi_{en'}^K) = \frac{1}{K} \sum_i^K (\varphi_e^{o(i)} | V_{EN}'' | \varphi_e^{o(i)}) (\chi_{en}^{o(i)} | (q - q^0)^2 | \chi_{en'}^{o(i)})$$

Off-diagonal $e \neq e'$, all K, K', n, n'

$$\begin{aligned} & (\Phi_{en}^K | \mathcal{H}' | \Phi_{en'}^{K'}) \\ &= \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} | V_{EN}' | \varphi_{e'}^{o(j)}) (\chi_{en}^{o(i)} | (q - q^0) | \chi_{en'}^{o(j)}) \\ &+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} | V_{EN}'' | \varphi_{e'}^{o(j)}) (\chi_{en}^{o(i)} | (q - q^0)^2 | \chi_{en'}^{o(j)}) \end{aligned}$$

H. Vibronic Sum of Products - Adiabatic

Zero-order basis functions

$$(IX H-1) \quad \Phi_{en}^K = \frac{1}{\sqrt{K}} \sum_i^K \varphi_e^{o(i)}(x, q) \chi_{en}^{o(i)}(q)$$

First-order Hamiltonian

$$\begin{aligned} (IX H-2) \quad \mathcal{H}' = & T_E(x) + V_E(x) + V_{EN}(x, q) \\ & + T_N(q) + V_N(q) \end{aligned}$$

Schroedinger Equation

$$(IX\ H-3) \quad [T_E(x) + V_E(x) + V_{EN}(x, q)] \varphi_e^{o(j)}(x, q) = W_e^{o(j)}(q) \varphi_e^{o(j)}(x, q)$$

$$(IX\ H-4) \quad [T_N(q) + V_N(q) + W_e^{o(j)}(q)] \chi_{en}^{o(j)}(q) = E_{en}^{o(j)} \chi_{en}^{o(j)}(q)$$

We may evaluate the matrix elements of the Hamiltonian representation.

$$(IX\ H-5) \quad (\Phi_{en}^K | \mathcal{H}' | \Phi_{en}^{K'}) \\ = \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} \chi_{en}^{o(i)} | T_E + V_E + V_{EN} | \varphi_e^{o(j)} \chi_{en}^{o(j)}) \\ + \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} \chi_{en}^{o(i)} | T_N + V_N | \varphi_e^{o(j)} \chi_{en}^{o(j)})$$

Using the Schroedinger equation (IX H-3) and the orthogonality properties of the electronic wave functions, we have:

$$(IX\ H-6) \quad (\Phi_{en}^K | \mathcal{H}' | \Phi_{en}^{K'}) \\ = \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\varphi_e^{o(i)} \chi_{en}^{o(i)} | T_N | \varphi_e^{o(j)} \chi_{en}^{o(j)}) \\ + \frac{1}{K} \sum_i^K (\chi_{en}^{o(i)} | V_N + W_e^{o(i)} | \chi_{en}^{o(i)}) \delta_{ee'} \delta_{KK'}$$

We have the parallel to equation (IX F-7)

$$(IX\ H-7) \quad (\varphi_e^{o(i)} \chi_{en}^{o(i)} | T_N | \varphi_e^{o(j)} \chi_{en}^{o(j)}) = (\chi_{en}^{o(i)} | (\varphi_e^{o(i)} | T_N | \varphi_e^{o(j)}) | \chi_{en}^{o(j)}) \\ + (\chi_{en}^{o(i)} | T_N | \chi_{en}^{o(i)}) \delta_{ee'} \delta_{ij} \\ + \frac{1}{2M} (\chi_{en}^{o(i)} | (\varphi_e^{o(i)} | P_N | \varphi_e^{o(i)}) P_N | \chi_{en}^{o(j)})$$

Substituting equation (IX H-7) into equation (IX H-6), we have:

$$\begin{aligned}
 \text{(IX H-8)} \quad & (\Phi_{en}^K | \mathcal{H}' | \Phi_{e'n'}^{K'}) \\
 &= \frac{1}{K} \sum_i^K (\chi_{en}^{o(i)} | T_N + V_N + W_{e'}^{o(i)} | \chi_{e'n'}^{o(i)}) \delta_{ee'} \delta_{KK'} \\
 &+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\chi_{en}^{o(i)} | (\varphi_e^{o(i)} | T_N | \varphi_{e'}^{o(j)}) | \chi_{e'n'}^{o(j)}) \\
 &+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} \frac{1}{2M} (\chi_{en}^{o(i)} | (\varphi_e^{o(i)} | P_N | \varphi_{e'}^{o(j)}) P_N | \chi_{e'n'}^{o(j)})
 \end{aligned}$$

Substituting the Schroedinger equation (IX H-4) into equation (IX H-8), we have:

$$\begin{aligned}
 \text{(IX H-9)} \quad & (\Phi_{en}^K | \mathcal{H}' | \Phi_{e'n'}^{K'}) \\
 &= \frac{1}{K} \sum_i^K E_{e'n'}^{o(i)} \delta_{ee'} \delta_{nn'} \delta_{KK'} \\
 &+ \left(\frac{1}{KK'}\right)^{1/2} \sum_i^K \sum_j^{K'} (\chi_{en}^{o(i)} | \{ (\varphi_e^{o(i)} | T_N | \varphi_{e'}^{o(j)}) + \frac{1}{2M} (\varphi_e^{o(i)} | P_N | \varphi_{e'}^{o(j)}) P_N \} | \chi_{e'n'}^{o(j)})
 \end{aligned}$$

Using the relation $(\varphi_e^{o(i)} | P_N | \varphi_{e'}^{o(j)}) = (1 - \delta_{ij} \delta_{ee'}) (\varphi_e^{o(i)} | P_N | \varphi_{e'}^{o(j)})$ we find for the matrix elements.

Diagonal

$$\begin{aligned}
 (\Phi_{en}^K | \mathcal{H}' | \Phi_{en}^K) &= \frac{1}{K} \sum_i^K E_{en}^{o(i)} \\
 &+ \frac{1}{K} \sum_i^K \sum_j^K (\chi_{en}^{o(i)} | \{ (\varphi_e^{o(i)} | T_N | \varphi_e^{o(j)}) \} | \chi_{en}^{o(j)}) \\
 &+ \frac{1}{K} \sum_i^K \sum_j^K (\chi_{en}^{o(i)} | \frac{1}{2M} (\varphi_e^{o(i)} | P_N | \varphi_e^{o(j)}) P_N | \chi_{en}^{o(j)})
 \end{aligned}$$

Off-diagonal $e = e'$ ($\therefore k = k'$), $n \neq n'$

$$\begin{aligned}
 (\Phi_{en}^k | \mathcal{H}' | \Phi_{en'}^k) &= \frac{1}{k} \sum_i^k \sum_j^k (\chi_{en}^{o(i)} | \{ (\varphi_e^{o(i)} | T_N | \varphi_e^{o(j)}) \} | \chi_{en'}^{o(j)}) \\
 &+ \frac{1}{k} \sum_i^k \sum_{j \neq i}^k (\chi_{en}^{o(i)} | \frac{1}{2M} (\varphi_e^{o(i)} | P_N | \varphi_e^{o(j)}) P_N | \chi_{en'}^{o(j)})
 \end{aligned}$$

Off-diagonal $e \neq e'$, all k, k', n, n'

$$\begin{aligned}
 (\Phi_{en}^k | \mathcal{H}' | \Phi_{e'n'}^{k'}) &= \left(\frac{1}{kk'} \right)^{1/2} \sum_i^k \sum_j^{k'} (\chi_{en}^{o(i)} | \{ (\varphi_e^{o(i)} | T_N | \varphi_{e'}^{o(j)}) \} | \chi_{e'n'}^{o(j)}) \\
 &+ \left(\frac{1}{kk'} \right)^{1/2} \sum_i^k \sum_j^{k'} (\chi_{en}^{o(i)} | \frac{1}{2M} (\varphi_e^{o(i)} | P_N | \varphi_{e'}^{o(j)}) P_N | \chi_{e'n'}^{o(j)})
 \end{aligned}$$

Again the vibrational wave functions are normally chosen via a variational procedure such that the matrix elements between $\varphi_e^{o(i)} \chi_{en}^{o(i)}$ and $\varphi_{e'}^{o(j)} \chi_{e'n'}^{o(j)}$ are zero. The above elements become:

Diagonal

$$(\Phi_{en}^k | \mathcal{H}' | \Phi_{en}^k) = \frac{1}{k} \sum_i^k E_{en}^{o(i)} + \frac{1}{k} \sum_i^k (\chi_{en}^{o(i)} | \{ (\varphi_e^{o(i)} | T_N | \varphi_e^{o(i)}) \} | \chi_{en}^{o(i)})$$

Off-diagonal $e = e'$ ($\therefore k = k'$), $n \neq n'$

$$(\Phi_{en}^k | \mathcal{H}' | \Phi_{en'}^k) = \frac{1}{k} \sum_i^k (\chi_{en}^{o(i)} | \{ (\varphi_e^{o(i)} | T_N | \varphi_e^{o(i)}) \} | \chi_{en'}^{o(i)})$$

Off-diagonal $e \neq e'$, all k, k', n, n'

$$\begin{aligned}
 (\Phi_{en}^k | \mathcal{H}' | \Phi_{e'n'}^{k'}) &= \left(\frac{1}{kk'} \right)^{1/2} \sum_i^k \sum_j^{k'} (\chi_{en}^{o(i)} | \{ (\varphi_e^{o(i)} | T_N | \varphi_{e'}^{o(j)}) \} | \chi_{e'n'}^{o(j)}) \\
 &+ \left(\frac{1}{kk'} \right)^{1/2} \sum_i^k \sum_j^{k'} (\chi_{en}^{o(i)} | \frac{1}{2M} (\varphi_e^{o(i)} | P_N | \varphi_{e'}^{o(j)}) P_N | \chi_{e'n'}^{o(j)})
 \end{aligned}$$

Appendix X

Third-order Degenerate Perturbation Expansions for Ground and Excited States

Let the perturbation be $\mathcal{P}$.

We use Table 5.1, Chapter V on page 84 of Perturbation Methods in Quantum Mechanics of n-Electron Systems by Corson (88).

$$\begin{aligned}
 (X-1) \quad |K^{\Lambda S}\rangle &= \sum_{j,k} \langle H^{jk} | K^{\Lambda S} \rangle |H^{jk}\rangle \\
 &= |H^{jk}\rangle + \sum_{j,k} \langle H^{jk} | K^{\Lambda S}; 1 \rangle |H^{jk}\rangle \\
 &\quad + \sum_{j,k} \langle H^{jk} | K^{\Lambda S}; 2 \rangle |H^{jk}\rangle \\
 &\quad + \sum_{j,k} \langle H^{jk} | K^{\Lambda S}; 3 \rangle |H^{jk}\rangle
 \end{aligned}$$

The H terms are the zeroth order states, the K terms are the perturbed states. Of the superscripts, the first indicates the particular electronic state and the second, the particular degenerate member of that state (if degenerate). For our convenience, we change the notation. The capital arabic letter signifies the particular electronic state, the small arabic subscript signifies the degenerate member. Zeroth order states are signified by a 0 superscript. Thus L_m is the true m degenerate member of the L electronic state. L_m^0 is the zeroth order m degenerate member of this state. We, therefore rewrite the above equation (switching to the |) notation as we shall reserve | > for time dependent states).

$$(X-2) \quad |K_s) = |K_s^0) + \sum_{L^0} \sum_m (L_m^0 | K_s; 1) |L_m^0) \\ + \sum_{L^0} \sum_m (L_m^0 | K_s; 2) |L_m^0) \\ + \sum_{L^0} \sum_m (L_m^0 | K_s; 3) |L_m^0)$$

We now must define the terms used in this equation.

$$(X-3) \quad (L_m^0 | K_s; 1) = \frac{(L_m^0 | P | K_s^0)}{E_K^0 - E_L^0} \quad L^0 \neq K^0$$

$$(K_m^0 | K_s; 1) = \sum_{M^0} \sum_q \frac{(K_m^0 | P | M_q^0)(M_q^0 | P | K_s^0)}{(E_K^0 - E_M^0)(E_{Ks} - E_{Kmq})} \quad M^0 \neq K^0, m \neq s$$

$$(K_s^0 | K_s; 1) = 0$$

$$(L_m^0 | K_s; 2) = \sum_{M^0} \sum_q \frac{(L_m^0 | P | M_q^0)(M_q^0 | K_s; 1)}{E_K^0 - E_L^0} \\ - \frac{\Delta_1^{(s)} E_K (L_m^0 | K_s; 1)}{E_K^0 - E_L^0} \quad L^0 \neq K^0$$

$$(K_m^0 | K_s; 2) = \sum_{M^0} \sum_q \frac{(K_m^0 | P | M_q^0)(M_q^0 | K_s; 2)}{E_{Ks} - E_{Kmq}} \\ - \frac{\Delta_2^{(s)} E_K (K_m^0 | K_s; 1)}{E_{Ks} - E_{Kmq}} \quad M^0 \neq K^0, m \neq s$$

$$(K_s^0 | K_s; 2) = -\frac{1}{2} \sum_{M^0} \sum_q |(M_q^0 | K_s; 1)|^2$$

$$(L_m^0 | K_s; 3) = \sum_{M^0} \sum_q \frac{(L_m^0 | P | M_q^0)(M_q^0 | K_s; 2)}{E_K^0 - E_L^0} \\ - \frac{\Delta_1^{(s)} E_K (L_m^0 | K_s; 2)}{E_K^0 - E_L^0} \\ - \frac{\Delta_2^{(s)} E_K (L_m^0 | K_s; 1)}{E_K^0 - E_L^0} \quad L^0 \neq K^0$$

$$(K_m^0 | K_s; 3) = \sum_{M^0} \sum_q \frac{(K_m^0 | P | M_q^0)(M_q^0 | K_s; 3)}{E_{Ks} - E_{Kmq}} \\ - \frac{\Delta_2^{(s)} E_K (K_m^0 | K_s; 2)}{E_{Ks} - E_{Kmq}}$$

$$- \frac{\Delta_3^{(s)} E_K (K_m^0 | K_s; 1)}{E_{Ks} - E_{Km}} \quad M^0 \neq K^0, m \neq s$$

$$(K_s^0 | K_s; 3) = -\frac{1}{2} \sum_{M^0} \sum_l \left[(K_s; 1 | M_l^0) (M_l^0 | K_s; 2) + (K_s; 2 | M_l^0) (M_l^0 | K_s; 1) \right]$$

where

(X-4)

$$\Delta_1^{(s)} E_K = (K_s^0 | P | K_s^0)$$

$$\Delta_2^{(s)} E_K = \sum_{M^0} \sum_l \frac{|(K_s^0 | P | M_l^0)|^2}{E_K^0 - E_M^0} \quad M^0 \neq K^0$$

$$\Delta_3^{(s)} E_K = \sum_{M^0} \sum_l (K_s^0 | P | M_l^0) (M_l^0 | K_s; 2) \quad M^0 \neq K^0$$

$$= \sum_{M^0 \neq K^0} \sum_{N^0} \sum_l \sum_{\lambda} \frac{(K_s^0 | P | M_l^0) (M_l^0 | P | N_{\lambda}^0) (N_{\lambda}^0 | K_s; 1)}{E_K^0 - E_M^0}$$

$$- \sum_{M^0 \neq K^0} \sum_l \Delta_1^{(s)} E_K \frac{(K_s^0 | P | M_l^0) (M_l^0 | K_s; 1)}{E_K^0 - E_M^0}$$

$$\therefore \Delta_3^{(s)} E_K = \sum_{M^0 \neq K^0} \sum_{N^0 \neq K^0} \sum_l \sum_{\lambda} \frac{(K_s^0 | P | M_l^0) (M_l^0 | P | N_{\lambda}^0) (N_{\lambda}^0 | P | K_s^0)}{(E_K^0 - E_M^0) (E_K^0 - E_N^0)}$$

$$- \sum_{M^0 \neq K^0} \sum_{N^0 \neq K^0} \sum_l \sum_{\lambda \neq s} \frac{(K_s^0 | P | M_l^0) (M_l^0 | P | K_{\lambda}^0) (K_{\lambda}^0 | P | N_{\lambda}^0) (N_{\lambda}^0 | P | K_s^0)}{(E_K^0 - E_M^0) (E_K^0 - E_N^0) (E_{Ks} - E_{K\lambda})}$$

Now we are only considering perturbations of order 3 or less. By

examining the equation for $\Delta_3^{(s)} E_K$ and the next to last of equation (X-3),

we see that if we can consider terms such as $\frac{(K_{\lambda}^0 | P | N_{\lambda}^0)}{E_{Ks} - E_{Kt}} < 1$ then we

can treat these also as lowering the order, and thus omit many terms.

Thus we can ignore any contribution in 3rd order of $\Delta_3^{(s)} E_K$.

Similarly, we can ignore any contribution of $\Delta_2^{(s)} E_K$ to $(K_m^0 | K_S; 3)$.

Let us now write out the 0th, 1st, 2nd, and 3rd order terms of the perturbation expansion of $|K_S\rangle$.

$$(X-5) \quad 0^{TH} \quad |K_S^0\rangle$$

$$1^{ST} \quad \sum_{L^0 \neq K^0} \sum_m \frac{(L_m^0 | P | K_S^0)}{E_K^0 - E_L^0} |L_m^0\rangle \\ + \sum_{t \neq S} \sum_{M^0 \neq K^0} \sum_L \frac{(K_t^0 | P | M_L^0)(M_L^0 | P | K_S^0)}{(E_K^0 - E_M^0)(E_{K_S} - E_{K_t})} |K_t^0\rangle$$

$$2^{ND} \quad \sum_{L^0 \neq K^0} \sum_m \sum_{M^0 \neq K^0} \sum_L \frac{(L_m^0 | P | M_L^0)(M_L^0 | P | K_S^0)}{(E_K^0 - E_L^0)(E_K^0 - E_M^0)} |L_m^0\rangle \\ + \sum_{t \neq S} \sum_{L^0 \neq K^0} \sum_m \sum_{M^0 \neq K^0} \sum_L \frac{(L_m^0 | P | K_t^0)(K_t^0 | P | M_L^0)(M_L^0 | P | K_S^0)}{(E_K^0 - E_L^0)(E_K^0 - E_M^0)(E_{K_S} - E_{K_t})} |L_m^0\rangle \\ - \sum_{L^0 \neq K^0} \sum_m \frac{(K_S^0 | P | K_S^0)(L_m^0 | P | K_S^0)}{(E_K^0 - E_L^0)^2} |L_m^0\rangle \\ + \sum_{t \neq S} \sum_{L^0 \neq K^0} \sum_m \sum_{M^0 \neq K^0} \sum_L \frac{(K_t^0 | P | L_m^0)(L_m^0 | P | M_L^0)(M_L^0 | P | K_S^0)}{(E_{K_S} - E_{K_t})(E_K^0 - E_L^0)(E_K^0 - E_M^0)} |K_t^0\rangle \\ - \sum_{t \neq S} \sum_{L^0 \neq K^0} \sum_m \frac{(K_t^0 | P | L_m^0)(L_m^0 | P | K_S^0)(K_S^0 | P | K_S^0)}{(E_{K_S} - E_{K_t})(E_K^0 - E_L^0)^2} |K_t^0\rangle \\ - \frac{1}{2} \sum_{L^0 \neq K^0} \sum_m \frac{|(L_m^0 | P | K_S^0)|^2}{(E_K^0 - E_L^0)^2} |K_S^0\rangle$$

$$3^{RD} \quad \sum_{L^0 \neq K^0} \sum_m \sum_{M^0 \neq K^0} \sum_L \sum_{N^0 \neq K^0} \sum_N \frac{(L_m^0 | P | M_L^0)(M_L^0 | P | N_N^0)(N_N^0 | P | K_S^0)}{(E_K^0 - E_L^0)(E_K^0 - E_M^0)(E_K^0 - E_N^0)} |L_m^0\rangle \\ - \sum_{L^0 \neq K^0} \sum_m \sum_{M^0 \neq K^0} \sum_L \frac{(L_m^0 | P | M_L^0)(M_L^0 | P | K_S^0)(K_S^0 | P | K_S^0)}{(E_K^0 - E_L^0)(E_K^0 - E_M^0)^2} |L_m^0\rangle$$

$$\begin{aligned}
& -\frac{1}{2} \sum_{L^0 \neq K^0} \sum_m \sum_{M^0 \neq K^0} \sum_L \frac{(L_m^0 | P | K_s^0) |(M_e^0 | P | K_s^0)|^2}{(E_K^0 - E_L^0)(E_K^0 - E_M^0)^2} |L_m^0\rangle \\
& - \sum_{L^0 \neq K^0} \sum_m \sum_{M^0 \neq K^0} \sum_L \frac{(K_s^0 | P | K_s^0)(L_m^0 | P | M_e^0)(M_e^0 | P | K_s^0)}{(E_K^0 - E_L^0)^2 (E_K^0 - E_M^0)} |L_m^0\rangle \\
& + \sum_{L^0 \neq K^0} \sum_m \frac{(K_s^0 | P | K_s^0)^2 (L_m^0 | P | K_s^0)}{(E_K^0 - E_L^0)^3} |L_m^0\rangle \\
& - \sum_{L^0 \neq K^0} \sum_m \sum_{M^0 \neq K^0} \sum_L \frac{|(K_s^0 | P | M_e^0)|^2 (L_m^0 | P | K_s^0)}{(E_K^0 - E_L^0)^2 (E_K^0 - E_M^0)} |L_m^0\rangle \\
& - \frac{1}{2} \sum_{L^0 \neq K^0} \sum_m \sum_{M^0 \neq K^0} \sum_L \frac{(K_s^0 | P | L_m^0)(L_m^0 | P | M_e^0)(M_e^0 | P | K_s^0)}{(E_K^0 - E_L^0)^2 (E_K^0 - E_M^0)} |K_s^0\rangle \\
& - \frac{1}{2} \sum_{L^0 \neq K^0} \sum_m \sum_{M^0 \neq K^0} \sum_L \frac{(L_m^0 | P | K_s^0)(K_s^0 | P | M_e^0)(M_e^0 | P | L_m^0)}{(E_K^0 - E_L^0)^2 (E_K^0 - E_M^0)} |K_s^0\rangle \\
& + \sum_{L^0 \neq K^0} \sum_m \frac{(K_s^0 | P | L_m^0)(L_m^0 | P | K_s^0)(K_s^0 | P | K_s^0)}{(E_K^0 - E_L^0)^3} |K_s^0\rangle
\end{aligned}$$

In tabulating these terms, we have ignored terms of perturbation of order higher than 3.

We can make further reductions of these terms by noting that the $(K_s^0 | K_s; 3)$ and $(K_s^0 | K; 2)$ sets are small corrections on the 0th order wave function $|K_s^0\rangle$ and give no new symmetry sets. Furthermore, as can be shown, for certain conditions which are almost always fulfilled, we can ignore any terms which include $(E_{K_s} - E_{K_t})$ in the denominator. Therefore, if we combine the various terms of (X-5) under these conditions, and drop the subscripts denoting members of the degenerate set, we may write the equations for $(J|$ and $|K)$ as are given in Chapter 4, equations (4-23) and (4-24). Although we drop the notation indicating the members of degenerate sets, we do not forget that it

exists, and in the case of a degenerate representation, we must sum over all members in doing the symmetry evaluation.

Appendix XIListing for Computer Program SYMDET
and Associated Subroutines

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PROGRAM SYMDET(INPUT,OUTPUT,TAPE 2=INPUT,TAPE 3=OUTPUT)
115 COMPLEX COCOME,COUPCF,CCPROD,DDPROD,CURSCC,CCTSTS,CDIMAG,CTSTS,
    IDCPROD,CPRD,CXPRD,CYPRD,CZPRD,CPRD
115 INTEGER AOPF1,BOPE2,COPE3,AOPM1,BOPM2,COPM3,DOPV,AWFJ,BWFK,CWFL,
    IDWFM,EFWN,ROPE(2),ROPM(2)
120 DIMENSION CURSCC(5),CPROD(4)
122 DIMENSION LVIB(3),LCPRD(4)
125 COMMON/GNOTER/INDZJJ(6),INDZJK(6),INDZKJ(6)
126 COMMON/GNDPRO/NRIP(12,12),IGP(12,12,4)
128 COMMON/TERPRO/KOP(5),KWF(5),IOPQ(5),IWFQ(5)
130 COMMON/SUBGND/MOELEC(2),MOMAGN(2)
132 COMMON/SUBTER/LABOP(5),LABWF(5),INZ(28),NNSQIN,IOPADE,ITPADE,
    IOPADM
134 COMMON/SUBPRO/IOPQA(5),IWFQA(5),JOSLWF(4),JOSOP(4),JDSTWF(4),
    IMATELQ(5),NRIPS,IREFSB(9)
135 COMMON/SUBSER/IDEGRR(12),IPARTM(12),IRDEG(12),MEMREP(10,10,4),
    ICOCOME(5,4,4),COUPCF(10,10,4),NNDREP,MATCH(4)
136 COMMON/SUBSYM/ITECM(28),KAROP(28),KARWF(28),NIX(6),NIY(6,50),
    INADD(4),JVIB(28,90)
137 COMMON/IDCG/IVISB(6,50,35),IEXGD(6,50,35)
138 COMMON/2000/INONOP(28,90,3),INONWF(28,90,3),LPRU(28,90)
139 COMMON/3000/NDOP(6,50),NDWF(6,50,35)
140 DIMENSION ICCSSA(5),ICCSSB(5),IDOCCE(5),IOPDEG(5),
    IOPMPI(5),IOPQB(5),ISTACK(5),IWFDEG(5),IWFMPI(5),IWFQB(5),
    INCORIP(5),NDEGMP(5),NUMUME(10),ILWFB(5,4),
    3IOPRS(5,4),ITWFB(5,4),JOPGPD(5,128),JWFGPD(5,128)
145 DIMENSION MODEL(70),JSTOWF(70),KSTOWF(70)
147 DIMENSION NSUBWF(35),NBOTWF(35),NVIBWF(35),NS(7),NB(7),NV(7)
150 READ 151, NUMBMO
151 FORMAT (20X,I2)
156 READ 157, IPOS
157 FORMAT (20X,I2)
158 READ 159, (MATCH(I), I=1,4)
159 FORMAT (3X, 4(11X,I2))
162 READ 163, ISKIP
163 FORMAT (20X,I2)
165 READ 170, (JSTOWF(I), KSTOWF(I), MODEL(I), I=1,NUMBMO)
170 FORMAT (2X,3(20X,I3))
180 READ 190, NUMIRK, NNDREP
190 FORMAT (49X, I3/49X, I3)
200 READ 210, MOELEC, MOMAGN
210 FORMAT (45X, 2(14X,I2)/45X, 2(14X,I2))
220 READ 230, IRDEG
230 FORMAT (43X, 2(11X, I2)/6(11X, I2)/4(11X, I2))
240 READ 250, IDEGRR
250 FORMAT (48X, 2(12X, I2)/ 5(12X, I2)/5(12X, I2))
260 READ 270, IREFSB
270 FORMAT (74X, I2/ 4(12X, I2)/4(12X, I2))
280 READ 290, IPARTM
290 FORMAT (/17X,4(12X,I2)/13X,I2,3(12X,I2)/13X,I2,3(12X,I2))
300 READ 310, NRIP
310 FORMAT (16X,I2(1X,I2))
320 READ 330, IGP
330 FORMAT (17X,I2(1X,I2))
340 READ 350, MEMREP
350 FORMAT (21X,10(1X,I4))
360 READ 370, COUPCF

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370 FORMAT (2X,8(2X,F3,1X,F3))
400 READ 410, AOPE1,BOPE2,COPE3,AUPM1,BOPM2,COPM3,DOPV,AWFJ,BWFK,
    ICWFL,DWFM,EWFN
410 FORMAT(4X,7(A2,1X),5(A1,1X))
420 READ 430,AQ,DAQ,EAQ,DBQ,EBQ,DCQ,ECQ,DDQ,EDQ,DEQ,EEQ
430 FORMAT(4X,A3,4X,A10,A8,A10,A8,A10,A8/4X,A10,A8,A10,A8)
    NADD(1) = 1
    NADD(2) = 10
    NADD(3) = 100
    NADD(4) = 1000
431 DO 9916 MODNUM = 1,NUMBMD
    DO 432 I = 1,6
        INDZJK(I) = 0
        INDZKJ(I) = 0
        INDZJJ(I) = 0
432 CONTINUE
    NUMCOM = 2
    COIMAG = (0.,1.)
433 MODE = MODEL(MODNUM)
434 MODEPI = MODE + 1
    IWFJ = JSTOWF(MODNUM)
    IWFK = KSTOWF(MODNUM)
436 IF (ISKIP) 438,438,1004
438 GO TO (442,450,458,466,474), MODEPI
440 FORMAT(//,9X,15HSYMMETRY GROUP ,A3,5X,32HINITIAL WAVE FUNCTION SYM
    METRY = ,I2,4X,31HFINAL WAVE FUNCTION SYMMETRY = ,I2,4X,7HMODE = ,
    2A10,A8,/)
442 PRINT 440, AQ,IWFJ,IWFK,DAQ,EAQ
446 GO TO 1004
450 PRINT 440, AQ,IWFJ,IWFK,DBQ,EBQ
454 GO TO 1004
458 PRINT 440, AQ,IWFJ,IWFK,DCQ,ECQ
462 GO TO 1004
466 PRINT 440, AQ,IWFJ,IWFK,DDQ,EDQ
470 GO TO 1004
474 PRINT 440, AQ,IWFJ,IWFK,DEQ,EEQ
1004 CONTINUE
1008 GO TO (1009,1013,1015,1015,1017), MODEPI
1009 NUTCOM = NUMCOM
1010 GO TO 1020
1013 NUTCOM = NUMCOM + NUMCOM
1014 GO TO 1020
1015 NUTCOM = 3
1016 GO TO 1020
1017 NUTCOM = 6
1020 CALL GONOGO(NUTCOM,MODEPI,IWFJ,IWFK)
2004 ROPE(1) = AOPE1
2005 ROPE(2) = BOPE2
2006 ROPM(1) = AOPM1
2007 ROPM(2) = BOPM2
2020 DO 8372 NCOM = 1, NUTCOM
    IF (ISKIP) 2021,2021,2026
2021 PRINT 2022, NCOM
2022 FORMAT(25H                                COMPONENT,I2/)
2023 PRINT 2025
2025 FORMAT(24X,4HTERM,6X,3HWF1,4X,3HOP1,6X,3HWF2,4X,3HOP2,6X,3HWF3,4X,
    13HOP3,6X,3HWF4,4X,3HOP4,6X,3HWF5,4X,3HOP5)
2026 IF (MODE - 1) 2027,2027,2140

```

```

2027 IF (NCOM - NUMCOM) 2028,2028,2052
C
C   THIS PORTION STORES THE DESIGNATED SYMMETRIES OF THE ELECTRIC (AND
C   MAGNETIC IF CIRCULAR DICHROISM IS BEING CALCULATED) DIPOLE MOMENTS
C   IN THE OPERATOR STORAGE SLOTS KOP(2), KOP(3).
C
2028 KOP(2) = MUELEC(NCOM)
2029 LABOP(2) = ROPE(NCOM)
2032 IF (MODE) 2034,2036,2044
2034 CALL ERROR( 4)
2036 KOP(3) = MUELEC(NCOM)
2037 LABOP(3) = ROPE(NCOM)
2040 GO TO 2060
2044 KOP(3) = MOMAGN(NCOM)
2045 LABOP(3) = ROPM(NCOM)
2048 GO TO 2060
2052 KOP(2) = MOMAGN(NCOM - NUMCOM)
2056 KOP(3) = MUELEC(NCOM - NUMCOM)
2057 LABOP(2) = ROPM(NCOM - NUMCOM)
2058 LABOP(3) = ROPE(NCOM - NUMCOM)
C
C   THE NEXT TWO STATEMENTS STORE THE SYMMETRIES OF THE INITIAL STATE J
C   AND FINAL STATE K IN THE WAVE FUNCTION STORAGE SLOTS KWF(2), KWF(3).
C   THESE ASSIGNMENTS ALONG WITH THE OPERATOR ASSIGNMENTS ARE INITIAL
C   ASSIGNMENTS AND ARE LATER PERMUTED IN THE TERM DO LOOP.
C
2060 KWF(2) = IWFJ
2064 KWF(3) = IWFK
2065 LABWF(2) = AWFJ
2066 LABWF(3) = BWEK
2068 KOP(1) = 0
2072 KOP(4) = 0
2076 KOP(5) = 0
2077 LABOP(1) = DOPV
2078 LABOP(4) = DOPV
2079 LABOP(5) = DOPV
2080 KWF(1) = 0
2084 KWF(4) = 0
2088 KWF(5) = 0
2089 LABWF(1) = CWFL
2090 LABWF(4) = DWFM
2091 LABWF(5) = EWFN
C
C
C   THESE LAST SIX STATEMENTS INITIALIZE THE OPERATOR AND WAVE FUNCTION
C   STORAGE SLOTS THAT ARE NOT INITIALLY ASSIGNED ELECTRONIC STATE AND
C   TRANSITION MOMENT SYMMETRIES.
C
2092 IOPQ(1) = 0
2094 IOPQ(2) = 1
2096 IOPQ(3) = 1
2098 IOPQ(4) = 0
2100 IOPQ(5) = 0
2102 IWFQ(1) = 0
2104 IWFQ(2) = 1
2106 IWFQ(3) = 1
2108 IWFQ(4) = 0
2110 IWFQ(5) = 0

```

```

C
C   THESE LAST TEN STATEMENTS INDICATE THE KNOWLEDGE OF THE FIVE WAVE
C   FUNCTIONS AND THE FIVE OPERATORS. A 1 INDICATES A KNOWLEDGE, A 0
C   INDICATES A LACK OF KNOWLEDGE. AGAIN THESE ARE INITIAL ASSIGNMENTS
C   AND CHANGE DURING THE TERM PERMUTATIONS.
C
2111 NFITER = 18
2112 DO 2126 NUMMAT = 1,5
2114 IOQ = IOPQ(NUMMAT)
2116 IWQ = IWFQ(NUMMAT)
C
C   IOQ AND IWQ ARE DUMMY VARIABLES FOR STORING INFORMATION REGARDING
C   KNOWLEDGE OF THE UNIT SYMMETRIES OF WAVE FUNCTIONS AND OPERATORS.
C   THEY ARE USED AS INTERMEDIARIES IN THIS DO LOOP TO TRANSFER DATA
C   FROM THE ARRAYS IWFQ(NUMMAT), IOPQ(NUMMAT) TO THE ARRAYS
C   IWFQ(NUMMAT), IOPQA(NUMMAT) AND IWFQB(NUMMAT), IOPQB(NUMMAT).
C   THE ARRAYS IWFQB(NUMMAT), IOPQB(NUMMAT) HOLD FOR EACH TERM THE
C   SPECIFICATION OF THE INITIAL KNOWLEDGE OF WAVE FUNCTION AND OPERATOR
C   SYMMETRIES WITHOUT THE SUPPLEMENTARY SYMMETRIES SUPPLIED FOR N AND
C   N**2 TERMS AND BEFORE ANY MATRIX ELEMENTS ARE EVALUATED. THE ARRAYS
C   IWFQA(NUMMAT), IOPQA(NUMMAT) HOLD FOR EACH TERM SPECIFICATION OF THE
C   INITIAL KNOWLEDGE OF WAVE FUNCTION AND OPERATOR SYMMETRIES WITH
C   MODIFICATION DUE TO SUPPLEMENTARY SYMMETRY KNOWLEDGE BUT WITHOUT
C   THE MODIFICATION DUE TO MATRIX ELEMENT EVALUATION. THE ARRAYS
C   IWFQ(NUMMAT), IOPQ(NUMMAT) HOLD FOR EACH TERM ALL CURRENT KNOWLEDGE
C   OF WAVE FUNCTION AND OPERATOR SYMMETRIES.
C
2118 IOPQA(NUMMAT) = IOQ
2120 IWFQA(NUMMAT) = IWQ
2122 IOPQB(NUMMAT) = IOQ
2124 IWFQB(NUMMAT) = IWQ
2126 CONTINUE
2130 GO TO 2340
2140 IF (NCOM - 3) 2148,2148,2156
2148 NDCOM = NCOM
2152 GO TO 2160
2156 NDCOM = NCOM - 3
C   THIS IS THE PORTION OF THE 2000 SECTION THAT DOES THE PRELIMINARY
C   SETUP FOR THE TERM PERMUTATIONS FOR MAGNETIC CIRCULAR DICHROISM.
2160 GO TO (2164,2180,2196), NDCOM
2164 KOP(1) = MOELEC(2)
2168 KOP(2) = MOELEC(1)
2172 KOP(3) = MOMAGN(1)
2173 LABOP(1) = BOPE2
2174 LABOP(2) = AOPE1
2175 LABOP(3) = AOPM1
2176 GO TO 2208
2180 KOP(1) = MOELEC(1)
2184 KOP(2) = MOELEC(1)
2188 KOP(3) = MOMAGN(2)
2189 LABOP(1) = AOPE1
2190 LABOP(2) = AOPE1
2191 LABOP(3) = BOPE2
2192 GO TO 2208
2196 KOP(1) = MOELEC(1)
2200 KOP(2) = MOELEC(2)
2204 KOP(3) = MOMAGN(1)
2205 LABOP(1) = AOPE1

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2206 LABOP(2) = BOPE2
2207 LABOP(3) = AOPM1
2208 KOP(4) = C
2212 KOP(5) = C
2213 LABOP(4) = DOPV
2214 LABOP(5) = DOPV
2216 IOPQ(1) = 1
2220 IOPQ(2) = 1
2224 IOPQ(3) = 1
2228 IOPQ(4) = C
2232 IOPQ(5) = C
2236 KWF(2) = IWFK
2240 KWF(3) = IWFJ
2241 LABWF(2) = BWFK
2242 LABWF(3) = AWFJ
2244 KWF(4) = C
2248 KWF(5) = C
2249 LABWF(4) = CWFL
2250 LABWF(5) = DWFM
2252 IWFQ(2) = 1
2256 IWFQ(3) = 1
2260 IWFQ(4) = C
2264 IWFQ(5) = C
2268 IF (MODE - 2) 2272,2276,2292
2272 CALL ERROR(86)
2276 KWF(1) = C
2280 IWFQ(1) = C
2281 LABWF(1) = EWFN
2284 NFITER = 28
2288 GO TO 2112
2292 NFITER = 14
2296 IF (NCOM - 3) 2300,230C,2312
2300 KWF(1) = IWFJ
2304 IWFQ(1) = 1
2305 LABWF(1) = AWFJ
2308 GO TO 2112
2312 KWF(1) = IWFK
2316 KWF(2) = IWFJ
2320 KWF(3) = IWFK
2324 IWFQ(1) = 1
2325 LABWF(1) = BWFK
2326 LABWF(2) = AWFJ
2327 LABWF(3) = BWFK
2328 GO TO 2112
2340 IQPAOF = 4
2344 ITPADE = 1
2345 ICAC = C
2346 ICBC = C
2347 ICABC = C
2352 DO 8364 NTER = 1,NFITER
2353 ITECOM = C
2354 GO TO (2355,2355,2366,2366,2366), MODEPI
2355 NTRE = NTER - 12
2356 IF (NTRE) 2366,2366,2357
2357 GO TO (2358,2358,2360,2360,2363,2363), NTRE
2358 ICBC = 1
2359 GO TO 2366
2360 ICBC = C

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2361 ICAC = 1
2362 GO TO 2366
2363 ICAC = 0
2364 ICBC = 1
2365 ICABC = 1
2366 INZ(INTER) = 1
2367 CALL TERPER(NCOM, NTER, NMATEL, MODEPI)
2370 IF (ISKIP) 2372, 2372, 2402
2372 GO TO (2376, 2376, 2384, 2392, 2400), NMATEL
2376 CALL ERROR(87)
2380 FORMAT (/25X, I2, 1X, 5(7X, A1, 6X, A2))
2384 PRINT 2380, NTER, (LABWF(N), LABOP(N), N = 1, 3)
2388 GO TO 2402
2392 PRINT 2380, NTER, (LABWF(N), LABOP(N), N = 1, 4)
2396 GO TO 2402
2400 PRINT 2380, NTER, (LABWF(N), LABOP(N), N = 1, 5)
2402 IF (INZ(INTER)) 2403, 2484, 2404
2403 CALL ERROR(86)
2404 DO 2432 NUMMAT = 1, NMATEL
2408 IOQ = IOPQ(NUMMAT)
2412 IWQ = IWFQ(NUMMAT)
2416 IOPQA(NUMMAT) = IOQ
2420 IWFQA(NUMMAT) = IWQ
2424 IOPQB(NUMMAT) = IOQ
2428 IWFQB(NUMMAT) = IWQ
2432 CONTINUE
2436 IF (MODE - 1) 2440, 2440, 2468
2440 IOPONE = IOPADE
2444 IOPTWO = IOPADM
2448 IF (IOPADE - IOPADM) 2478, 2452, 2460
2452 CALL ERROR(88)
2456 GO TO 2480
2460 CALL SWAP (IOPONE, IOPTWO)
2462 ITAC = 1
2464 GO TO 2480
2468 IOPONE = ITPADE
2472 IOPTWO = IUPADE
2476 IOPTRF = IOPADM
2478 ITAC = 0
2480 GO TO 2700
2484 DO 2512 NA = 1, NMATEL
2488 IOQ = IOPQ(NA)
2492 IWQ = IWFQ(NA)
2496 IOPQB(NA) = IOQ
2500 IWFQB(NA) = IWQ
2504 IOPQA(NA) = IOQ
2508 IWFQA(NA) = IWQ
2512 CONTINUE
2516 GO TO 8360
2700 IF (MODE - 1) 2704, 2704, 2724
2704 IF (NMATEL - 3) 2708, 2708, 2716
2708 ICHVIB = 0
2712 GO TO 2764
2716 ICHVIB = 1
2720 GO TO 2728
2724 IF (NMATEL - 4) 2708, 2708, 2716
2728 NE = 0
2732 DO 2760 IMED = 1, NMATEL

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2740 IF (IMED - IOPONE) 2744,2760,2744
2744 IF (IMED - IOPTWO) 2748,2760,2748
2748 IF (MODE - 1) 2756,2756,2752
2752 IF (IMED - IOPTRE) 2756,2760,2756
2756 NE = NE + 1
2758 LVIB(NE) = IMED
2760 CONTINUE
2764 NTOT = NE

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C
C   IN THIS SECTION THE TERM PERMUTATIONS WERE OBTAINED BY INTERCHANGING
C   UNIT SYMMETRIES. A SWAP OF UNIT SYMMETRIES NECESSITATES ALSO A SWAP
C   OF THE STATE OF KNOWLEDGE OF THESE SYMMETRIES. SINCE ACTUAL
C   INTERCHANGE ONLY TAKES PLACE IN THE ARRAYS IOPQ(NUMMAT) AND
C   IWFQ(NUMMAT), THE PRECEEDING DO LOOP TRANSFERS THE INTRACHANGE
C   INFORMATION TO THE ARRAYS IOPQA(NUMMAT), IWFQA(NUMMAT) AND
C   IOPQB(NUMMAT), IWFQB(NUMMAT).
C   THE PROGRAM NOW ENTERS THE MATRIX ELEMENT PRODUCT SYMMETRY
C   CALCULATIONS SECTION, SECTION 3000.
C

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3004 NALL = 1
3012 NSQALL = 1

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C
C   THESE TWO STATEMENTS INITIALIZE THE CLOCKS USED FOR KEEPING TRACK
C   OF THE N AND N**2 TERMS WHEN THESE NEED BE COMPUTED. THE N
C   ADDITIONAL SYMMETRIES MUST BE COMPUTED FOR TERMS NTER=3-5,13-18.
C   THE N**2 ADDITIONAL SYMMETRIES ARE COMPUTED FOR NTER=9-12. THE
C   CHOOSING OF THE SYMMETRIES IS DONE IN THE 8000 SECTION, THE
C   SYMMETRY WRITE AND N,N**2 SELECTION SECTION. THE SUBSTITUTION OF
C   THESE SYMMETRIES IS DONE IN THE SUBROUTINE PROD. THE VALUES OF
C   LUNONQ AND NORNSQ (WHICH ARE INITIALIZED IN THE STATEMENTS 3016,
C   3018) DETERMINE WHETHER OR NOT THE N (OR N**2) SYMMETRY TERMS NEED
C   BE COMPUTED.
C

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3016 LUNONQ = 0
3018 NORNSQ = 0
3024 INDHCS = 0
3028 INDVGS = 0
3032 IDEGPM = 0
3036 IPRCLK = 0
3038 ISERCH = 0

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C
C   THE LAST 7 STATEMENTS ARE INITIALIZATION STATEMENTS. LUNONQ AND
C   NORNSQ ARE DESCRIBED ABOVE. INDHCS AND INDVGS ARE INDICES FOR
C   STORAGE OF SYMMETRIES FOR WAVE FUNCTIONS AND OPERATORS. IDEGPM AND
C   IPRCLK ARE DECISION VARIABLES USED IN SECTIONS 4000 AND 3000.
C   ISERCH IS USED TO SEARCH FOR THE CORRECT STARTING POINT IN
C   CALCULATING MATRIX ELEMENTS
C

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3040 DO 3052 NUMMAT = 1,NMATEL
3044 NDEGMP(NUMMAT) = 1
3048 MATELQ(NUMMAT) = 2
3052 CONTINUE

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C
C   THIS 3040 DO LOOP INITIALIZES NDEGMP(NUMMAT),MATELQ(NUMMAT).
C   THE FOLLOWING DO LOOP IS THE MAIN DO LOOP OF THE MATRIX ELEMENT
C   PRODUCT SYMMETRY CALCULATION SECTION. IT DOES THE GROUP
C   MULTIPLICATION FOR THE NMATEL=3,4,OR 5 MATRIX ELEMENT PRODUCTS.(THE
C   VALUE OF NMATEL DEPENDS ON THE TERM WE ARE DEALING WITH) THIS

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C SECTION STARTS WITH KNOWN WAVE FUNCTIONS AND OPERATORS AND SOLVES
C FOR THE UNKNOWN ONES USING THE GROUP MULTIPLICATION TABLES. IF ONE
C UNIT (UNKNOWN WAVE FUNCTION OR OPERATOR) HAS MORE THAN ONE POSSIBLE
C SYMMETRY SPECIES SOLUTION (DUE TO DIRECT PRODUCTS OF DEGENERATE
C SPECIES) ONE OF THESE POSSIBLE SPECIES IS CHOSEN AND THE REMAINDER
C PLACED IN A BUFFER STORAGE (THE VARIABLES ILWFB(S,INDHCS,NRS),
C ITWFB(S,INDHCS,NRS),IOPBS(S,INDHCS,NRS) ARE BUFFER STORAGE ARRAYS FOR
C THE LEADING WAVE FUNCTION, TRAILING WAVE FUNCTION, AND OPERATOR.
C A MATRIX ELEMENT IS REPRESENTED AS (LWF/OP/TWF). INDHCS INDEXES
C THE HORIZONTAL DIMENSION OF THE ARRAY AND THE UNITS ARE IN CALCULATE
C ORDER. NRS INDEXES THE VERTICAL DIMENSION OF THE ARRAY AND LABELS
C THE VARIOUS POSSIBLE SYMMETRY SPECIES FOR THE UNITS). THE SPECIES
C CHOSEN IS USED FOR CALCULATING THE REMAINING UNITS OF THE MATRIX
C ELEMENTS. IF OTHER MULTIPLE SPECIES OCCUR THE SAME PROCEDURE IS
C FOLLOWED AND MORE UNITS ARE STORED IN BUFFER. WHEN THE LAST MATRIX
C ELEMENT (IN CALCULATE ORDER) IS REACHED, IF THERE ARE MULTIPLE
C SPECIES NONE ARE STORED IN BUFFER - THAT IS ALL ARE CHOSEN. THESE
C UNITS ALONG WITH THE PREVIOUSLY CHOSEN UNITS (BY UNITS WE MEAN THE
C SYMMETRY SPECIES OF THE UNITS) ARE SENT TO BE ORDERED AND STORED
C IN THE GROUP STORER SECTION. THEN USING THE PROGRAM SET FORTH IN
C THE DEGENERATE PERMUTATION EXECUTION SECTION, STORED UNIT SYMMETRIES
C ARE EXTRACTED FROM THE BUFFER AREA AND USED FOR FURTHER
C CALCULATIONS IN THIS SECTION, THE MATRIX ELEMENT PRODUCT SYMMETRY
C CALCULATIONS SECTION.
C
C 3056 DO 3152 NUMMAT = 1,NMATL
C
C NMATL IS THE NUMBER OF MATRIX ELEMENTS. FOR TERMS 1,2 IT IS 3,
C FOR TERMS 3-8 IT IS 4, FOR TERMS 9-18 IT IS 5.
C
C 3060 IF (ISERCH) 3072,3072,3064
C
C AFTER EXTRACTING SYMMETRIES FROM THE BUFFER AREA WE RETURN TO THIS
C SECTION AND START TO RECALCULATE THE UNIT SYMMETRIES. FOR MOST OF
C THE RECALCULATIONS SOME OF THE PREVIOUS SYMMETRY CALCULATIONS WILL
C STILL BE VALID. IF WE FIND THE CORRECT STARTING POINT WE CAN AVOID
C DUPLICATING CALCULATIONS. IF ISERCH=1 WE MUST CONTINUE TO SEARCH
C FOR THIS POINT, IF ISERCH=0 WE HAVE FOUND THIS POINT, THE VALUE OF
C MELNDO, THE KEY MATRIX ELEMENT NUMBER, DICTIONARY ORDER, TELLS US
C WHERE THAT POINT IS. DICTIONARY ORDER IS THE ORIGINAL ORDER OF THE
C MATRIX ELEMENTS.
C
C 3064 IF (NUMMAT - MELNDO) 3152,3068,3152
C 3068 ISERCH = 0
C 3072 IF (MATELQ(NUMMAT)) 3074,3076,3152
C 3074 CALL ERROR( 6)
C
C WHEN MATELQ(NUMMAT)=1, THEN THE NUMMAT MATRIX ELEMENT (DICTIONARY
C ORDER) HAS ALREADY BEEN CALCULATED AND THUS THE SUBROUTINE PROD
C IS BYPASSED.
C
C 3076 CALL PROD(LUNONQ,NORNSQ,NALL,NSQALL,NUMMAT,NMATL)
C
C SUBROUTINE PROD COMPUTES THE MISSING SYMMETRIES OF THE THREE PART
C MATRIX ELEMENT (LWF/OP/TWF). IF ALL 3 SYMMETRIES ARE GIVEN IT
C DETERMINES WHETHER OR NOT THE ELEMENT IS ZERO. IF 2 OF 3 SYMMETRIES
C ARE GIVEN IT COMPUTES THE UNKNOWN ONE. IF ONE OR NONE OF THE 3
C SYMMETRIES ARE GIVEN THERE ARE TWO POSSIBILITIES. IF CALCULATION

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C   ON THE OTHER NMATL-1 MATRIX ELEMENTS DO NOT EVENTUALLY LEAD TO
C   KNOWLEDGE OF AT LEAST 2 OF THE 3 SYMMETRIES THEN THE N OR N**2
C   SECTION IS USED TO PROVIDE THE UNKNOWN SYMMETRIES. IF THESE
C   CALCULATIONS DO LEAD TO THE KNOWLEDGE OF AT LEAST 2 OF THE 3
C   SYMMETRIES, THEN THE N OR N**2 SECTION IS NOT NEEDED. IN THESE
C   CALCULATIONS, THE WAVE FUNCTIONS AND OPERATOR SYMMETRIES ARE STORED
C   BY THE SUBROUTINE IN THE ARRAYS JDSLWF(NRS), JDSTWF(NRS), AND
C   JDSOP(NRS) WHERE NRS IS THE INDEX LISTING THE SYMMETRY
C   POSSIBILITIES RESULTING FROM DIRECT PRODUCTS OF DEGENERATE SPECIES.
C
C   3080 IF (MATLQ(NUMMAT)) 3082,3152,3084
C   3082 CALL ERROR( 7)
C   3083 GO TO 3152
C
C   HERE IT IS CHECKED WHETHER THE SUBROUTINE HAS EVALUATED THE
C   UNKNOWN SYMMETRIES OF THE UNITS (WAVE FUNCTIONS AND OPERATOR) OF
C   THE MATRIX ELEMENTS. IF MATLQ(NUMMAT)=1, THE SYMMETRIES HAVE BEEN
C   EVALUATED.
C
C   3084 INDHCS = INDHCS + 1
C   3088 IDUCCO(INDHCS) = NUMMAT
C
C   INDHCS IS THE HORIZONTAL (ROW) INDEX FOR THE MATRIX ELEMENT UNIT
C   SYMMETRIES IN CALCULATE ORDER. THE DICTIONARY ORDER (NUMMAT)
C   CORRESPONDING TO CALCULATE ORDER (INDHCS) IS STORED IN IDUCCO(INDHCS).
C
C   3090 IF (NRIPS) 3091,3092,3096
C   3091 CALL ERROR(18)
C
C   NRIPS IS GREATER THAN ZERO EXCEPT FOR THE CASE WHERE THE SUBROUTINE
C   PROD, HAVING BEEN CALLED ON TO DEAL WITH A MATRIX ELEMENT WHERE ALL
C   3 UNIT SYMMETRIES ARE KNOWN, DETERMINES THAT IN THIS CASE THE UNIT
C   SYMMETRIES ARE INCOMPATIBLE AND THE MATRIX ELEMENT IS ZERO. IF THIS
C   IS SO NRIPS IS SET EQUAL TO ZERO, THERE IS NO STORAGE IN THE BUFFER
C   STORAGE OF WAVE FUNCTION AND OPERATOR SYMMETRIES.
C
C   3092 NCORIP(INDHCS) = 0
C   3094 GO TO 3152
C   3096 DO 3112 NRS = 1,NRIPS
C
C   THIS DO LOOP STORES THE SYMMETRY SPECIES GENERATED BY SUBROUTINE
C   PROD AND INDEXED BY NRS IN THE BUFFER STORAGE ARRAYS
C   ILWFBS(INDHCS,NRS), ITWFBS(INDHCS,NRS), IOPBS(INDHCS,NRS).
C
C   3100 ILWFBS(INDHCS,NRS) = JDSLWF(NRS)
C   3104 IOPBS(INDHCS,NRS) = JDSOP(NRS)
C   3108 ITWFBS(INDHCS,NRS) = JDSTWF(NRS)
C   3112 CONTINUE
C   3116 NCORIP(INDHCS) = NRIPS
C
C   NRIPS IS THE TOTAL NUMBER OF SYMMETRY POSSIBILITIES RESULTING FROM
C   THE GROUP PRODUCT OF DEGENERATE*DEGENERATE (NRIPS=2,3, OR 4),
C   DEGENERATE*NON-DEGENERATE (NRIPS=1), NON-DEGENERATE*NON-DEGENERATE
C   (NRIPS=1). IT IS STORED IN CALCULATE ORDER IN NCORIP(INDHCS) TO BE
C   LATER USED IN SECTION 5000, THE DEGENERATE PERMUTATION EXECUTION
C   SECTION
C
C   3120 IF (INDHCS - NMATL) 3124,3152,3122

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3122 CALL ERROR( 9)
3123 GO TO 3152
C
C   THIS BRANCH DETERMINES WHETHER OR NOT WE HAVE CALCULATED AND STORED
C   THE SYMMETRY SPECIES FOR ALL THE MATRIX ELEMENTS. IF SO WE HAVE
C   SYMMETRY SPECIES VALUES ASSIGNED TO ALL KWF(NUMMAT),KOP(NUMMAT),
C   NUMMAT =1,NMATEL. IF NOT WE CHOOSE FROM THE NRIPS SETS OF UNIT
C   SYMMETRIES, THE SET DESIGNATED BY NDEGMP(NUMMAT). ALL THE
C   NDEGMP(NUMMAT), NUMMAT =1,NMATEL, ARE INITIALLY SET EQUAL TO 1,
C   THEREBY SPECIFYING THE CHOOSING OF THE FIRST SETS. FOR THE CURRENT
C   NUMMAT THE FIRST SET OF UNIT SYMMETRIES ARE SET IN KWF(NUMMAT + 1),
C   KOP(NUMMAT), KWF(NUMMAT). THESE ARE THEN USED IN THE SUBROUTINE
C   PROD TO CALCULATE THE UNIT SYMMETRIES FOR REMAINING UNCALCULATED
C   MATRIX ELEMENTS. IN THE CASE OF ANY MATRIX ELEMENT HAVING MORE THAN
C   ONE SET OF UNIT SYMMETRIES, THAT IS NRIPS=2,3, OR 4, THE VALUE OF
C   NDEGMP(NUMMAT) WILL BE REASSIGNED IN TURN BY THE DEGENERATE
C   PERMUTATION EXECUTION SECTION ALL INTEGER VALUES UP TO NRIPS, THUS
C   CAUSING THE CHOOSING OF AND CALCULATION WITH THE APPROPRIATE SETS.
C   SINCE ALL CURRENTLY UNUSED SETS ARE STORED IN THE BUFFER AREA, THEY
C   CAN BE DRAWN UPON WHEN NEEDED.
C
3124 NDEGPS = NDEGMP(NUMMAT)
3128 KOP(NUMMAT) = JDSOP(NDEGPS)
3132 KWF(NUMMAT) = JDSTWF(NDEGPS)
3136 IF (NUMMAT - NMATEL) 3140,3148,3138
3138 CALL ERROR(10)
3139 GO TO 3148
3140 KWF(NUMMAT + 1) = JDSLWF(NDEGPS)
3144 GO TO 3152
3148 KWF(1) = JDSLWF(NDEGPS)
3152 CONTINUE
C
C   WE NOW CALCULATE WHETHER THIS SET OF PASSES THROUGH THE 3056 NUMMAT
C   DO LOOP HAS FINISHED THE CALCULATION OF UNIT SYMMETRIES FOR ALL
C   NMATEL MATRIX ELEMENTS.
C
3156 MALLEC = 0
3160 DO 3168 IM = 1,NMATEL
3164 MALLEC = MALLEC + MATELQ(IM)
3168 CONTINUE
3172 IF (MALLEC - NMATEL) 3176,4002,3174
3174 CALL ERROR(11)
3175 GO TO 4002
C
C   IF ALL MATRIX ELEMENTS HAVE BEEN CALCULATED THEN MALLEC=NMATEL. IF
C   MALLEC IS LESS THAN NMATEL THEN NOT ALL MATRIX ELEMENTS HAVE BEEN
C   CALCULATED AND WE MUST GO BACK FOR ANOTHER SET OF PASSES THROUGH
C   THE 3056 NUMMAT DO LOOP. IF, HOWEVER, SUCCESSIVE SETS OF PASSES
C   THROUGH THE LOOP DO NOT INCREASE THE NUMBER OF CALCULATED MATRIX
C   ELEMENTS, WE ARE THEN DEALING WITH EITHER AN N OR N**2 CASE. THE
C   FOLLOWING STATEMENTS PRECEEDING THE RETURN TO THE 3056 LOOP DECIDE
C   WHETHER THE LAST SET OF PASSES THROUGH THE DO LOOP CALCULATED ANY
C   NEW MATRIX ELEMENTS.
C
3176 IPRCLK = IPRCLK + 1
3180 NUMUME(IPRCLK) = MALLEC
3184 IF (IPRCLK - 1) 3186,3056,3188
3186 CALL ERROR(12)

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3187 GO TO 3056
C
C   THE NUMBER OF MATRIX ELEMENTS CALCULATED BY THE TIME WE DO THE SET
C   OF PASSES OF THE 3056 DO LOOP IPRCLK TIMES IS STORED IN THE SLOTS
C   NUMUME(IPRCLK). ONCE WE HAVE GONE THROUGH THE LOOP TWO OR MORE
C   TIMES WE CHECK BY STATEMENTS 3188 AND 3192 WHETHER THERE HAS BEEN
C   AN INCREASE IN THE NUMBER OF MATRIX ELEMENTS CALCULATED. IF NOT WE
C   REINITIALIZE IPRCLK AND SET NEW VALUES OF LUNONQ AND NORNSQ SO AS
C   TO ACTIVATE THE N OR N**2 PROCEDURE. WE THEN RETURN TO THE 3056
C   DO LOOP. THIS CHECK IS TERMED A FURTHER PROGRESS CHECK.
C
3188 NAGAIN = NUMUME(IPRCLK) - NUMUME(IPRCLK - 1)
3192 IF (NAGAIN) 3194,3196,3056
3194 CALL ERROR(13)
3196 IPRCLK = 0
3200 LUNONQ = LUNONQ + 1
3204 NORNSQ = NORNSQ + 1
3208 GO TO 3056
C
3300 NIRP = 0
3304 DO 3320 N = 1,NMATEL
3308 IF (NCORIP(N)) 3312,3320,3316
3312 CALL ERROR(98)
3316 NIRP = NIRP + 1
3320 CONTINUE
3324 IF (NIRP - NMATEL) 4056,4008,4006
C
C   THE 4006 SECTION, THE GROUP STORER AND LOOP DETERMINATION SECTION,
C   IS NOW BEGUN. THE UNIT SYMMETRIES OF THE NMATEL MATRIX ELEMENTS
C   ARE STORED IN THE ARRAYS JWFGPO(IHDOME,INDVGS) (FOR WAVE FUNCTIONS)
C   AND JOPGPO(IHDOME,INDVGS) (FOR OPERATORS). THE WAVE FUNCTION STORED
C   IS THE TRAILING WAVE FUNCTION. SINCE THE SYMMETRY OF THE NUMMAT
C   LEADING WAVE FUNCTION IS IDENTICAL TO THAT OF THE NUMMAT+1 TRAILING
C   WAVE FUNCTION, ALL INFORMATION REGARDING LEADING WAVE FUNCTION
C   SYMMETRIES IS INCLUDED IN THE TRAILING WAVE FUNCTION SYMMETRIES.
C   IHDOME INDEXES THE HORIZONTAL DIMENSION OF THE ARRAY, THE MATRIX
C   ELEMENTS IN DICTIONARY ORDER. THUS THE GROUP STORER SECTION ACTS AS
C   A MATRIX ELEMENT ORDER CONVERTER, FROM CALCULATE ORDER TO
C   DICTIONARY ORDER. INDVGS INDEXES THE VERTICAL DIMENSION OF THE
C   ARRAY, THE GROUP PRODUCT TERMS IN GROUP ORDER. THUS A GROUP PRODUCT
C   TERM CONSISTS OF THE UNIT SYMMETRY SPECIES OF NMATEL MATRIX
C   ELEMENTS IN DICTIONARY ORDER (HORIZONTAL DIMENSION). GROUP PRODUCT
C   TERMS ARE STORED VERTICALLY IN BLOCKS OF NRIPS. NRIPS VARIES AND IT
C   IS THE NUMBER OF POSSIBLE UNIT SYMMETRY COMBINATIONS FOR THE LAST
C   (CALCULATE ORDER) MATRIX ELEMENT. FOR THE OTHER MATRIX ELEMENTS
C   THE UNIT SYMMETRY SPECIES ARE IDENTICAL FOR ALL THE NRIPS GROUP
C   PRODUCT TERMS. WHICH OF THE VARIOUS CALCULATED UNIT SYMMETRY
C   SPECIES ARE CHOSEN TO BE STORED BY THE GROUP STORER SECTION IS
C   DETERMINED BY THIS SECTION ALONG WITH SECTIONS 3000 AND 5000.
C
4002 IPRCLK = 0
4003 LUNONQ = 0
4004 NORNSQ = 0
4005 GO TO 3300
C
C   IPRCLK, NORNSQ ARE REINITIALIZED. IN THE DEGENERATE PERMUTATION EXECUTION
C   SECTION SYMMETRY PERMUTATIONS ARE PERFORMED AND THE MATRIX ELEMENT
C   PRODUCTS PREPARED FOR FURTHER CALCULATION. FOR THESE CALCULATIONS
C   ONE RETURNS TO THE MATRIX ELEMENT PRODUCT SYMMETRY CALCULATIONS

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C   SECTION. IN SUCH CALCULATIONS A FURTHER PROGRESS CHECK MAY BE
C   REQUIRED. THUS NORNSQ IS REINITIALIZED HERE.
C
C   4006 CALL ERROR(14)
C   4007 GO TO 4056
C
C   IF NRIPS IS EQUAL TO ZERO, THEN ONE OF THE NMATEL MATRIX
C   ELEMENTS FOR THIS GROUP PRODUCT TERM IS ZERO AND WE SKIP THE
C   REORDERING AND STORAGE OF THIS GROUP PRODUCTS UNIT SYMMETRIES (AS
C   THE GROUP PRODUCT TERM IS ZERO).
C
C   4008 DO 4052 NRS = 1,NRIPS
C
C   THIS DO LOOP ORDERS THE VERTICAL DIMENSION OF THE ARRAY, THE GROUP
C   PRODUCT TERMS. IT IS A REORDERING LOOP, WITH AN OLD INDEX NRS.
C   A SET OF UNIT SYMMETRIES HAVING BEEN DETERMINED FOR ALL BUT THE
C   LAST MATRIX ELEMENT, NRS INDEXES THE NRIPS POSSIBLE UNIT SYMMETRIES
C   FOR THE LAST MATRIX ELEMENT GIVEN THESE UNIT SYMMETRIES FOR THE
C   OTHER NMATEL-1 MATRIX ELEMENTS. THE NEW INDEX IS INDVGS. THIS
C   INDEXES GROUP PRODUCT TERMS, EACH OF WHICH CONSISTS OF UNIT
C   SYMMETRIES FOR NMATEL MATRIX ELEMENTS. IT STACKS VERTICALLY ALL THE
C   NRIPS BLOCKS OF NMATEL MATRIX ELEMENTS.
C
C   4012 INDVGS = INDVGS + 1
C   4016 DO 4052 NUMMAC = 1,NMATEL
C
C   THIS DO LOOP ORDERS THE HORIZONTAL DIMENSION OF THE ARRAY, THE
C   MATRIX ELEMENTS. IT IS A REORDERING LOOP, GOING FROM CALCULATE
C   ORDER, INDEXED BY NUMMAC, TO DICTIONARY ORDER, INDEXED BY IHDOME,
C   WHERE IHDOME IS RELATED TO NUMMAC BY IHDOME=IDOC(NUMAC).
C
C   4020 IHDOME = IDOC(NUMAC)
C   4024 IF (NUMMAC - NMATEL) 4028,4044,4026
C   4026 CALL ERROR(15)
C   4027 GO TO 4044
C
C   FOR EACH MATRIX ELEMENT BUT THE LAST, THE UNIT SYMMETRIES STORED
C   ARE INDEPENDENT OF NRS. FOR THE LAST MATRIX ELEMENT (CALCULATE
C   ORDER), THE UNIT SYMMETRIES STORED ARE DIFFERENT FOR EACH VALUE
C   OF NRS.
C
C   4028 NOEGPS = NOEGMP(IHDOME)
C
C   FOR EACH OF THE MATRIX ELEMENTS THERE MAY BE MORE THAN ONE POSSIBLE
C   SET OF UNIT SYMMETRIES. IN SECTION 3000 AND 5000 WE CALCULATE OUR
C   GROUP PRODUCT TERMS FROM A PYRAMIDAL POINT OF VIEW. THAT IS WE
C   CALCULATE THE FIRST MATRIX ELEMENT, CHOOSE ONE OF THE SETS OF UNIT
C   SYMMETRIES, USE THIS SET TO CALCULATE THE SECOND MATRIX ELEMENT,
C   CHOOSE ONE OF ITS SETS AND SO ON UNTIL ALL MATRIX ELEMENTS HAVE
C   BEEN CALCULATED. WE THEN STORE THESE UNIT SYMMETRIES IN THIS SECTION
C   KEEPING TRACK OF WHICH SETS WE HAVE CHOSEN BY STORAGE IN THE ARRAY
C   NOEGMP(IHDOME). THEN OF COURSE WE MUST RETURN TO CONSIDER THE
C   UNCHOSEN SETS AND MAKE FURTHER PYRAMIDAL CALCULATIONS AND STORAGE.
C
C   4032 JOPGPO(IHDOME,INDVGS) = IOPBS(NUMMAC,NOEGPS)
C   4036 JWFGPO(IHDOME,INDVGS) = ITWFB(NUMMAC,NOEGPS)
C   4040 GO TO 4052
C   4044 JOPGPO(IHDOME,INDVGS) = IOPBS(NUMMAC,NRS)

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4048 JWF6PO(IHDOME,INDVGS) = ITWFB5(NUMMAC,NRS)
4052 CONTINUE
4056 IF (IDEGPM) 4058,4060,4068
4058 CALL ERROR(16)
C
C   IF IDEGPM=C THIS IS THE FIRST TIME THROUGH THE GROUP STORER SECTION
C   AND WE HAVE NOT DONE ANY DEGENERATE PERMUTATIONS. IF IDEGPM=1, WE
C   HAVE ALREADY BEGUN THE PERMUTATIONS
C
4060 IDEGPM = 1
4064 GO TO 5004
4068 IF (ILPYES) 4070,4072,5104
4070 CALL ERROR(17)
C
C   IF ILPYES=C WE CHECK JLPYES. IF ILPYES=1, WE TRANSFER INTO THE
C   I-LOOP PORTION OF THE DEGENERATE PERMUTATION EXECUTION SECTION.
C   THIS IS WHERE WE CHOOSE NEW UNIT SYMMETRY SETS FOR THE FIRST
C   (CALCULATE ORDER) MATRIX ELEMENT. CORRESPONDINGLY JLPYES CAN
C   TRANSFER US TO J-LOOP WHICH CONSIDERS PERMUTATIONS FOR THE SECOND
C   MATRIX ELEMENT. FINALLY KLPYES CAN TRANSFER TO EITHER K-LOOP FOR
C   THE THIRD MATRIX ELEMENT OR L-LOOP FOR THE FOURTH MATRIX ELEMENT.
C   THE L-LOOP IS USED ONLY FOR NMATEL=5, THE K-LOOP ONLY FOR
C   NMATEL=4,5.
C
4072 IF (JLPYES) 4074,4076,5184
4074 CALL ERROR(18)
4076 IF (KLPYES) 4078,5340,5264
4078 CALL ERROR(19)
4080 GO TO 5340
C
C   THE DEGENERATE PERMUTATION EXECUTION SECTION, SECTION 5000, IS NOW
C   BEGUN. THIS SECTION WORKS IN CONJUNCTION WITH THE MATRIX ELEMENT
C   PRODUCT SYMMETRY CALCULATIONS SECTION TO CALCULATE THE UNIT
C   SYMMETRIES FOR ALL THE MATRIX ELEMENTS OF ALL THE PERMUTATIONS
C   DUE TO MULTIPLE PRODUCTS OF DEGENERATE REPRESENTATIONS. THERE ARE
C   FOUR LOOPS, I,J,K,L, IN SECTION 5000. THESE LOOPS DO THE
C   PERMUTATIONS FOR FIRST, SECOND, THIRD, AND FOURTH MATRIX ELEMENT
C   UNIT SYMMETRIES, RESPECTIVELY. DEPENDING UPON WHICH LOOP IS
C   OPERATING THE VALUES ICLKRP, JCLKRP, KCLKRP, LCLKRP ARE USED TO
C   RESET THE UNIT SYMMETRIES. WITH THE I-LOOP OPERATING, NEW UNIT
C   SYMMETRY SETS ARE SUPPLIED FOR THE IELNDO MATRIX ELEMENT, THAT IS
C   KWF(IELNDO+1), KOP(IELNDO), KWF(IELNDO). IELNDO IS THE ELEMENT
C   NUMBER, DICTIONARY ORDER, THAT IS BEING HANDLED BY THE I-LOOP.
C   ICLKRP VARIES FROM 1 TO ICORIP, WHERE ICORIP=NCURIP(1), THE TOTAL
C   NUMBER OF POSSIBLE SETS FOR THE FIRST MATRIX ELEMENT. THE PARTICULAR
C   SET OF UNIT SYMMETRIES TO BE CHOSEN FOR THE FIRST MATRIX ELEMENT
C   IS SPECIFIED BY NDEGMP(IELNDO) WHICH IS SET EQUAL TO THE CURRENT
C   VALUE OF ICLKRP. THIS VALUE CONTAINS THE BUFFER STORAGE INDEX FOR
C   THE CORRECT SET. THE J,K,L-LOOPS OPERATE IN AN IDENTICAL MANNER
C   WITH THE VARIABLES IELNDO, ICURIP REPLACED BY JELNDO, JCORIP FOR
C   THE J-LOOP, KELNDO, KCURIP FOR THE K-LOOP, AND LELNDO,LCORIP FOR
C   THE L-LOOP
C
5004 ILPYES = 0
5008 JLPYES = 0
5012 KLPYES = 0
5016 INMERD = NMATEL - 1
5020 JNMERD = NMATEL - 2

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5024 KNMERD = NMATEL - 3
5028 LNMERD = NMATEL - 4
C
C   INNERD, JNMERD, KNMERD, LNMERD GIVE THE TOTAL NUMBER OF MATRIX
C   ELEMENTS THAT MUST BE DETERMINED BY THE I,J,K,L-LOOPS.
C
5032 IELNDO = IDOCCO(1)
C
C   IELNDO IS THE DICTIONARY ORDER NUMBER OF THE FIRST (CALCULATE
C   ORDER) MATRIX ELEMENT.
C
5036 ICORIP = NCORIP(1)
5037 IF (ICORIP) 5038,5364,5040
5038 CALL ERROR(20)
5039 GO TO 5364
C
C   IF NCORIP(1)=0 THIS INDICATES THAT THE FIRST CALCULATE ORDER MATRIX
C   ELEMENT IS ZERO AND WE DO NOT DO PERMUTATIONS ON THIS OR ANY OF THE
C   SUCCEEDING MATRIX ELEMENTS. IN THE J,K,L LOOPS SIMILAR BRANCHINGS
C   EXIST FOR THE SECOND, THIRD, FOURTH ELEMENTS. IF ICORIP IS NOT ZERO,
C   ICORIP IS THE PRESENT NUMBER OF POSSIBLE UNIT SYMMETRY SETS FOR THE
C   FIRST (CALCULATE ORDER) MATRIX ELEMENT.
C
5040 DO 5360 ICLKRP = 1, ICORIP
C
C   THIS I-LOOP CONSIDERS IN TURN ALL OF THE POSSIBLE SETS OF UNIT
C   SYMMETRIES FOR THE FIRST MATRIX ELEMENT (CALCULATE ORDER). AS THE
C   FIRST SET (ICLKRP=1) HAS ALREADY BEEN USED TO CALCULATE SYMMETRIES
C   OF SUBSEQUENT MATRIX ELEMENTS, IT IS BYPASSED. FOR ALL OTHER VALUES
C   OF ICLKRP ALL UNIT SYMMETRIES OF SUBSEQUENT MATRIX ELEMENTS ARE
C   RECALCULATED. THIS IS DONE BY A RETURN TO SECTION 3000 AND STORAGE
C   IN SECTION 4000. IN THE I-LOOP THERE IS A BRANCH POINT TO THE
C   J-LOOP FOR EACH VALUE OF ICLKRP=1, ICORIP. THUS FOR EACH VALUE OF
C   ICLKRP, THE J-LOOP CONSIDERS IN TURN ALL POSSIBLE SETS OF UNIT
C   SYMMETRIES FOR THE SECOND MATRIX ELEMENT (CALCULATE ORDER). AN
C   IDENTICAL DESCRIPTION PROCEEDS FOR THE K-LOOP TREATING THE THIRD
C   MATRIX ELEMENT FOR NMATEL=4,5, AND FOR THE L-LOOP TREATING THE
C   FOURTH MATRIX ELEMENT FOR NMATEL=5. IN THIS MANNER ALL UNIT
C   SYMMETRY PERMUTATIONS ARE CONSIDERED.
C
5044 IF (ICLKRP - 1) 5046,5104,5048
5046 CALL ERROR(21)
5047 GO TO 5104
5048 NDEGMP(IELNDO) = ICLKRP
C
C   THIS VALUE SPECIFIES THE SET OF UNIT SYMMETRIES OF THE IELNDO
C   MATRIX ELEMENT THAT IS TO BE DRAWN FROM BUFFER TO BE USED IN THE
C   CALCULATIONS OF SECTION 3000.
C
5052 DO 5064 IERCLK = 1, INNERD
C
C   THIS DO LOOP RESETS THE SECOND THROUGH INNERD=NMATEL-1 MATRIX
C   ELEMENTS (CALCULATE ORDER) SO THAT THEY CAN BE RECALCULATED. MEIND
C   IS DUMMY STORAGE FOR THE DICTIONARY ORDER MATRIX ELEMENT INDEX FOR
C   EACH OF THESE MATRIX ELEMENTS IN TURN. ALL MATELQ(MEIND) AND
C   NDEGMP(MEIND) ARE REINITIALIZED AT 0 AND 1 RESPECTIVELY. THIS
C   INDICATES THAT PRIOR TO RETURN TO SECTION 3000 THE MEIND MATRIX
C   ELEMENT (DICTIONARY ORDER) HAS NOT BEEN RECALCULATED (DESIGNATED BY

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C   MATELQ(MEIND)=C) AND THAT WHEN RECALCULATED, THE INITIAL CHOICE
C   OF UNIT SYMMETRY SETS WILL BE THE FIRST ONE (NDEGMP(MEIND)=1).
C
5054 MEIND = IDUCCO(NMATEL - IERCLK + 1)
5056 MATELQ(MEIND) = 0
5058 NDEGMP(MEIND) = 1
5060 IWFQ(MEIND) = IWFQA(MEIND)
5062 IOPQ(MEIND) = IOPQA(MEIND)
C
C   IWFQ(MEIND) AND IOPQ(MEIND), WHICH HOLD THE PRESENT STATE OF
C   KNOWLEDGE OF THE WAVE FUNCTION AND OPERATOR UNIT SYMMETRIES OF THE
C   MEIND MATRIX ELEMENT ARE SET TO THE ORIGINAL STATE OF KNOWLEDGE
C   OF THESE UNIT SYMMETRIES (INCLUDING THE SUPPLEMENTARY SYMMETRIES)
C   FOR ALL THE MEIND MATRIX ELEMENTS THAT MUST BE RECALCULATED. THIS
C   LOOP CAN LOSE INFORMATION WITH REGARD TO THE STATE OF KNOWLEDGE OF
C   THE WAVEFUNCTION UNIT SYMMETRIES. IN ORDER TO AVOID THIS IWFQ(MEIND)
C   AND IWFQ(MEIND + 1) ARE SET EQUAL TO ONE FOR ALL MEIND MATRIX
C   ELEMENTS THAT ARE NOT RECALCULATED. THIS IS DONE IN THE FOLLOWING
C   STATEMENTS 5066, 5068, 5070. IN THE J,K,L-LOOPS IT IS DONE BY
C   DO LOOPS
C
5064 CONTINUE
5065 NFIND = IDUCCO(1)
5066 IWFQ(NFIND) = 1
5067 IF (NMATEL - NFIND) 5068,5069,5071
5068 CALL ERROR(74)
5069 IWFQ(1) = 1
5070 GO TO 5072
5071 IWFQ(NFIND + 1) = 1
5072 INDHCS = 1
5076 ISERCH = 1
5080 MELNDO = IELNDO
C
C   INITIALIZATION FOR SECTION 3000 IN STATEMENTS 5072, 5076, 5080.
C
5084 ILPYES = 1
C
C   REINITIALIZING FOR SECTION 4000 IN STATEMENT 5084.
C
5085 IF (NMATEL - IELNDO) 5086,5087,5090
5086 CALL ERROR(75)
5087 KWF(1) = ILWFRS(1,ICLKRP)
5088 GO TO 5092
5090 KWF(IELNDO + 1) = ILWFRS(1,ICLKRP)
5092 KOP(IELNDO) = IOPBS(1,ICLKRP)
5096 KWF(IELNDO) = ILWFRS(1,ICLKRP)
C
C   UNIT SYMMETRIES DRAWN FROM BUFFER STORAGE AND PLACED IN KWF(IELNDO),
C   KWF(IELNDO+1),KOP(IELNDO) TO BE USED FOR CALCULATIONS IN SECTION
C   3000.
C
5100 GO TO 3056
C
C   HERE WE RETURN TO MATRIX ELEMENT PRODUCT SYMMETRY CALCULATIONS
C   SECTION, SECTION 3000. REENTRIES TO THE I-LOOP ARE AT STATEMENT 5104.
C
5104 IF (JNMERO) 5106,5106,5108
5106 CALL ERROR(22)

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C
C   THIS IS OUR BRANCH POINT TO THE J-LOOP. IN ALL CASES THAT WE
C   CONSIDER JNMRD IS GREATER THAN ZERO. THEREFORE IT IS NOT REALLY
C   A BRANCH POINT, BUT A DISGUISED GO TO. IT IS DONE THIS WAY TO
C   MAINTAIN UNIFORMITY IN FLOW CHART FORM WITH KNMRD AND LNMRD. THUS
C   THIS STATEMENT COULD BE WRITTEN GO TO 5128 AND WE GO TO THE J-LOOP.
C
5108 ILPYES = 0
5112 JELNDO = IDOCCO(2)
5116 JCORIP = NCORIP(2)
5117 IF (JCORIP) 5118,5356,5120
5118 CALL ERROR(23)
5119 GO TO 5356
5120 DO 5352 JCLKRP = 1, JCORIP
5123 IF (JCLKRP - 1) 5124,5184,5126
5124 CALL ERROR(24)
5125 GO TO 5184
5126 NDEGMP(JELNDO) = JCLKRP
5128 DO 5140 JERCLK = 1, JNMRD
5130 MEIND = IDOCCO(NMATEL - JERCLK + 1)
5132 MATELQ(MEIND) = 0
5134 NDEGMP(MEIND) = 1
5136 IWFQ(MEIND) = IWFQA(MEIND)
5138 IOPQ(MEIND) = IOPQA(MEIND)
5140 CONTINUE
5142 DO 5150 NIND = 1,2
5143 NEIND = IDOCCO(NIND)
5144 IWFQ(NEIND) = 1
5145 IF (NMATEL - NEIND) 5146,5147,5149
5146 CALL ERROR(75)
5147 IWFQ(1) = 1
5148 GO TO 5150
5149 IWFQ(NEIND + 1) = 1
5150 CONTINUE
5152 INDHCS = 2
5156 ISERCH = 1
5160 MELNDO = JELNDO
5164 JLPYES = 1
5165 IF (NMATEL - JELNDO) 5166,5167,5170
5166 CALL ERROR(71)
5167 KWF(1) = ILWFBS(2, JCLKRP)
5168 GO TO 5172
5170 KWF(JELNDO + 1) = ILWFBS(2, JCLKRP)
5172 KOP(JELNDO) = IOPBS(2, JCLKRP)
5176 KWF(JELNDO) = ITWFBS(2, JCLKRP)
5180 GO TO 3056
5184 IF (KNMRD) 5186,5352,5188
5186 CALL ERROR(25)
5187 GO TO 5352
C
C   BRANCH POINT TO K-LOOP. WE ENTER K-LOOP ONLY FOR NMATEL=4,5.
C   OTHERWISE WE IMMEDIATELY FINISH THE J-LOOP AND RETURN TO THE
C   I-LOOP
C
5188 JLPYES = 0
5192 KELNDO = IDOCCO(3)
5196 KCORIP = NCORIP(3)
5197 IF (KCORIP) 5198,5348,5200

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5198 CALL ERROR(26)
5199 GO TO 5348
5200 DO 5344 KCLKRP = 1,KCORIP
5203 IF (KCLKRP - 1) 5204,5264,5206
5204 CALL ERROR(27)
5205 GO TO 5264
5206 NDEGMP(KELNDO) = KCLKRP
5208 DO 5220 KERCLK = 1,KNMERD
5210 MEIND = 100000(NMATL - KERCLK + 1)
5212 MATLQ(MEIND) = 0
5214 NDEGMP(MEIND) = 1
5216 IWFQ(MEIND) = IWFQA(MEIND)
5218 IOPQ(MEIND) = IOPQA(MEIND)
5220 CONTINUE
5222 DO 5230 NIND = 1,3
5223 NEIND = 100000(NIND)
5224 IWFQ(NEIND) = 1
5225 IF (NMATL - NEIND) 5226,5227,5229
5226 CALL ERROR(76)
5227 IWFQ(1) = 1
5228 GO TO 5230
5229 IWFQ(NEIND + 1) = 1
5230 CONTINUE
5232 INDHCS = 3
5236 ISERCH = 1
5240 MELNDO = KELNDO
5244 KLPYES = 1
5245 IF (NMATL - KELNDO) 5246,5247,5250
5246 CALL ERROR(72)
5247 KWF(1) = ILWFBS(3,KCLKRP)
5248 GO TO 5252
5250 KWF(KELNDO + 1) = ILWFBS(3,KCLKRP)
5252 KOP(KELNDO) = IOPBS(3,KCLKRP)
5256 KWF(KELNDO) = ITWFBS(3,KCLKRP)
5260 GO TO 5056
5264 IF (LNMERD) 5266,5344,5268
5266 CALL ERROR(28)
5267 GO TO 5344
C
C   BRANCH POINT TO L-LOOP. WE ENTER THE L-LOOP ONLY FOR NMATL=5.
C   OTHERWISE WE IMMEDIATELY FINISH THE K-LOOP AND RETURN TO THE
C   J-LOOP
C
5268 KLPYES = 0
5272 LELNDO = 100000(4)
5276 LKORIP = NKORIP(4)
5277 IF (LKORIP) 5278,5344,5280
5278 CALL ERROR(29)
5279 GO TO 5344
5280 DO 5340 LCLKRP = 1,LKORIP
5283 IF (LCLKRP - 1) 5284,5340,5286
5284 CALL ERROR(30)
5285 GO TO 5340
5286 NDEGMP(LELNDO) = LCLKRP
5288 DO 5300 LERCLK = 1,LNMERD
5290 MEIND = 100000(NMATL - LERCLK + 1)
5292 MATLQ(MEIND) = 0
5294 NDEGMP(MEIND) = 1

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5296 IWFQ(MEIND) = IWFQA(MEIND)
5298 IOPQ(MEIND) = IOPQA(MEIND)
5300 CONTINUE
5302 DO 5310 NIND = 1,4
5303 NEIND = IDOCCO(NIND)
5304 IWFQ(NEIND) = 1
5305 IF (NMATEL - NEIND) 5306,5307,5309
5306 CALL ERROR(77)
5307 IWFQ(1) = 1
5308 GO TO 5310
5309 IWFQ(NEIND + 1) = 1
5310 CONTINUE
5312 INDHCS = 4
5316 ISERCH = 1
5320 MELNDO = LELNDO

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C
C   UNLIKE THE I,J,K-LOOPS WHICH SET ILPYES, JLPYES, KLPYES=1, THERE IS
C   NO LLPYES
C

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5321 IF (NMATEL - LELNDO) 5322,5323,5326
5322 CALL ERROR(73)
5323 KWF(1) = ILWFS(4,LCLKRP)
5324 GO TO 5328
5326 KWF(LELNDO + 1) = ILWFS(4,LCLKRP)
5328 KOP(LELNDO) = IOPBS(4,LCLKRP)
5332 KWF(LELNDO) = ITWFS(4,LCLKRP)
5336 GO TO 3056

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C
C   HERE WE GO TO SECTION 3000. WHEN WE RETURN WE DO NOT BRANCH BUT
C   CONTINUE ON WITH THE L DO LOOP UNTIL DONE.
C

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5340 CONTINUE
5344 CONTINUE
5348 KLPYES = 0
5352 CONTINUE
5356 JLPYES = 0
5360 CONTINUE
5364 ILPYCS = 0
5368 GO TO 6002
5400 IF (LPOS) 5404,5404,5412
5404 LPOS = 0
5408 GO TO 6008
5412 GO TO (5416,5424,5444,5444,5444), MODEPI
5416 LPOS = 0
5420 GO TO 6008
5424 IF (ITAC) 5428,5428,5436
5428 LPOS = IOPTW0
5432 GO TO 6008
5436 LPOS = IOPTW1
5440 GO TO 6008
5444 LPOS = IOPTRE
5448 GO TO 6008

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C
C   SECTION 6000, THE COUPLING COEFFICIENT SET AND INITIAL PRODUCT
C   DETERMINATION SECTION INCLUDES A CALL FOR THE SUBROUTINE SEARCH.
C   THIS SUBROUTINE HAS AS INPUT THE UNIT SYMMETRIES OF THE PARTICULAR
C   MATRIX ELEMENT OF THE PARTICULAR GROUP PRODUCT TERM BEING
C   INVESTIGATED. THE OUTPUT IS AN ORDERED SET OF COUPLING COEFFICIENTS.

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C   IF ALL UNITS (TWO WAVE FUNCTIONS AND ONE OPERATOR) ARE OF A
C   NON-DEGENERATE NATURE, THEN THE COUPLING COEFFICIENT SET IS TRIVIAL
C   AND CONSISTS OF ONE REAL VALUE OF UNITY. WHEN ONE, TWO, OR THREE
C   OF THE UNITS ARE DOUBLY-DEGENERATE, THEN THERE ARE 2**1, 2**2, OR
C   2**3 COUPLING COEFFICIENTS, SOME OF WHICH ARE ZERO. THESE SETS
C   ARISE SINCE EACH DOUBLY-DEGENERATE REPRESENTATION HAS TWO MEMBERS
C   AND EACH PERMUTATION OF THE MEMBERS OF THESE DOUBLY-DEGENERATE
C   REPRESENTATIONS IS ASSIGNED A UNIQUE COUPLING COEFFICIENT. IN THIS
C   PROGRAM DEGENERACIES HIGHER THAN TWO ARE NOT CONSIDERED. FOR EACH
C   GROUP PRODUCT TERM, THERE IS A COUPLING COEFFICIENT SET CALCULATED
C   FOR EACH MATRIX ELEMENT. IT SOMETIMES HAPPENS THAT IN GOING FROM
C   ONE GROUP PRODUCT TERM TO THE NEXT THERE IS NO CHANGE IN THE UNIT
C   SYMMETRIES OF ONE PARTICULAR MATRIX ELEMENT. IF THIS IS THE CASE
C   IT WOULD BE REDUNDANT TO RECALCULATE THE SET OF COUPLING
C   COEFFICIENTS FOR THIS MATRIX ELEMENT. A LARGE PORTION OF THIS
C   SECTION 6000 IS USED TO AVOID THIS TYPE OF DOUBLE CALCULATION. THE
C   LAST PART OF THE SECTION IS USED TO CALCULATE THE INITIAL COUPLING
C   COEFFICIENT PRODUCT FOR EACH GROUP PRODUCT TERM. THIS IS THE
C   PRODUCT OF THE FIRST COUPLING COEFFICIENTS IN EACH MATRIX ELEMENT
C   SET OF COEFFICIENTS. THERE IS ALSO SOME INITIALIZATION DONE HERE
C   FOR SECTION 7000, THE SECTION WHICH GENERATES ALL OTHER COUPLING
C   COEFFICIENT PRODUCTS RESULTING FROM PERMUTATIONS IN THE COUPLING
C   COEFFICIENT SETS.
C
6002 IF (INDVGS) 6003,8244,6006
6003 CALL ERROR(96)
6005 GO TO 8244
6006 ILGOS = INDVGS
6007 GO TO 5400
C
C   THE FINAL VALUE OF INDVGS, WHICH IS THE TOTAL NUMBER OF GROUP
C   PRODUCT TERMS, IS STORED IN ILGOS. THE FOLLOWING DO LOOP GOES
C   THROUGH EACH GROUP PRODUCT TERM ONE BY ONE, CALCULATING ALL OF THEIR
C   COUPLING PRODUCT PERMUTATIONS AND DETERMINING WHETHER EACH GROUP
C   PRODUCT TERM IS ZERO OR NONZERO. THIS IS DONE IN SECTIONS 6000 AND
C   7000. IN SECTION 8000 THE UNIT SYMMETRIES OF THE MATRIX ELEMENTS
C   OF A NONZERO GROUP PRODUCT TERM ARE STORED. THERE IS THEN A RETURN
C   TO STATEMENT 6008 FOR CONSIDERATION OF ANOTHER OF THE ILGOS GROUP
C   PRODUCT TERMS.
C
6008 DO 8240 INDVGS = 1,ILGOS
6012 DO 6132 IMECCD = 1,NMATL
C
C   THIS MATRIX ELEMENT DO LOOP IS RUN FOR EACH GROUP PRODUCT TERM AND
C   DETERMINES THE SET OF COUPLING COEFFICIENTS FOR EACH MATRIX ELEMENT.
C   FOR A PARTICULAR MATRIX ELEMENT OF A PARTICULAR GROUP PRODUCT TERM
C   THE UNIT SYMMETRIES OF THAT MATRIX ELEMENT ARE COMPARED WITH THOSE
C   FOR THE SAME MATRIX ELEMENT BUT OF THE PREVIOUS GROUP PRODUCT TERM.
C   IF ALL OF THESE UNIT SYMMETRIES ARE THE SAME, THERE IS NO NEED TO
C   RECALCULATE THE SET OF COUPLING COEFFICIENTS FOR THIS MATRIX
C   ELEMENT AS THEY ARE THE SAME AS BEFORE. IF HOWEVER SOME OF THE UNIT
C   SYMMETRIES ARE DIFFERENT, THEN THE SET OF COUPLING COEFFICIENTS
C   WILL ALSO BE DIFFERENT AND MUST BE RECALCULATED.
C
6016 JOPN = JOPGPU(IMECCD,INDVGS)
C
C   JOPN IS STORAGE FOR THE SYMMETRY OF THE OPERATOR OF THE IMECCD
C   MATRIX ELEMENT OF THE CURRENT GROUP PRODUCT TERM.

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C
6020 JWFN = JWFGPO(IMECCD,INDVGS)
C
C   SAME AS JOPN BUT FOR TRAILING WAVE FUNCTION OF IMECCD MATRIX
C   ELEMENT.
C
6024 IF (INDVGS - 1) 6026,6028,6060
6026 CALL ERROR(31)
C
C   IF IT IS THE FIRST TIME THROUGH THE 6008 INDVGS LOOP, THE VALUES
C   OF JOPP, JWFP, KWFP ARE SET EQUAL TO ZERO AS THIS INSURES WE
C   CALCULATE ALL SETS OF COUPLING COEFFICIENTS. ALL SUBSEQUENT TIMES
C   THROUGH THE INDVGS LOOP THESE ARE SET EQUAL TO THE APPROPRIATE UNIT
C   SYMMETRY OF THE PARTICULAR MATRIX ELEMENT OF THE PREVIOUS GROUP
C   PRODUCT TERM.
C
6028 JOPP = 0
6032 JWFP = 0
6036 KWFP = 0
6040 IF (IMECCD - NMATEL) 6044,6052,6042
6042 CALL ERROR(68)
6043 GO TO 6052
C
C   THIS SETS THE VALUE OF KWFN FOR THE FIRST GROUP PRODUCT TERM. SINCE
C   THIS IS THE LEADING WAVE FUNCTION SYMMETRY, IT IS RELATED TO THE
C   TRAILING WAVE FUNCTION SYMMETRY OF ANOTHER MATRIX ELEMENT, THE
C   RELATION GIVEN IN STATEMENTS 6044 AND 6052.
C
6044 KWFN = JWFGPO(IMECCD + 1,1)
6048 GO TO 6092
6052 KWFN = JWFGPO(1,1)
6056 GO TO 6092
6060 JOPP = JOPGPO(IMECCD,INDVGS - 1)
6064 JWFP = JWFGPO(IMECCD,INDVGS - 1)
6068 IF (IMECCD - NMATEL) 6072,6084,6070
6070 CALL ERROR(32)
6071 GO TO 6084
C
C   SAME AS 6040 BRANCH BUT FOR ALL GROUP PRODUCT TERMS BUT THE FIRST.
C   ALSO IT SETS BOTH KWFP AND KWFN.
C
6072 KWFP = JWFGPO(IMECCD + 1,INDVGS - 1)
6076 KWFN = JWFGPO(IMECCD + 1,INDVGS)
6080 GO TO 6092
6084 KWFP = JWFGPO(1,INDVGS - 1)
6088 KWFN = JWFGPO(1,INDVGS)
6092 IOPDEG(IMECCD) = IRDEG(JOPN)
6096 IWFDEG(IMECCD) = IRDEG(JWFN)
6100 IF (JOPN - JOPP) 6120,6104,6120
6104 IF (JWFN - JWFP) 6120,6108,6120
6108 IF (KWFN - KWFP) 6120,6112,6120
6112 IWDCC = 0
6116 GO TO 6121
6120 IWDCC = 1
6121 IF (IWDCC) 6122,6132,6124
6122 CALL ERROR(33)
6123 GO TO 6132
6124 KPOS = 0

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6125 IF (LPOS) 6129,6129,6126
6126 IF (LPOS - IMECCD) 6129,6127,6129
6127 IF (IRDEG(JOPN) - 1) 6129,6129,6128
6128 KPOS = 1
6129 CALL SEARCH(IMECCD,JOPN,JWFN,KWFN,KPOS)
6132 CONTINUE

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C
C   STATEMENTS 6092,6096 STORE THE DEGENERACIES OF THE UNIT SYMMETRIES
C   (TRAILING WAVE FUNCTION AND OPERATOR) OF THE IMECCD MATRIX ELEMENTS
C   FOR IMECCD=1,NMATEL. THESE ARE USED IN SECTION 7000. STATEMENTS
C   6100,6104,6108 CHECK TO SEE IF FOR THE IMECCD MATRIX ELEMENT THERE
C   HAS BEEN ANY CHANGE IN ANY OF THE THREE UNIT SYMMETRIES FROM THOSE
C   OF THE PREVIOUS GROUP PRODUCT TERM. IF THERE HAS THE SUBROUTINE
C   SEARCH IS CALLED. THE SUBROUTINE SEARCH MAKES AVAILABLE AS
C   COCME(IMECCD,NEWDA,NEWDB) A SET (DEFINED BY THE INDEXES NEWIA,
C   NEWIB) OF COUPLING COEFFICIENTS FOR THE IMECCD MATRIX ELEMENT. IN
C   THE LAST PART OF SECTION 6000 WE FORM THE INITIAL COUPLING
C   COEFFICIENT PRODUCT (WITH COCME(IMECCD,1,1), IMECCD=1,NMATEL) AND
C   WE INITIALIZE SOME ARRAYS NEEDED IN SECTION 7000. THE COUPLING
C   COEFFICIENTS CAN BE COMPLEX.
C

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6136 IF (ICHVIB) 6140,6140,6148
6140 IVIBCH = 0
6144 GO TO 6280
6148 LFL = LVIB(1)
6152 MEL = LVIB(2)
6156 JOPA = JOPGPD(LEL,INDVGS)
6160 JOPB = JOPGPD(MEL,INDVGS)
6164 IF (NTOT - 2) 6168,6168,6212
6168 NEL = 0
6172 JOPC = 0
6176 IF (JOPA - JOPB) 6180,6188,618
6180 IVIBCH = 0
6184 GO TO 6280
6188 MATVIB = 1
6192 IF (IRDEG(JOPA) - 1) 6196,6196,6204
6196 IVIBCH = 1
6200 GO TO 6280
6204 IVIBCH = 2
6208 GO TO 6280
6212 NEL = LVIB(3)
6216 JOPC = JOPGPD(NEL,INDVGS)
6220 IF (JOPA - JOPB) 6244,6224,6244
6224 IF (JOPA - JOPC) 6236,6225,6236
6225 IF (ICAC) 6226,6226,6232
6226 IF (ICBC) 6236,6236,6227
6227 IF (ICABC) 6228,6228,6230
6228 MATVIB = 4
6229 GO TO 6192
6230 MATVIB = 6
6231 GO TO 6192
6232 MAIVIB = 5
6233 GO TO 6192
6236 MATVIB = 1
6240 GO TO 6192
6244 IF (JOPA - JOPC) 6256,6245,6256
6245 IF (ICAC) 6180,6180,6248
6248 MAIVIB = 2

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6252 GO TO 6192
6256 IF (JOPB - JOPC) 6180,6257,6180
6257 IF (ICBC) 6180,6180,6260
6260 MATVIB = 3
6264 IF (IRDEG(JOPB) - 1) 6268,6268,6276
6268 IVIBCH = 1
6272 GO TO 6280
6276 IVIBCH = 2
6280 IF (IVIBCH - 1) 6284,6284,6292
6284 INVIB = 1
6288 GO TO 6328
6292 GO TO (6296,6308,6320,6328,6328,6328), MATVIB
6296 KELO = LEL
6300 KELT = MEL
6304 GO TO 6328
6308 KELO = LEL
6312 KELT = NEL
6316 GO TO 6328
6320 KELO = MEL
6324 KELT = NEL
6328 IF (MODE - 1) 6332,6332,6340
6332 CCPROD = (1.,0.)
6336 GO TO 6344
6340 CCPROD = (0.,0.)
6344 DO 6372 IMECCD = 1,NMATEL
6348 CURSCC(IMECCD) = CCOME(IMECCD,1,1)
6352 ICCSSA(IMECCD) = 1
6356 ICCSSB(IMECCD) = 1
6360 ISTACK(IMECCD) = -2
6364 IQPMPI(IMECCD) = 1
6368 IWFMPI(IMECCD) = 1
6372 CONTINUE
6376 IF (MODE - 1) 6380,6380,6392
6380 DO 6388 IMECCD = 1,NMATEL
6384 CCPROD = CCPROD * CURSCC(IMECCD)
6388 CONTINUE
6392 IF (IVIBCH - 1) 6396,6396,6412
6396 CXPROD = (0.,0.)
6400 CYPROD = (0.,0.)
6404 CZPROD = (0.,0.)
6408 GO TO 6436
6412 IF (MATVIB - 3) 6416,6416,6424
6416 CXPROD = CCPROD
6418 INVIB = 2
6420 GO TO 6430
6424 INVIB = 3
6426 CXPROD = CCPROD
6428 CYPROD = CCPROD
6432 CZPROD = CCPROD
6436 INDUV = 1
6440 JNDUV = 1
6444 KNDUV = 1

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C
C SECTION 7000, THE COUPLING COEFFICIENT PRODUCT DETERMINATION FOR
C MEMBER PERMUTATIONS AND GROUP PRODUCT TERM GO-NOGO CALCULATION
C SECTION, TAKES THE NMATEL SETS OF COUPLING COEFFICIENTS FOR A GROUP
C PRODUCT TERM AND USING ONE FROM EACH SET, FORMS ALL LEGITIMATE
C PERMUTATIONS INTO PRODUCTS. THESE PERMUTATIONS ARE ARRIVED AT IN

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C THE FOLLOWING WAY. CONSIDER A PARTICULAR MATRIX ELEMENT. IF SOME OF
 C THE UNIT SYMMETRIES ARE DOUBLY DEGENERATE, THEN WHEN WE CHANGE THE
 C MEMBER OF ONE OF THESE SYMMETRIES (THERE TWO MEMBERS FOR A DOUBLY
 C DEGENERATE REPRESENTATION) WE HAVE A NEW COUPLING COEFFICIENT TO
 C CONSIDER. INSTEAD OF CONSIDERING THE PERMUTATIONS BY MATRIX ELEMENT
 C IT MAKES MORE SENSE TO DO IT BY OPERATOR (NMATEL OF THEM) AND BY
 C WAVEFUNCTION (NMATEL OF THEM). IF ALL OPERATORS AND WAVE FUNCTIONS
 C WERE DOUBLY DEGENERATE THEN ONE WOULD HAVE $2^{**}(2*NMATEL)$ NUMBER OF
 C PERMUTATIONS. FOR NMATEL=5 THIS WOULD BE 1024 PERMUTATIONS AND IS
 C THE WORST POSSIBLE CASE. IT ALSO IS AN UNLIKELY SITUATION. SECTION
 C 7000 IS DIVIDED INTO TWO SECTIONS, ONE TO PERMUTE OPERATORS AND THE
 C OTHER TO PERMUTE WAVE FUNCTIONS. THE PROGRAM IS SUCH THAT WE DO AN
 C OPERATOR PERMUTATION, CALCULATE THE COUPLING COEFFICIENT PRODUCT,
 C THEN DO ALL WAVE FUNCTION PERMUTATIONS CALCULATING COUPLING
 C COEFFICIENT PRODUCTS FOR EACH OF THESE PERMUTATIONS. WE THEN DO A
 C SECOND OPERATOR PERMUTATION, CALCULATE THE COUPLING COEFFICIENT
 C PRODUCT, AGAIN DO ALL WAVE FUNCTION PERMUTATIONS CALCULATING
 C COUPLING COEFFICIENT PRODUCTS, DO A THIRD OPERATOR PERMUTATION AND
 C SO ON UNTIL ALL THE OPERATOR PERMUTATIONS ARE DONE. AN OPERATOR
 C PERMUTATION CONSISTS OF SWITCHING MEMBERS OF ONE OF THE DOUBLY
 C DEGENERATE OPERATOR SYMMETRIES SUCH THAT ONE GETS A NEW COMBINATION
 C OF THE NMATEL OPERATOR MEMBERS. A WAVE FUNCTION PERMUTATION IS
 C SIMILARLY DEFINED. THERE IS ONE DIFFERENCE HOWEVER. FOR THE WAVE
 C FUNCTION MEMBERS ONE MUST INTRASET SWITCH TWO WAVE FUNCTION MEMBER
 C SETS, SAY THE TRAILING WAVE FUNCTION SET FOR THE THIRD MATRIX
 C ELEMENT AND THE LEADING WAVE FUNCTION SET FOR THE SECOND MATRIX
 C ELEMENT. THE WAY IT IS DETERMINED WHETHER A GROUP PRODUCT TERM IS
 C ZERO OR NONZERO IS STRAIGHTFORWARD. IF ALL OF THE NONZERO COUPLING
 C COEFFICIENT PRODUCTS ARE NOT IDENTICAL, THE GROUP PRODUCT TERM IS
 C ZERO. THE NONZERO GROUP PRODUCT TERMS ARE OUTPUTED IN SECTION 8000.
 C

7001 IF (MODE - 1) 7005,7005,7002
 7002 NEGLEK = 1
 7004 GO TO 7007
 7005 NEGLEK = 0
 7006 DCPROD = (1.,0.)
 7007 IOPPCO = 0
 7008 IWFCO = 0
 7010 ISWCWF = 0

C
 C IOPPCO AND IWFCO ARE DECISION VARIABLES TO DETERMINE WHETHER ALL
 C OPERATOR AND WAVE FUNCTION MEMBER PERMUTATIONS ARE COMPLETE.
 C

7012 NUMMAT = 0

C
 C HERE NUMMAT IS A CLOCK TO KEEP TRACK OF THE MATRIX ELEMENTS DURING
 C THE PERMUTATIONS
 C

7016 NUMMAT = NUMMAT + 1
 7020 IF (NUMMAT - NMATEL) 7024,7024,7021
 7021 IF (ISWCWF) 7022,7022,7216
 7022 IF (NEGLEK) 7176,7176,7216

C
 C IF A PERMUTATION HAS BEEN DONE AND THE NEW COUPLING COEFFICIENT(S)
 C DETERMINED, THEN WE GO TO THE COUPLING COEFFICIENT PRODUCT PORTION
 C OF THIS SECTION. IF NOT (NUMMAT NOT GREATER THAN NMATEL) WE CONTINUE
 C IN THE PERMUTATION GENERATION PORTION UNTIL WE OBTAIN A PERMUTATION.
 C


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7024 IF (IWFDEG(NUMMAT) - 1) 7026,7028,7036
7026 CALL ERROR(34)
C
C   IF IWFDEG(NUMMAT)=2, THEN THE TRAILING WAVE FUNCTION OF THE NUMMAT
C   MATRIX ELEMENT IS DOUBLY DEGENERATE AND WE HAVE TO CONSIDER THE
C   POSSIBILITY OF MEMBER INTERCHANGE. IF IT IS 1, THEN THIS WAVE
C   FUNCTION IS NON-DEGENERATE, IT CAN BE IGNORED AS FAR AS
C   PERMUTATIONS ARE CONCERNED AND WE GO ON TO CONSIDER THE NEXT MATRIX
C   ELEMENT TRAILING WAVE FUNCTION
C
7028 IWPCO = IWPCO + 1
7029 IF (IWPCO - NMATEL) 7016,7030,7030
7030 ISWCWF = 1
C
C   WHEN THE LAST WAVE FUNCTION PERMUTATION IS COMPLETED THE PROGRAM,
C   AFTER INITIALIZING IWPCO=C, DOES THIS STATEMENT NMATEL TIMES,
C   GIVING IWPCO=NMATEL. AFTER GOING THROUGH THE COUPLING COEFFICIENT
C   PRODUCT PORTION (AN UNNECESSARY TIME) THIS VALUE IS USED IN
C   STATEMENT 7216 TO INDICATE ALL WAVE FUNCTION MEMBER PERMUTATIONS
C   ARE DONE. THERE IS THEN A CHECK TO SEE IF ALL OPERATOR PERMUTATIONS
C   ARE DONE. IF SO ONE GOES TO SECTION 8000. IF NOT THERE IS A NEW
C   OPERATOR PERMUTATION AND ALL WAVE FUNCTION PERMUTATIONS ARE RERUN.
C   THIS CONTINUES UNTIL THE OPERATOR PERMUTATIONS ARE COMPLETE
C
7032 GO TO 7016
7036 IF (IWFMPI(NUMMAT)) 7038,7040,7048
7038 CALL ERROR(35)
C
C   THE VALUE OF IWFMPI(NUMMAT) DETERMINES WHETHER OR NOT WE PERMUTE
C   THE NUMMAT MATRIX ELEMENT TRAILING WAVE FUNCTION MEMBERS. IF IT IS
C   EQUAL TO ONE THE PERMUTATION IS DONE, IF ZERO IT IS NOT DONE.
C
7040 IWFMPI(NUMMAT) = 1
7044 GO TO 7028
C
C   THIS TIME THE NUMMAT MATRIX ELEMENT TRAILING WAVE FUNCTION MEMBERS
C   WERE NOT PERMUTED. THE LOOP PERMUTES THE FIRST WAVEFUNCTION WHOSE
C   VALUE OF IWFMPI(NUMMAT)=1.
C
7048 IWFMPI(NUMMAT) = 0
C
C   THIS TIME THE NUMMAT MATRIX ELEMENT TRAILING WAVE FUNCTION MEMBERS
C   ARE TO BE PERMUTED. THE VALUE OF IWFMPI(NUMMAT) IS SET EQUAL TO
C   ZERO SO THAT THE NEXT PERMUTATION WILL NOT BE OF THE SAME MATRIX
C   ELEMENT TRAILING WAVE FUNCTION, SINCE THIS WOULD NOT BE A NEW
C   PERMUTATION.
C
7052 IF (NUMMAT - 1) 7054,7064,7056
7054 CALL ERROR(36)
7055 GO TO 7064
7056 NMINUS = NUMMAT - 1
7060 GO TO 7068
7064 NMINUS = NMATEL
C
C   WHEN WE PERMUTE THE MEMBERS OF THE NUMMAT MATRIX ELEMENT TRAILING
C   WAVE FUNCTION, WE MUST ALSO PERMUTE THE MEMBERS OF THE LEADING WAVE
C   FUNCTION OF THE PRIOR (TO NUMMAT) MATRIX ELEMENT. FOR NUMMAT=1,
C   THIS IS THE NMATEL MATRIX ELEMENT. FOR ALL OTHER NUMMAT THIS IS THE

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C   NUMMAT-1 MATRIX ELEMENT. WE STORE THE APPROPRIATE NUMBER OF THE
C   LEADING WAVE FUNCTION MATRIX ELEMENT IN NMINUS.
C
7068 INDWFP = 0
7072 NDAB = ICCSSA(NUMMAT)
C
C   THE COUPLING COEFFICIENTS ARE STORED IN COCOME(NUMMAT,NEWDA,NEWDB).
C   NEWDA AND NEWDB ARE SUFFICIENT TO SPECIFY THE COUPLING COEFFICIENT.
C   NUMMAT SPECIFIES THE MATRIX ELEMENT. THE CURRENT VALUES FOR NEWDA
C   AND NEWDB FOR THE NUMMAT MATRIX ELEMENT ARE STORED IN ICCSSA(NUMMAT)
C   AND ICCSSB(NUMMAT). IN ORDER TO PERMUTE THE NUMMAT MATRIX ELEMENT
C   TRAILING WAVE FUNCTION MEMBERS ONE MUST CHANGE THE VALUE OF
C   ICCSSA(NUMMAT). TO PERMUTE THE NMINUS MATRIX ELEMENT LEADING WAVE
C   FUNCTION MEMBERS ONE MUST CHANGE THE VALUE OF ICCSSB(NMINUS). THE
C   INFORMATION NEEDED TO CHANGE THESE VALUES IS CONTAINED IN THE
C   VALUES THEMSELVES. IN TURN THESE VALUES ARE PLACED IN THE DUMMY
C   VARIABLE NDAB. NDAB IS THEN CHANGED BY THE FOLLOWING SCHEDULE. IF
C   NDAB IS ORIGINALLY 1, IT IS CHANGED TO 2, IF 2 TO 1, IF 3 TO 4, IF
C   4 TO 3. THE NEW VALUE OF NDAB IS THEN REINSERTED INTO THE SAME
C   FUNCTION FROM WHICH IT CAME, EITHER ICCSSA(NUMMAT) OR ICCSSB(NMINUS).
C   THE INFORMATION NEEDED TO SPECIFY THE LOCATION OF THE NEW COUPLING
C   COEFFICIENTS FOR THE PERMUTED (WAVE FUNCTION MEMBERS) NUMMAT AND
C   NMINUS MATRIX ELEMENTS IS CONTAINED IN THESE TWO STORAGE SPACES.
C
7076 IF (NDAB - 2) 7080,7080,7100
7080 IF (NDAB - 1) 7084,7084,7092
7084 NDAB = 2
7088 GO TO 7116
7092 NDAB = 1
7096 GO TO 7116
7100 IF (NDAB - 3) 7104,7104,7112
7104 NDAB = 4
7108 GO TO 7116
7112 NDAB = 3
7116 IF (INDWFP) 7120,7120,7136
7120 ICCSSA(NUMMAT) = NDAB
7124 INDWFP = 1
7128 NDAB = ICCSSB(NMINUS)
7132 GO TO 7076
7136 ICCSSB(NMINUS) = NDAB
7140 NEWDA = ICCSSA(NUMMAT)
7144 NEWDB = ICCSSB(NUMMAT)
7148 CURSCC(NUMMAT) = COCOME(NUMMAT,NEWDA,NEWDB)
C
C   CURSCC(NUMMAT) IS STORAGE FOR THE CURRENT COUPLING COEFFICIENT OF
C   THE NUMMAT MATRIX ELEMENT. THEY WERE INITIALLY SET EQUAL TO
C   COCOME(NUMMAT,1,1) BY STATEMENT 6142 AND ARE PROGRESSIVELY CHANGED
C   DURING UNIT SYMMETRY MEMBER PERMUTATIONS. FOR THE WAVE FUNCTION
C   PERMUTATIONS WE CHANGE BOTH CURSCC(NUMMAT) AND CURSCC(NMINUS).
C
7152 NEWDA = ICCSSA(NMINUS)
7156 NEWDB = ICCSSB(NMINUS)
7160 CURSCC(NMINUS) = COCOME(NMINUS,NEWDA,NEWDB)
7164 IWFPCC = 0
C
C   WE MUST RESET IWFPCC TO ZERO SO AS TO BE ABLE TO DETERMINE WHEN THE
C   WAVE FUNCTION PERMUTATIONS ARE COMPLETE.
C

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7168 NUMMAT = NMATEL + 1
C
C   WE HAVE DONE A PERMUTATION AND THEREFORE MUST SET NUMMAT SO THAT
C   STATEMENT 7020 WILL DIRECT US INTO THE COUPLING COEFFICIENT PRODUCT
C   PORTION OF SECTION 7000.
C
7172 GO TO 7020
C
C   WE NOW ENTER THE COUPLING COEFFICIENT PRODUCT UPON THE CONDITIONS
C   SPECIFIED BY STATEMENT 7020
C   DDPROD ANALOGOUS TO CCPROD AND AFTER COMPUTATION OF THE COUPLING
C   COEFFICIENT PRODUCT OF THE CURRENT PERMUTATION (IT IS STORED IN
C   DDPROD), NONZERO VALUES OF DDPROD ARE COMPARED WITH THE VALUE IN
C   CCPROD (IF CCPROD IS ZERO THE VALUE OF DDPROD IS PUT INTO CCPROD).
C   IF CCPROD IS THE SAME AS DDPROD THEN THE PERMUTATIONS ARE CONTINUED.
C   IF NONZERO VALUES ARE DIFFERENT THEN THE GROUP PRODUCT TERM IS ZERO
C   AND WE GO ON TO CONSIDER THE NEXT GROUP PRODUCT TERM.
C
7176 DDPROD = DCPROD
7180 DO 7196 IMECCD = 1, NMATEL
7184 CCTSTS = CURSCC(IMECCD)
C
C   STATEMENT 7186 CHECKS THE REAL PART OF CCTSTS, 7190 THE IMAGINARY PART.
C
7186 IF (CCTSTS) 7192, 7188, 7192
7188 CTSTS = COIMAG * CCTSTS
7190 IF (CTSTS) 7192, 7216, 7192
C
C   IF ANY OF THE NMATEL COUPLING COEFFICIENTS ARE ZERO, THEN THE
C   COUPLING COEFFICIENT PRODUCT WILL BE ZERO. THEREFORE THERE IS NO
C   SENSE IN GOING THROUGH ALL THE MULTIPLICATION STEPS FOR THIS CASE.
C   THUS WE HAVE A BRANCH OUT OF THE MULTIPLICATION LOOP FOR ANY OF
C   THE COUPLING COEFFICIENTS EQUAL TO ZERO.
C
7192 DDPROD = DDPROD * CCTSTS
7196 CONTINUE
7198 CCPROD = CCPROD + DDPROD
7200 GO TO (7216, 7210, 7202), INVI8
7202 IF (KNDDV) 7206, 7206, 7205
7205 CZPROD = CZPROD + DDPROD
7206 IF (JNDUV) 7210, 7210, 7209
7209 CYPROD = CYPROD + DDPROD
7210 IF (INDUV) 7216, 7216, 7213
7213 CXPROD = CXPROD + DDPROD
7216 IF (IWFPCD - NMATEL) 7008, 7220, 7218
7218 CALL ERROR(37)
C
C   A CHECK TO SEE IF ALL WAVE FUNCTION PERMUTATIONS ARE COMPLETE (FOR
C   A PARTICULAR OPERATOR PERMUTATION)
C
7220 IF (IOPPCD - NMATEL) 7224, 8004, 7222
7222 CALL ERROR(38)
7223 GO TO 8004
C
C   A CHECK TO SEE IF ALL OPERATOR PERMUTATIONS ARE COMPLETE. IN BOTH
C   STATEMENTS 7216 AND 7220 COMPLETION IS INDICATED BY A ZERO VALUE
C   OF THE ARGUMENT.
C   WE NOW ENTER THE OPERATOR PERMUTATION PORTION. FOR THE MOST PART

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C IT IS DIRECTLY ANALOGOUS TO THE WAVE FUNCTION PERMUTATION PORTION
C OF SECTION 7000.

C
7224 IOPPCO = 0
7225 NEGLEK = 0
7226 ISWCOP = 0
7228 NUMMAT = 0
7232 NUMMAT = NUMMAT + 1
7236 IF (NUMMAT - NMATEL) 7240,7240,7237
7237 IF (ISWCOP) 7316,7316,8004
7240 IF (IOPDEG(NUMMAT) - 1) 7242,7244,7252
7242 CALL ERROR(39)
7244 IOPPCO = IOPPCO + 1
7245 IF (IOPPCO - NMATEL) 7232,7246,7246
7246 ISWCOP = 1
7248 GO TO 7232
7252 IF (IOPMPI(NUMMAT)) 7254,7256,7264
7254 CALL ERROR(40)
7256 IOPMPI(NUMMAT) = 1
7260 GO TO 7244
7264 IOPMPI(NUMMAT) = 0
7268 IF (ISTACK(NUMMAT)) 7272,7270,7280
7270 CALL ERROR(41)

C
C EACH MATRIX ELEMENT HAS THREE UNIT SYMMETRIES, TWO WAVE FUNCTIONS
C AND AN OPERATOR. THUS THE EASIEST WAY TO SPECIFY COUPLING
C COEFFICIENTS IS BY THREE SUBSCRIPTS FOR THE THREE UNIT SYMMETRIES.
C HOWEVER SINCE NO MORE THAN THREE SUBSCRIPTS ARE ALLOWED IN FORTRAN
C IV AND SINCE ONE OF THESE IS ALREADY ACCOUNTED FOR BY THE MATRIX
C ELEMENT NUMBER NUMMAT, THUS ONE MUST INCLUDE IN TWO SUBSCRIPTS THE
C INFORMATION THAT WOULD BE CONTAINED IN THREE. IN ORDER TO DO THIS
C ONE STACKS SETS OF TWO SUBSCRIPTS. SINCE THE THIRD SUBSCRIPT
C CORRESPONDING TO THE OPERATOR HAS ONLY TWO VALUES (LIKE THE TWO
C OTHERS CORRESPONDING TO LEADING AND TRAILING WAVE FUNCTIONS) ONE
C NEEDS ONLY TWO SETS OF TWO SUBSCRIPTS, ONE SET CORRESPONDING TO
C ONE VALUE OF THE HIDDEN THIRD SUBSCRIPT AND THE OTHER SET TO THE
C OTHER VALUE OF THE HIDDEN THIRD SUBSCRIPT. EACH OF THE TWO VISIBLE
C SUBSCRIPTS CAN HAVE THE VALUES 1,2 FOR THE FIRST (LOWER) SET AND
C THE VALUES 3,4 FOR THE SECOND (UPPER) SET. SINCE THIS HIDDEN THIRD
C SUBSCRIPT IDENTIFIES THE OPERATOR SYMMETRY MEMBERS, ALL THAT IS
C NEEDED TO PERMUTE THE OPERATOR MEMBERS IS TO ADD 2 TO THE LOWER SET
C OR SUBTRACT 2 FROM THE UPPER SET. THIS PROCEDURE IS FOLLOWED WITH
C THE AID OF ISTACK(NUMMAT). IF THE PREVIOUS PERMUTATION OF THE
C NUMMAT OPERATOR ENTAILED ADDITION OF 2, THIS PERMUTATION INVOLVES
C THE SUBTRACTION OF 2 (TO OR FROM EACH OF THE TWO VISIBLE
C SUBSCRIPTS). TO DO THIS ISTACK(NUMMAT) IS ADDED TO EACH OF THE TWO
C VISIBLE SUBSCRIPTS ICCSSA(NUMMAT) AND ICCSSB(NUMMAT). IF ON THE
C PREVIOUS PERMUTATION ISTACK(NUMMAT) WAS -2, IT IS SET EQUAL TO +2
C FOR THE PRESENT PERMUTATION, AND VISA VERSA.

C
7272 ISTACK(NUMMAT) = 2
7276 GO TO 7284
7280 ISTACK(NUMMAT) = -2
7284 ICCSSA(NUMMAT) = ICCSSA(NUMMAT) + ISTACK(NUMMAT)
7288 ICCSSB(NUMMAT) = ICCSSB(NUMMAT) + ISTACK(NUMMAT)
7292 NEWDA = ICCSSA(NUMMAT)
7296 NEWDB = ICCSSB(NUMMAT)
7300 CURSCC(NUMMAT) = COCUME(NUMMAT,NEWDA,NEWDB)

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7304 IOPPCO = 0
7308 NUMMAT = NMATEL + 1
7312 GO TO 7236
7316 IF (MODE - 1) 7320,7320,7332
7320 IF (ISTACK(IOPONE) - ISTACK(IOPTWO)) 7324,7364,7324
7324 NEGLEK = 1
7328 GO TO 7008
7332 IF (NCOM - 3) 7336,7336,7344
7336 NDCOM = NCOM
7340 GO TO 7348
7344 NDCOM = NCOM - 3
7348 GO TO (7352,7356,7360), NDCOM
7352 IF (ISTACK(IOPTR) - ISTACK(IOPTWO)) 7364,7324,7366
7356 IF (ISTACK(IOPTWO) - ISTACK(IOPONE)) 7364,7324,7366
7360 IF (ISTACK(IOPONE) - ISTACK(IOPTR)) 7364,7324,7366
7364 DCPROD = (1.,0.)
7365 GO TO 7367
7366 DCPROD = (-1.,0.)
7367 IF (IVIBCH - 1) 7580,7580,7372
7372 IF (MATVIB - 3) 7376,7376,7436
7376 ISTK = ISTACK(KELO)
7380 IF (ISTK - ISTACK(KELT)) 7384,7400,7384
7384 INUV = 0
7386 INVIB = 1
7388 GO TO 7580
7400 INUV = 1
7404 INVIB = 2
7424 GO TO 7580
7436 ISTK = ISTACK(LEL)
7440 IF (ISTK - ISTACK(MEL)) 7444,7460,7444
7444 INUV = 0
7448 GO TO 7476
7460 INUV = 1
7476 IF (MATVIB - 5) 7477,7479,7479
7477 JNDUV = 0
7478 GO TO 7512
7479 IF (ISTK - ISTACK(NEL)) 7480,7496,7480
7480 JNDUV = 0
7484 GO TO 7512
7496 JNDUV = 1
7512 IF (MATVIB - 5) 7515,7513,7515
7513 KNDUV = 0
7514 GO TO 7564
7515 ISTK = ISTACK(MEL)
7516 IF (ISTK - ISTACK(NEL)) 7520,7536,7520
7520 KNDUV = 0
7524 GO TO 7564
7536 KNDUV = 1
7564 IF (INUV + JNDUV + KNDUV) 7568,7568,7576
7568 INVIB = 1
7572 GO TO 7580
7576 INVIB = 3
7580 DOPROD = DCPROD
7584 DU 7608 IMECCD = 1,NMATEL
7588 CCTSTS = CURSCC(IMECCD)
7592 IF (CCTSTS) 7604,7596,7604
7596 CTSTS = CDIMAG * CCTSTS
7600 IF (CTSTS) 7604,7608,7604

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7604 DOPROD = DOPROD * CCTSTS
7608 CONTINUE
7612 CCPROD = CCPROD + DOPROD
7616 GO TO (7008,7652,7620), INVIS
7620 IF (KNDUV) 7636,7636,7632
7632 CZPROD = CZPROD + DOPROD
7636 IF (JNDUV) 7652,7652,7648
7648 CYPROD = CYPROD + DOPROD
7652 IF (INDUV) 7008,7008,7664
7664 CXPROD = CXPROD + DOPROD
7668 GO TO 7008

C
C   WE NOW ENTER SECTION 8000, THE SYMMETRY WRITE AND N,N**2 SELECTION
C   SECTION. THE SECTION IS ENTERED FOR EACH NONZERO GROUP PRODUCT TERM
C   AND FOR EACH OF THESE TERMS THE 2*NMATEL UNIT SYMMETRIES, NMATEL
C   WAVE FUNCTION SYMMETRIES AND NMATEL OPERATOR SYMMETRIES, ARE
C   WRITTEN. THE FIRST STATEMENT IN THIS SECTION IS A BRANCH. IT IS
C   PRECAUTIONARY TO AVOID WRITING OUT UNIT SYMMETRIES IF ALL COUPLING
C   COEFFICIENT PRODUCTS ARE ZERO. WE WILL NEVER ENTER THIS FIRST
C   PORTION OF THE 8000 SECTION UNLESS ALL NONZERO COUPLING COEFFICIENT
C   PRODUCTS ARE IDENTICAL. IF THERE IS AT LEAST ONE NONZERO COUPLING
C   COEFFICIENT PRODUCT IT WILL BE AT THIS POINT, STORED IN CCPROD.
C   THUS IF CCPROD=0 AFTER ENTRY TO SECTION 8000, THEN ALL COUPLING
C   COEFFICIENT PRODUCTS ARE ZERO AND THERE IS NO SYMMETRY WRITING TO
C   BE DONE FOR THAT GROUP PRODUCT TERM.
C
8004 CPROD(1) = CCPROD
8008 CPROD(2) = CXPROD
8012 CPROD(3) = CYPROD
8016 CPROD(4) = CZPROD
8020 DO 8052 NCP = 1,4
8024 CPRD = CPROD(NCP)
8028 IF (CPRD) 8048,8032,8048
8032 CCTSTS = COIMAG * CPRD
8036 IF (CCTSTS) 8048,8040,8048
8040 LCPRD(NCP) = 0
8044 GO TO 8052
8048 LCPRD(NCP) = 1
8052 CONTINUE
8056 LPRSUM = 1000*LCPRD(1) + 100*LCPRD(2) + 10*LCPRD(3) + LCPRD(4)
8060 IF (LPRSUM) 8240,8240,8064
8064 ITECOM = ITECOM + 1
8068 LPRO(INTER,ITECOM) = LPRSUM
8072 KNWF = 0
8076 KNOP = 0
8078 JVIR(INTER,ITECOM) = JVIRCH
8080 DO 8140 N = 1,NMATEL
8084 IF (IWFQB(N)) 8088,8092,8112
8088 CALL ERROR(96)
8092 KNWF = KNWF + 1
8108 INONWF(INTER,ITECOM,KNWF) = JWFGPO(N,INDVGS)
8112 IF (IOPQB(N)) 8116,8120,8140
8116 CALL ERROR(97)
8120 KNOP = KNOP + 1
8136 INONOP(INTER,ITECOM,KNOP) = JOPGPO(N,INDVGS)
8140 CONTINUE
8144 KARWF(INTER) = KNWF
8148 KAROP(INTER) = KNOP

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8152 IF (ISKIP) 8156,8156,8240
8156 GO TO (8160,8160,8188,8216,8216), MODEPT
8160 IF (NMATEL - 4) 8164,8172,8180
8164 PRINT 8166, (INONWF(INTER,ITECOM,N), N = 1,KNWF),
      1(INONOP(INTER,ITECOM,N), N = 1,KNOP),
      2(JWFGPO(IPR,INDVGS), JOPGPO(IPR,INDVGS), IPR = 1,NMATEL),
      3LPRSUM
8166 FORMAT (9X,I2,9X,I2,I2X,3(I2,5X,I2,7X),40X,I4)
8168 GO TO 8240
8172 PRINT 8174, (INONWF(INTER,ITECOM,N), N = 1,KNWF),
      1(INONOP(INTER,ITECOM,N), N = 1,KNOP),
      2(JWFGPO(IPR,INDVGS), JOPGPO(IPR,INDVGS), IPR = 1,NMATEL),
      3LPRSUM
8174 FORMAT (7X,2I2,7X,2I2,I2X,4(I2,5X,I2,7X),24X,I4)
8176 GO TO 8240
8180 PRINT 8182, (INONWF(INTER,ITECOM,N),N=1,KNWF),
      1(INONOP(INTER,ITECOM,N),N=1,KNOP),
      2(JWFGPO(IPR,INDVGS), JOPGPO(IPR,INDVGS), IPR = 1,NMATEL),
      3LPRSUM
8182 FORMAT (5X,3I2,5X,3I2,I2X,5(I2,5X,I2,7X),8X,I4)
8184 GO TO 8240
8188 IF (NMATEL - 4) 8192,8200,8208
8192 PRINT 8194, (INONWF(INTER,ITECOM,N), N = 1,KNWF),
      1(JWFGPO(IPR,INDVGS), JOPGPO(IPR,INDVGS), IPR = 1,NMATEL),
      2LPRSUM
8194 FORMAT (9X,I2,23X,3(I2,5X,I2,7X),40X,I4)
8196 GO TO 8240
8200 PRINT 8202, (INONWF(INTER,ITECOM,N), N = 1,KNWF),
      1(INONOP(INTER,ITECOM,N), N = 1,KNOP),
      2(JWFGPO(IPR,INDVGS), JOPGPO(IPR,INDVGS), IPR = 1,NMATEL),
      3LPRSUM
8202 FORMAT (7X,2I2,9X,I2,I2X,4(I2,5X,I2,7X),24X,I4)
8204 GO TO 8240
8208 PRINT 8210, (INONWF(INTER,ITECOM,N), N = 1,KNWF),
      1(INONOP(INTER,ITECOM,N), N = 1,KNOP),
      2(JWFGPO(IPR,INDVGS), JOPGPO(IPR,INDVGS), IPR = 1,NMATEL),
      3LPRSUM
8210 FORMAT (5X,3I2,7X,2I2,I2X,5(I2,5X,I2,7X),8X,I4)
8212 GO TO 8240
8216 IF (NMATEL - 4) 8220,8228,8236
8220 PRINT 8222, (JWFGPO(IPR,INDVGS), JOPGPO(IPR,INDVGS), IPR=1,NMATEL)
      1,LPRSUM
8222 FORMAT (34X,3(I2,5X,I2,7X),40X,I4)
8224 GO TO 8240
8228 PRINT 8230, (INONWF(INTER,ITECOM,N), N = 1,KNWF),
      1(INONOP(INTER,ITECOM,N), N = 1,KNOP),
      2(JWFGPO(IPR,INDVGS), JOPGPO(IPR,INDVGS), IPR = 1,NMATEL),
      3LPRSUM
8230 FORMAT (9X,I2,9X,I2,I2X,4(I2,5X,I2,7X),24X,I4)
8232 GO TO 8240
8236 PRINT 8238, (INONWF(INTER,ITECOM,N), N = 1,KNWF),
      1(INONOP(INTER,ITECOM,N), N = 1,KNOP),
      2(JWFGPO(IPR,INDVGS), JOPGPO(IPR,INDVGS), IPR = 1,NMATEL),
      3LPRSUM
8238 FORMAT (7X,2I2,7X,2I2,I2X,5(I2,5X,I2,7X),8X,I4)
8240 CONTINUE

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C
C   THIS IS THE END OF THE INDVGS GROUP PRODUCT TERM EVALUATION DO LOOP

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C      WHICH STARTS AT STATEMENT 6008. THE FOLLOWING LOOP RESETS THE
C      IWFQ(NUMMAT), IOPQ(NUMMAT) AND IWFQA(NUMMAT), IOPQA(NUMMAT) TO THE
C      ORIGINAL STATES OF KNOWLEDGE STORED IN THE SLOTS IWFQB(NUMMAT),
C      IOPQB(NUMMAT). THUS FOR NEW TERMS OR FOR NEW SUPPLEMENTARY SYMMETRY
C      INSERTIONS, ALL STATES OF KNOWLEDGE OF THE UNIT SYMMETRIES ARE
C      RESET TO THE VALUES IN IWFQB(NUMMAT), IOPQB(NUMMAT).
C
C      8244 DO 8272 NUMMAT = 1, NMATEL
C      8248 IOQ = IOPQB(NUMMAT)
C      8252 IWQ = IWFQB(NUMMAT)
C      8256 IOPQ(NUMMAT) = IOQ
C      8260 IWFQ(NUMMAT) = IWQ
C      8264 IOPQA(NUMMAT) = IOQ
C      8268 IWFQA(NUMMAT) = IWQ
C      8272 CONTINUE
C
C      WE NOW ENTER THE PORTION OF SECTION 8000 CONCERNED WITH SELECTING,
C      IF NECESSARY, THE ADDITIONAL N OR N**2 SYMMETRIES
C
C      8276 IF (NNSQIN) 8280, 8360, 8288
C      8280 CALL ERROR(42)
C      8284 GO TO 8360
C
C      IF NNSQIN=0 WE ARE DEALING WITH TERMS FOR WHICH NO ADDITIONAL
C      SYMMETRIES NEED BE SUPPLIED. IF THIS IS THE CASE WE CONTINUE WITH
C      THE COMPONENT AND TERM DO LOOP. IF NNSQIN IS GREATER THAN ZERO
C      THEN WE WILL HAVE TO DEAL WITH N OR N**2 TERMS.
C
C      8288 IF (NNSQIN - 1) 8292, 8296, 8316
C      8292 CALL ERROR(43)
C
C      IF NNSQIN=1 WE ARE DEALING WITH N ADDITIONAL SYMMETRIES. IF
C      NNSQIN=2 WE ARE DEALING WITH N**2 ADDITIONAL SYMMETRIES.
C
C      8296 IF (NALL - NUMIRR) 8308, 8360, 8300
C      8300 CALL ERROR(44)
C      8304 GO TO 8360
C      8308 NALL = NALL + 1
C
C      WE ARE INVESTIGATING. NALL IS THE NUMBER OF THE REPRESENTATION WE
C      ARE USING AS THE ADDITIONAL SYMMETRY FOR THIS RUN. IF NALL IS LESS
C      THAN NUMIRR WE ADVANCE NALL BY 1 AND RETURN TO SECTION 3000 FOR
C      CALCULATION OF GROUP PRODUCT TERMS CORRESPONDING TO THE INTRODUCED
C      SYMMETRY IREPSB(NALL+1). IF NALL=NUMIRR WE HAVE FINISHED ALL THE
C      ADDITIONAL N=NUMIRR SYMMETRIES AND WE CONTINUE WITH THE COMPONENT
C      AND TERM DO LOOPS.
C
C      8312 GO TO 3016
C      8316 IF (NSQALL - NUMIRR) 8328, 8336, 8320
C      8320 CALL ERROR(45)
C      8324 GO TO 8336
C
C      WE ARE NOW DEALING WITH THE CASE OF N**2 ADDITIONAL SYMMETRIES. THE
C      TWO BRANCHES DEALING WITH THE VALUES OF NSQALL AND NALL (STATEMENTS
C      8108 AND 8120) AND THE ASSOCIATED STATEMENTS REVALUING NSQALL AND
C      NALL DO ALL COMBINATIONS OF THESE INDEXES
C
C      8328 NSQALL = NSQALL + 1

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8332 GO TO 3016
8336 IF (NALL - NUMIRR) 8348,8360,8340
8340 CALL ERROR(46)
8344 GO TO 8360
8348 NALL = NALL + 1
8352 NSQALL = 1
8356 GO TO 3016
8360 ITECM(INTER) = ITECOM
8364 CONTINUE
8368 CALL SYMANA(MODEPI,NCOM)
8372 CONTINUE
8376 GO TO (8384,8392,8400,8408,8416), MODEPI
8380 FORMAT(/,9X,15HSYMMETRY GROUP ,A3,5X,32HINITIAL WAVE FUNCTION SYM
      IMETRY = ,12,4X,31HFINAL WAVE FUNCTION SYMMETRY = ,12,4X,7HMODE = ,
      2A10,A9,/)
8384 PRINT 8380, AQ,IWFJ,IWFK,DAQ,EAQ
8388 GO TO 8420
8392 PRINT 8380, AQ,IWFJ,IWFK,DBQ,EBQ
8396 GO TO 8420
8400 PRINT 8380, AQ,IWFJ,IWFK,DCQ,ECQ
8404 GO TO 8420
8408 PRINT 8380, AQ,IWFJ,IWFK,DDQ,EDQ
8412 GO TO 8420
8416 PRINT 8380, AQ,IWFJ,IWFK,DEQ,EEQ
8420 NEXGD = 1
8424 DO 9864 NCOM = 1,NUTCOM
8428 PRINT 8432, NCOM
8432 FORMAT(/,5X,10HCOMPONENT ,12, 8X,13HSUBSTITUTIONS,10X,28HVIBRATION
      IS AND SUBSTITUTIONS,12X,10HVIBRATIONS)
8436 NFX = NIX(NCOM)
8440 IF (NFX) 9864,9864,8444
8444 DO 9864 NF = 1,NFX
8448 NFY = NIY(NCOM,NF)
8452 IF (NFY) 8456,9064,8464
8456 CALL ERROR(8)
8460 GO TO 9864
8464 KSUR = 0
8468 KBOTH = 0
8472 KVIB = 0
8476 DO 8796 N = 1,NFY
8480 NVS = IVISB(NCOM,NF,N)
8484 NEGD = IEXGD(NCOM,NF,N) + 1
8488 GO TO (8492,8504,8520,8540), NEXGD
8492 GO TO (8796,8496,8796,8496,8796,8496,8796,8496,8796,8496,8796,
      18496,8796,8496,8796,8496), NEGD
8496 LGEO = NVS/1000
8500 GO TO 8756
8504 GO TO (8796,8796,8508,8508,8796,8796,8508,8508,8796,8796,8508,
      18508,8796,8796,8508,8508), NEGD
8508 LGEO = NVS/1000
8512 LGEO = (NVS - 1000*LGEO)/100
8516 GO TO 8756
8520 GO TO (8796,8796,8796,8796,8796,8796,8796,8796,8524,8524,8524,
      18524,8524,8524,8524,8524), NEGD
8524 LGEO = NVS - 1000*(NVS/1000)
8528 LGEO = LGEO - 100*(LGEO/100)
8532 LGEO = LGEO - 10*(LGEO/10)
8536 GO TO 8756

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8540 GO TO (8796,8544,8544,8544,8544,8544,8544,8544,8544,8544,
 18544,8544,8544,8544,8544), NEG0
 8544 KAT = 0
 8548 KBT = 0
 8552 KCT = 0
 8556 KDT = 0
 8560 LGEO = NVS/1000
 8564 LEO = LGEO + 1
 8568 GO TO (8572,8580,8588,8596), LEO
 8572 KAT = 1
 8576 GO TO 8600
 8580 KBT = 2
 8584 GO TO 8600
 8588 KCT = 3
 8592 GO TO 8600
 8596 KDT = 4
 8600 NVGS = NVS - 1000*LGEO
 8604 LGEO = NVGS/100
 8608 LEO = LGEO + 1
 8612 GO TO (8616,8624,8632,8640), LEO
 8616 KAT = 1
 8620 GO TO 8644
 8624 KBT = 2
 8628 GO TO 8644
 8632 KCT = 3
 8636 GO TO 8644
 8640 KDT = 4
 8644 NVGS = NVGS - 100*LGEO
 8648 LGEO = NVGS/10
 8652 LEO = LGEO + 1
 8656 GO TO (8660,8668,8676,8684), LEO
 8660 KAT = 1
 8664 GO TO 8688
 8668 KBT = 2
 8672 GO TO 8688
 8676 KCT = 3
 8680 GO TO 8688
 8684 KDT = 4
 8688 NVGS = NVGS - 10*LGEO
 8692 LEO = NVGS + 1
 8696 GO TO (8700,8708,8716,8724), LEO
 8700 KAT = 1
 8704 GO TO 8728
 8708 KBT = 2
 8712 GO TO 8728
 8716 KCT = 3
 8720 GO TO 8728
 8724 KDT = 4
 8728 KTT = KAT + KBT + KCT + KDT
 8732 GO TO (8796,8736,8736,8744,8744,8744,8744,8752,8752,8744,8744,
 18744,8744,8744,8744), KTT
 8736 LGEO = 1
 8740 GO TO 8756
 8744 LGEO = 2
 8748 GO TO 8756
 8752 LGEO = 3
 8756 IF (LGEO) 8796,8796,8760
 8760 GO TO (8764,8776,8788), LGEO

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8764 KSUB = KSUB + 1
8768 NSUBWF(KSUB) = NDWF(NCOM,NF,N)
8772 GO TO 8796
8776 KBOTh = KBOTh + 1
8780 NBOTWF(KBOTh) = NDWF(NCOM,NF,N)
8784 GO TO 8796
8788 KVI8 = KVI8 + 1
8792 NVIBWF(KVI8) = NDWF(NCOM,NF,N)
8796 CONTINUE
9002 NP = NDOP(NCOM,NF)
9004 NVBS = 1
9008 NSUB = KSUB
9012 NBOTH = KBOTh
9016 NVIB = KVI8
9020 IF (NSUB - 7) 9024,9024,9032
9024 ISUB = NSUB
9028 GO TO 9036
9032 ISUB = 7
9036 IF (NBOTH - 7) 9040,9040,9048
9040 IBOTH = NBOTH
9044 GO TO 9052
9048 IBOTH = 7
9052 IF (NVIB - 7) 9056,9056,9064
9056 IVIB = NVIB
9060 GO TO 9068
9064 IVIB = 7
9068 LSUB = ISUB + 1
9072 LBOTH = IBOTH + 1
9076 NFSB = NVBS - 1 + ISUB
9080 NFBH = NVBS - 1 + IBOTH
9084 NFVB = NVBS - 1 + IVIB
9088 KO = 0
9092 DO 9104 KS = NVBS,NFSB
9096 KO = KO + 1
9100 NS(KO) = NSUBWF(KS)
9104 CONTINUE
9108 KO = 0
9112 DO 9124 KS = NVBS,NFBH
9116 KO = KO + 1
9120 NB(KO) = NBOTWF(KS)
9124 CONTINUE
9128 KO = 0
9132 DO 9144 KS = NVBS,NFVB
9136 KO = KO + 1
9140 NV(KO) = NVIBWF(KS)
9144 CONTINUE
9148 IF (IVIB) 9152,9152,9236
9152 IF (LBOTH - 1) 9156,9156,9168
9156 IF (LSUB - 1) 9864,9864,9160
9160 PRINT 9161,NP,(NS(K),K=1,ISUB)
9161 FORMAT(10X,I3,5X,7(I3,1X))
9162 GO TO 9784
9168 GO TO (9172,9180,9188,9196,9204,9212,9220,9228), LSUB
9172 PRINT 9173,NP,(NB(K),K=1,IBOTH)
9173 FORMAT(10X,I3,36X,7(I3,1X))
9174 GO TO 9784
9180 PRINT 9181,NP,(NS(K),K=1,ISUB),(NB(K),K=1,IBOTH)
9181 FORMAT(10X,I3,5X,1(I3,1X),27X,7(I3,1X))

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9182 GO TO 9784
9188 PRINT 9189, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH)
9189 FORMAT(10X, I3, 5X, 2(I3, 1X), 23X, 7(I3, 1X))
9190 GO TO 9784
9196 PRINT 9197, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH)
9197 FORMAT(10X, I3, 5X, 3(I3, 1X), 19X, 7(I3, 1X))
9198 GO TO 9784
9204 PRINT 9205, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH)
9205 FORMAT(10X, I3, 5X, 4(I3, 1X), 15X, 7(I3, 1X))
9206 GO TO 9784
9212 PRINT 9213, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH)
9213 FORMAT(10X, I3, 5X, 5(I3, 1X), 11X, 7(I3, 1X))
9214 GO TO 9784
9220 PRINT 9221, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH)
9221 FORMAT(10X, I3, 5X, 6(I3, 1X), 7X, 7(I3, 1X))
9222 GO TO 9784
9228 PRINT 9229, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH)
9229 FORMAT(10X, I3, 5X, 7(I3, 1X), 3X, 7(I3, 1X))
9230 GO TO 9784
9236 GO TO (9240, 9308, 9376, 9444, 9512, 9580, 9648, 9716), LSUB
9240 GO TO (9244, 9252, 9260, 9268, 9276, 9284, 9292, 9300), LBOOTH
9244 PRINT 9245, NP, (NV(K), K=1, IVIB)
9245 FORMAT(10X, I3, 67X, 7(I3, 1X))
9246 GO TO 9784
9252 PRINT 9253, NP, (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9253 FORMAT(10X, I3, 36X, 1(I3, 1X), 27X, 7(I3, 1X))
9254 GO TO 9784
9260 PRINT 9261, NP, (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9261 FORMAT(10X, I3, 36X, 2(I3, 1X), 23X, 7(I3, 1X))
9262 GO TO 9784
9268 PRINT 9269, NP, (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9269 FORMAT(10X, I3, 36X, 3(I3, 1X), 19X, 7(I3, 1X))
9270 GO TO 9784
9276 PRINT 9277, NP, (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9277 FORMAT(10X, I3, 36X, 4(I3, 1X), 15X, 7(I3, 1X))
9278 GO TO 9784
9284 PRINT 9285, NP, (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9285 FORMAT(10X, I3, 36X, 5(I3, 1X), 11X, 7(I3, 1X))
9286 GO TO 9784
9292 PRINT 9293, NP, (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9293 FORMAT(10X, I3, 36X, 6(I3, 1X), 7X, 7(I3, 1X))
9294 GO TO 9784
9300 PRINT 9301, NP, (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9301 FORMAT(10X, I3, 36X, 7(I3, 1X), 3X, 7(I3, 1X))
9302 GO TO 9784
9308 GO TO (9312, 9320, 9328, 9336, 9344, 9352, 9360, 9368), LBOOTH
9312 PRINT 9313, NP, (NS(K), K=1, ISUB), (NV(K), K=1, IVIB)
9313 FORMAT(10X, I3, 5X, 1(I3, 1X), 58X, 7(I3, 1X))
9314 GO TO 9784
9320 PRINT 9321, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9321 FORMAT(10X, I3, 5X, 1(I3, 1X), 27X, 1(I3, 1X), 27X, 7(I3, 1X))
9322 GO TO 9784
9328 PRINT 9329, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9329 FORMAT(10X, I3, 5X, 1(I3, 1X), 27X, 2(I3, 1X), 23X, 7(I3, 1X))
9330 GO TO 9784
9336 PRINT 9337, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9337 FORMAT(10X, I3, 5X, 1(I3, 1X), 27X, 3(I3, 1X), 19X, 7(I3, 1X))
9338 GO TO 9784

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9344 PRINT 9345, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9345 FORMAT(10X, I3, 5X, 1(I3, 1X), 27X, 4(I3, 1X), 15X, 7(I3, 1X))
9346 GO TO 9784
9352 PRINT 9353, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9353 FORMAT(10X, I3, 5X, 1(I3, 1X), 27X, 5(I3, 1X), 11X, 7(I3, 1X))
9354 GO TO 9784
9360 PRINT 9361, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9361 FORMAT(10X, I3, 5X, 1(I3, 1X), 27X, 6(I3, 1X), 7X, 7(I3, 1X))
9362 GO TO 9784
9368 PRINT 9369, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9369 FORMAT(10X, I3, 5X, 1(I3, 1X), 27X, 7(I3, 1X), 3X, 7(I3, 1X))
9370 GO TO 9784
9376 GO TO (9380, 9388, 9396, 9404, 9412, 9420, 9428, 9436), LBOOTH
9380 PRINT 9381, NP, (NS(K), K=1, ISUB), (NV(K), K=1, IVIB)
9381 FORMAT(10X, I3, 5X, 2(I3, 1X), 54X, 7(I3, 1X))
9382 GO TO 9784
9388 PRINT 9389, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9389 FORMAT(10X, I3, 5X, 2(I3, 1X), 23X, 1(I3, 1X), 27X, 7(I3, 1X))
9390 GO TO 9784
9396 PRINT 9397, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9397 FORMAT(10X, I3, 5X, 2(I3, 1X), 23X, 2(I3, 1X), 23X, 7(I3, 1X))
9398 GO TO 9784
9404 PRINT 9405, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9405 FORMAT(10X, I3, 5X, 2(I3, 1X), 23X, 3(I3, 1X), 19X, 7(I3, 1X))
9406 GO TO 9784
9412 PRINT 9413, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9413 FORMAT(10X, I3, 5X, 2(I3, 1X), 23X, 4(I3, 1X), 15X, 7(I3, 1X))
9414 GO TO 9784
9420 PRINT 9421, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9421 FORMAT(10X, I3, 5X, 2(I3, 1X), 23X, 5(I3, 1X), 11X, 7(I3, 1X))
9422 GO TO 9784
9428 PRINT 9429, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9429 FORMAT(10X, I3, 5X, 2(I3, 1X), 23X, 6(I3, 1X), 7X, 7(I3, 1X))
9430 GO TO 9784
9436 PRINT 9437, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9437 FORMAT(10X, I3, 5X, 2(I3, 1X), 23X, 7(I3, 1X), 3X, 7(I3, 1X))
9438 GO TO 9784
9444 GO TO (9448, 9456, 9464, 9472, 9480, 9488, 9496, 9504), LBOOTH
9448 PRINT 9449, NP, (NS(K), K=1, ISUB), (NV(K), K=1, IVIB)
9449 FORMAT(10X, I3, 5X, 3(I3, 1X), 50X, 7(I3, 1X))
9450 GO TO 9784
9456 PRINT 9457, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9457 FORMAT(10X, I3, 5X, 3(I3, 1X), 19X, 1(I3, 1X), 27X, 7(I3, 1X))
9458 GO TO 9784
9464 PRINT 9465, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9465 FORMAT(10X, I3, 5X, 3(I3, 1X), 19X, 2(I3, 1X), 23X, 7(I3, 1X))
9466 GO TO 9784
9472 PRINT 9473, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9473 FORMAT(10X, I3, 5X, 3(I3, 1X), 19X, 3(I3, 1X), 19X, 7(I3, 1X))
9474 GO TO 9784
9480 PRINT 9481, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9481 FORMAT(10X, I3, 5X, 3(I3, 1X), 19X, 4(I3, 1X), 15X, 7(I3, 1X))
9482 GO TO 9784
9488 PRINT 9489, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9489 FORMAT(10X, I3, 5X, 3(I3, 1X), 19X, 5(I3, 1X), 11X, 7(I3, 1X))
9490 GO TO 9784
9496 PRINT 9497, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9497 FORMAT(10X, I3, 5X, 3(I3, 1X), 19X, 6(I3, 1X), 7X, 7(I3, 1X))

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9498 GO TO 9784
9504 PRINT 9505, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9505 FORMAT(10X, I3, 5X, 3(I3, 1X), 19X, 7(I3, 1X), 3X, 7(I3, 1X))
9506 GO TO 9784
9512 GO TO (9516, 9524, 9532, 9540, 9548, 9556, 9564, 9572), LBOTH
9516 PRINT 9517, NP, (NS(K), K=1, ISUB), (NV(K), K=1, IVIB)
9517 FORMAT(10X, I3, 5X, 4(I3, 1X), 46X, 7(I3, 1X))
9518 GO TO 9784
9524 PRINT 9525, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9525 FORMAT(10X, I3, 5X, 4(I3, 1X), 15X, 1(I3, 1X), 27X, 7(I3, 1X))
9526 GO TO 9784
9532 PRINT 9533, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9533 FORMAT(10X, I3, 5X, 4(I3, 1X), 15X, 2(I3, 1X), 23X, 7(I3, 1X))
9534 GO TO 9784
9540 PRINT 9541, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9541 FORMAT(10X, I3, 5X, 4(I3, 1X), 15X, 3(I3, 1X), 19X, 7(I3, 1X))
9542 GO TO 9784
9548 PRINT 9549, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9549 FORMAT(10X, I3, 5X, 4(I3, 1X), 15X, 4(I3, 1X), 15X, 7(I3, 1X))
9550 GO TO 9784
9556 PRINT 9557, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9557 FORMAT(10X, I3, 5X, 4(I3, 1X), 15X, 5(I3, 1X), 11X, 7(I3, 1X))
9558 GO TO 9784
9564 PRINT 9565, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9565 FORMAT(10X, I3, 5X, 4(I3, 1X), 15X, 6(I3, 1X), 7X, 7(I3, 1X))
9566 GO TO 9784
9572 PRINT 9573, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9573 FORMAT(10X, I3, 5X, 4(I3, 1X), 15X, 7(I3, 1X), 3X, 7(I3, 1X))
9574 GO TO 9784
9580 GO TO (9584, 9592, 9600, 9608, 9616, 9624, 9632, 9640), LBOTH
9584 PRINT 9585, NP, (NS(K), K=1, ISUB), (NV(K), K=1, IVIB)
9585 FORMAT(10X, I3, 5X, 5(I3, 1X), 42X, 7(I3, 1X))
9586 GO TO 9784
9592 PRINT 9593, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9593 FORMAT(10X, I3, 5X, 5(I3, 1X), 11X, 1(I3, 1X), 27X, 7(I3, 1X))
9594 GO TO 9784
9600 PRINT 9601, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9601 FORMAT(10X, I3, 5X, 5(I3, 1X), 11X, 2(I3, 1X), 23X, 7(I3, 1X))
9602 GO TO 9784
9608 PRINT 9609, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9609 FORMAT(10X, I3, 5X, 5(I3, 1X), 11X, 3(I3, 1X), 19X, 7(I3, 1X))
9610 GO TO 9784
9616 PRINT 9617, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9617 FORMAT(10X, I3, 5X, 5(I3, 1X), 11X, 4(I3, 1X), 15X, 7(I3, 1X))
9618 GO TO 9784
9624 PRINT 9625, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9625 FORMAT(10X, I3, 5X, 5(I3, 1X), 11X, 5(I3, 1X), 11X, 7(I3, 1X))
9626 GO TO 9784
9632 PRINT 9633, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9633 FORMAT(10X, I3, 5X, 5(I3, 1X), 11X, 6(I3, 1X), 7X, 7(I3, 1X))
9634 GO TO 9784
9640 PRINT 9641, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9641 FORMAT(10X, I3, 5X, 5(I3, 1X), 11X, 7(I3, 1X), 3X, 7(I3, 1X))
9642 GO TO 9784
9648 GO TO (9652, 9660, 9668, 9676, 9684, 9692, 9700, 9708), LBOTH
9652 PRINT 9653, NP, (NS(K), K=1, ISUB), (NV(K), K=1, IVIB)
9653 FORMAT(10X, I3, 5X, 6(I3, 1X), 38X, 7(I3, 1X))
9654 GO TO 9784

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9660 PRINT 9661, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9661 FORMAT(10X, I3, 5X, 6(I3, 1X), 7X, 1(I3, 1X), 27X, 7(I3, 1X))
9662 GO TO 9784
9668 PRINT 9669, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9669 FORMAT(10X, I3, 5X, 6(I3, 1X), 7X, 2(I3, 1X), 23X, 7(I3, 1X))
9670 GO TO 9784
9676 PRINT 9677, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9677 FORMAT(10X, I3, 5X, 6(I3, 1X), 7X, 3(I3, 1X), 19X, 7(I3, 1X))
9678 GO TO 9784
9684 PRINT 9685, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9685 FORMAT(10X, I3, 5X, 6(I3, 1X), 7X, 4(I3, 1X), 15X, 7(I3, 1X))
9686 GO TO 9784
9692 PRINT 9693, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9693 FORMAT(10X, I3, 5X, 6(I3, 1X), 7X, 5(I3, 1X), 11X, 7(I3, 1X))
9694 GO TO 9784
9700 PRINT 9701, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9701 FORMAT(10X, I3, 5X, 6(I3, 1X), 7X, 6(I3, 1X), 7X, 7(I3, 1X))
9702 GO TO 9784
9708 PRINT 9709, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9709 FORMAT(10X, I3, 5X, 6(I3, 1X), 7X, 7(I3, 1X), 3X, 7(I3, 1X))
9710 GO TO 9704
9716 GO TO (9720, 9728, 9736, 9744, 9752, 9760, 9768, 9776), LBOOTH
9720 PRINT 9721, NP, (NS(K), K=1, ISUB), (NV(K), K=1, IVIB)
9721 FORMAT(10X, I3, 5X, 7(I3, 1X), 34X, 7(I3, 1X))
9722 GO TO 9784
9728 PRINT 9729, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9729 FORMAT(10X, I3, 5X, 7(I3, 1X), 3X, 1(I3, 1X), 27X, 7(I3, 1X))
9730 GO TO 9784
9736 PRINT 9737, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9737 FORMAT(10X, I3, 5X, 7(I3, 1X), 3X, 2(I3, 1X), 23X, 7(I3, 1X))
9738 GO TO 9784
9744 PRINT 9745, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9745 FORMAT(10X, I3, 5X, 7(I3, 1X), 3X, 3(I3, 1X), 19X, 7(I3, 1X))
9746 GO TO 9784
9752 PRINT 9753, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9753 FORMAT(10X, I3, 5X, 7(I3, 1X), 3X, 4(I3, 1X), 15X, 7(I3, 1X))
9754 GO TO 9784
9760 PRINT 9761, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9761 FORMAT(10X, I3, 5X, 7(I3, 1X), 3X, 5(I3, 1X), 11X, 7(I3, 1X))
9762 GO TO 9784
9768 PRINT 9769, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9769 FORMAT(10X, I3, 5X, 7(I3, 1X), 3X, 6(I3, 1X), 7X, 7(I3, 1X))
9770 GO TO 9784
9776 PRINT 9777, NP, (NS(K), K=1, ISUB), (NB(K), K=1, IBOTH), (NV(K), K=1, IVIB)
9777 FORMAT(10X, I3, 5X, 7(I3, 1X), 3X, 7(I3, 1X), 3X, 7(I3, 1X))
9778 GO TO 9784
9784 NVBS = NVBS + 7
9788 NSUB = NSUB - 7
9792 NBOTH = NBOTH - 7
9796 NVIB = NVIB - 7
9800 IF (NSUB) 9804, 9832, 9812
9804 NSUB = 0
9808 GO TO 9832
9812 IF (NBOTH) 9816, 9820, 9820
9816 NBOTH = 0
9820 IF (NVIB) 9824, 9020, 9020
9824 NVIB = 0
9828 GO TO 9020

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9832 IF (NR0TH) 9836,9856,9844
9836 NBOTH = 0
9840 GO TO 9856
9844 IF (NVIB) 9848,9020,9020
9848 NVIB = 0
9852 GO TO 9020
9856 IF (NVIB) 9860,9864,9020
9860 NVIB = 0
9864 CONTINUE
9868 GO TO (9872,9880,9900,9908), NEXGD
9872 NEXGD = 2
9876 GO TO 9912
9880 IF (MODEPI - 3) 9884,9892,9884
9884 NEXGD = 4
9888 GO TO 9912
9892 NEXGD = 3
9896 GO TO 9912
9900 NEXGD = 4
9904 GO TO 9912
9908 NEXGD = 5
9912 IF (NEXGD - 4) 8424,8424,9916
9916 CONTINUE
9920 END
```



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      SUBROUTINE TRANS(INTER,ITECOM,IOWTYP,ICHOSE,NUM,LINDI,LROP)
180 COMMON/2000/INONOP(28,90,3),INONWF(28,90,3),LPRO(28,90)
190 DIMENSION NSUB(3)
195 LINDI = 1
200 K = NUM
204 DO 224 N = 1,NUM
208 IF (ICHOSE - 1) 212,212,220
212 NSUB(N) = INONOP(INTER,ITECOM,N)
216 GO TO 224
220 NSUB(N) = INONWF(INTER,ITECOM,N)
224 CONTINUE
228 IF (NUM - 1) 300,300,232
232 DO 264 N = 1,NUM
236 IF (N - NUM) 240,252,250
240 IF (NSUB(N) - NSUB(N+1)) 264,241,246
241 IF (ICHOSE - 1) 242,242,264
242 LINDI = 0
244 GO TO 264
246 CALL SWAP(NSUB(N),NSUB(N+1))
248 GO TO 264
250 CALL ERROR(1)
252 IF (NSUB(N) - NSUB(1)) 254,258,264
254 CALL SWAP(NSUB(N),NSUB(1))
256 GO TO 264
258 IF (ICHOSE - 1) 260,260,264
260 LINDI = 0
264 CONTINUE
268 IF (K - 2) 280,280,272
272 K = 1
276 GO TO 232
280 IF (NUM - 2) 284,284,292
284 IOWTYP = NSUB(1) + 10*NSUB(2)
288 GO TO 304
292 IOWTYP = NSUB(1) + 10*NSUB(2) + 100*NSUB(3)
296 GO TO 304
300 IOWTYP = NSUB(1)
304 LROP = LPRO(INTER,ITECOM)
306 RETURN
308 END

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      SUBROUTINE SWAP(IOPWF,JOPWF)
10 IDUM = IOPWF
20 IOPWF = JOPWF
30 JOPWF = IDUM
40 RETURN
50 END

```

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      SUBROUTINE ERROR(N)
      PRINT 100,N
100 FORMAT(10X,9HERROR NO.,I5)
      RETURN
      END

```

```

      SUBROUTINE GONOGO(NUTCOM,MODEPI,IWFJ,IWFK)
150 COMMON/SUBGNO/MOELEC(2),MOMAGN(2)
160 COMMON/GNOTER/INDZJJ(6),INDZJK(6),INDZKJ(6)
180 COMMON/GNOPRO/NRIP(12,12),IGP(12,12,4)
200 NTYPE = 0
204 DO 484 N = 1,NUTCOM
208 IF (N-3) 212,212,220
212 KDIG = N
216 GO TO 224
220 KDIG = N - 3
224 GO TO (228,228,372,268,268), MODEPI
228 IF (N-2) 232,232,240
232 I = MOELEC(KDIG)
236 GO TO 248
240 KDIG = N - 2
244 I = MOMAGN(KDIG)
248 IWFONE = IWFJ
252 IWFTWO = IWFK
256 MOMONE = 0
260 NDEC = 1
264 GO TO 404
268 IF (NTYPE) 272,276,328
272 CALL ERROR(90)
276 IWFONE = IWFJ
280 IWFTWO = IWFK
284 GO TO (288,300,312), KDIG
288 MOMONE = MOELEC(1)
292 I = MOELEC(2)
296 GO TO 320
300 MOMONE = MOELEC(1)
304 I = MOELEC(1)
308 GO TO 320
312 MOMONE = MOELEC(2)
316 I = MOELEC(1)
320 NDEC = 0
324 GO TO 404
328 IF (N - 3) 332,332,344
332 IWFONE = IWFJ
336 IWFTWO = IWFJ
340 GO TO 352
344 IWFONE = IWFK
348 IWFTWO = IWFK
352 GO TO (356,364,356), KDIG
356 I = MOMAGN(1)
360 GO TO 404
364 I = MOMAGN(2)
368 GO TO 404
372 GO TO (376,376,384), N
376 I = MOELEC(1)
380 GO TO 388
384 I = MOELEC(2)
388 IWFONE = IWFJ
392 IWFTWO = IWFK
396 NDEC = 1
400 MOMONE = 0
404 NP = NRIP(I,IWFONE)
408 DO 460 L = 1,NP

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```
412 KD = IWFTWO - IGP(I,IWFONE,L)
416 IF (KD) 420,428,420
420 INQZ = 0
424 GO TO 432
428 INQZ = 1
432 IF (NTYPE) 436,436,456
436 IF (NDEC) 440,440,448
440 INDZKJ(N) = INDZKJ(N) + INQZ
444 GO TO 460
448 INDZJK(N) = INDZJK(N) + INQZ
452 GO TO 460
456 INDZJJ(N) = INDZJJ(N) + INQZ
460 CONTINUE
464 IF (MOMONE) 484,484,468
468 I = MOMONE
472 MOMONE = 0
476 NDEC = 1
480 GO TO 404
484 CONTINUE
488 IF (NTYPE) 492,492,504
492 GO TO (504,504,504,496,496), MODEPI
496 NTYPE = 1
500 GO TO 204
504 RETURN
508 END
```

```

SUBROUTINE TERPER(NCOM, NTER, NMATEL, MODEPI)
190 COMMON/GNOTER/INDZJJ(6), INDZJK(6), INDZKJ(6)
195 COMMON/TERPRO/KOP(5), KWF(5), IOPQ(5), IWFQ(5)
200 COMMON/SUBTER/LABOP(5), LABWF(5), INZ(28), NNSQIN, IOPADE, ITPADE,
    IOPADM
204 GO TO (208, 208, 516, 1004, 1004), MODEPI
C   THIS BRANCH DETERMINES WHETHER WE ARE DEALING WITH ABSORPTION OR
C   CIRCULAR DICHROISM (MODE=0,1) OR WITH THE MORE COMPLICATED TERMS
C   OF MAGNETIC CIRCULAR DICHROISM, MCD(B) (MODE=2), MCD(C) (MODE=3),
C   AND MCD(A) (MODE=4). HERE MODEPI=MODE+1.
208 IOPADM = 2
C   IOPADM, IOPADE, ITPADE GIVE THE MATRIX ELEMENT LOCATIONS FOR EACH
C   TERM OF THE MAGNETIC MOMENT, ELECTRIC MOMENT AND FOR MCD THE SECOND
C   COMPONENT OF THE ELECTRIC MOMENT. THESE ARE USED LATER IN THE MAIN
C   PROGRAM WHEN DEGENERATE SYMMETRIES MAKE IT NECESSARY TO ELIMINATE
C   MEMBER PERMUTATIONS NOT ALLOWED BY THE DOT PRODUCT (ABSORPTION AND
C   CIRCULAR DICHROISM) OR TRIPLE PRODUCT (MAGNETIC CIRCULAR DICHROISM)
212 IF (INDZJK(NCOM)) 216, 220, 232
C   IF INDZJK(NCOM)=1, THIS MEANS THAT FOR THE NCOM COMPONENT, THAT ALL
C   TERMS CONTAINING (J/U/K) (OR (J/M/K) FOR CIRCULAR DICHROISM) WILL
C   BE ZERO. IF INDZJK(NCOM)=0 THESE TERMS ARE NONZERO. IF THE NTER
C   TERM IS ZERO, THEN INZ(NTER)=0. IF NOT IT IS 1. THIS VALUE IS USED
C   IN THE 2000 SECTION OF THE MAIN PROGRAM TO DETERMINE WHETHER TO
C   CALCULATE THESE TERMS OR NOT (CALCULATE IF 1)
216 CALL ERROR(80)
220 GO TO (228, 228, 228, 228, 228, 232, 232, 232, 228, 228, 228, 232, 232,
    1232, 232, 232, 232), NTER
C   HERE WE SET THE VALUE OF INZ(NTER) ONLY FOR THE TERMS CONTAINING
C   (J/U/K) OR (J/M/K).
228 INZ(NTER) = 0
232 GO TO (236, 236, 244, 244, 280, 300, 320, 320, 364, 372, 280, 380, 400, 424,
    1424, 424, 424, 424), NTER
236 NNSQIN = 0
240 GO TO 248
244 NNSQIN = 1
C   THE VALUE OF NNSQIN INDICATES WHETHER WE HAVE FOR THE TERM WE ARE
C   CONSIDERING, NO ADDITIONAL SYMMETRIES (NNSQIN=0), N ADDITIONAL
C   SYMMETRIES (NNSQIN=1), OR N**2 ADDITIONAL SYMMETRIES (NNSQIN=2).
248 CALL SWAP (KOP(1), KOP(3))
252 CALL SWAP (IOPQ(1), IOPQ(3))
256 CALL SWAP (LABOP(1), LABOP(3))
C   THE SWAP SUBROUTINE SWAPS THE CONTENTS OF THE TWO ARGUMENTS, E.G.
C   THE CONTENTS OF KOP(1) AND KOP(3) AS IN STATEMENT 248.
260 IF (IOPADE - 2) 264, 264, 272
264 IOPADE = 3
268 GO TO 488
272 IOPADE = 1
276 GO TO 488
280 IOPADE = 4
284 CALL SWAP (KOP(3), KOP(4))
288 CALL SWAP (IOPQ(3), IOPQ(4))
292 CALL SWAP (LABOP(3), LABOP(4))
296 GO TO 488
300 NNSQIN = 0
304 CALL SWAP (KWF(3), KWF(4))
308 CALL SWAP (IWFQ(3), IWFQ(4))
312 CALL SWAP (LABWF(3), LABWF(4))

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C      THIS COMPLETES THE ABSORPTION, CIRCULAR DICHROISM PORTION OF THIS
C      SUBROUTINE. THE NEXT PORTION IS THE MCD(B) SECTION.
516 IF (INDZJK(NCOM)) 520,524,532
520 CALL ERROR(81)
524 GO TO (528,528,528,532,532,528,528,528,528,528,528,528,528,528,
      1532,532,532,528,528,528,532,532,532,532,532,532,532), NTER
528 INZ(NTER) = 0

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532 GO TO (536,536,556,576,596,616,632,652,664,672,692,700,732,752,
1772,596,804,812,832,840,576,632,860,692,868,896,904,596), NTER
536 NNSQIN = 0
540 IOPADE = 2
544 ITPADE = 1
548 IOPADM = 3
552 GO TO 912
556 IOPADM = 4
560 CALL SWAP (KOP(3),KOP(4))
564 CALL SWAP (IOPQ(3),IOPQ(4))
568 CALL SWAP (LABOP(3),LABOP(4))
572 GO TO 912
576 NNSQIN = 0
580 CALL SWAP (KWF(3),KWF(4))
584 CALL SWAP (IWFQ(3),IWFQ(4))
588 CALL SWAP (LABWF(3),LABWF(4))
592 GO TO 912
596 IOPADE = 3
600 CALL SWAP (KOP(2),KOP(3))
604 CALL SWAP (IOPQ(2),IOPQ(3))
608 CALL SWAP (LABOP(2),LABOP(3))
612 GO TO 912
616 CALL SWAP (KWF(2),KWF(3))
620 CALL SWAP (IWFQ(2),IWFQ(3))
624 CALL SWAP (LABWF(2),LABWF(3))
628 GO TO 912
632 ITPADE = 2
636 CALL SWAP (KOP(1),KOP(2))
640 CALL SWAP (IOPQ(1),IOPQ(2))
644 CALL SWAP (LABOP(1),LABOP(2))
648 GO TO 912
652 ITPADE = 1
656 NNSQIN = 1
660 GO TO 636
664 ITPADE = 2
668 GO TO 636
672 IOPADM = 5
676 CALL SWAP (KOP(4),KOP(5))
680 CALL SWAP (IOPQ(4),IOPQ(5))
684 CALL SWAP (LABOP(4),LABOP(5))
688 GO TO 912
692 ITPADE = 1
696 GO TO 636
700 IOPADE = 2
704 CALL SWAP (KWF(2),KWF(3))
708 CALL SWAP (IWFQ(2),IWFQ(3))
712 CALL SWAP (LABWF(2),LABWF(3))
716 CALL SWAP (KWF(3),KWF(4))
720 CALL SWAP (IWFQ(3),IWFQ(4))
724 CALL SWAP (LABWF(3),LABWF(4))
728 GO TO 600
732 IOPADM = 3
736 CALL SWAP (KOP(3),KOP(5))
740 CALL SWAP (IOPQ(3),IOPQ(5))
744 CALL SWAP (LABOP(3),LABOP(5))
748 GO TO 912
752 IOPADM = 4
756 CALL SWAP (KOP(3),KOP(4))

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760 CALL SWAP (IOPQ(3),IOPQ(4))
764 CALL SWAP (LABOP(3),LABOP(4))
768 GO TO 912
772 IOPADM = 5
776 CALL SWAP (KWF(3),KWF(5))
780 CALL SWAP (IWFQ(3),IWFQ(5))
784 CALL SWAP (LABWF(3),LABWF(5))
788 CALL SWAP (KOP(4),KOP(5))
792 CALL SWAP (IOPQ(4),IOPQ(5))
796 CALL SWAP (LABOP(4),LABOP(5))
800 GO TO 912
804 IOPADE = 4
808 GO TO 756
812 ITPADE = 2
816 CALL SWAP (KWF(2),KWF(4))
820 CALL SWAP (IWFQ(2),IWFQ(4))
824 CALL SWAP (LABWF(2),LABWF(4))
828 GO TO 636
832 ITPADE = 3
836 GO TO 600
840 ITPADE = 1
844 CALL SWAP (KOP(1),KOP(3))
848 CALL SWAP (IOPQ(1),IOPQ(3))
852 CALL SWAP (LABOP(1),LABOP(3))
856 GO TO 912
860 IOPADE = 3
864 GO TO 756
868 CALL SWAP (KWF(2),KWF(3))
872 CALL SWAP (IWFQ(2),IWFQ(3))
876 CALL SWAP (LABWF(2),LABWF(3))
880 CALL SWAP (KWF(4),KWF(5))
884 CALL SWAP (IWFQ(4),IWFQ(5))
888 CALL SWAP (LABWF(4),LABWF(5))
892 GO TO 912
896 IOPADE = 2
900 GO TO 600
904 IOPADM = 4
908 GO TO 676
912 GO TO (916,924,924,924,924,924,924,932,932,932,932,932,932,
1932,932,932,932,932,932,932,932,932,932,932,932), NTER
916 NMATEL = 3
920 GO TO 1316
924 NMATEL = 4
928 GO TO 1316
932 NMATEL = 5
936 GO TO 1316
C THIS COMPLETES THE MCD(B) SECTION. THE FINAL SECTION DEALS WITH THE
C MCD(A) AND MCD(C) TERMS
1004 IF (INDZJJ(NCOM)) 1008,1012,1016
C INDEJJ(NCOM) IS LIKE INDZJK(NCOM) BUT DEALS WITH TERMS THAT CONTAIN
C (J/M/J) OR (K/M/K).
1008 CALL ERROR(82)
1012 GO TO (1014,1014,1014,1016,1016,1016,1014,1014,1014,1014,1014,
11014,1016,1016), NTER
1014 INZ(INTER) = 0
1016 IF (INDZKJ(NCOM)) 1020,1022,1024
1020 CALL ERROR(83)
1022 GO TO (1023,1023,1023,1023,1023,1023,1023,1023,1023,1023,1024,1024,

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```

11024,1023,1023), NTER
1023 INZ(INTER) = 0
1024 IF (INDZJK(NCOM)) 1025,1026,1032
1025 CALL ERROR(90)
1026 GO TO (1028,1032,1032,1028,1028,1028,1032,1032,1032,1032,1032,
1032,1032,1032), NTER
1028 INZ(INTER) = 0
1032 GO TO (1036,1056,1076,1092,1112,1132,1152,1092,1168,1176,1192,
11212,1220,1268), NTER
1036 NNSQIN = 0
1040 IOPADE = 2
1044 ITPADE = 1
1048 IOPADM = 3
1052 GO TO 1292
1056 IOPADM = 4
1060 CALL SWAP (KOP(3),KOP(4))
1064 CALL SWAP (IOPQ(3),IOPQ(4))
1068 CALL SWAP (LABOP(3),LABOP(4))
1072 GO TO 1292
1076 CALL SWAP (KWF(3),KWF(4))
1080 CALL SWAP (IWFQ(3),IWFQ(4))
1084 CALL SWAP (LABWF(3),LABWF(4))
1088 GO TO 1292
1092 IOPADE = 3
1096 CALL SWAP (KOP(2),KOP(3))
1100 CALL SWAP (IOPQ(2),IOPQ(3))
1104 CALL SWAP (LABOP(2),LABOP(3))
1108 GO TO 1292
1112 IOPADE = 2
1116 CALL SWAP (KWF(3),KWF(4))
1120 CALL SWAP (IWFQ(3),IWFQ(4))
1124 CALL SWAP (LABWF(3),LABWF(4))
1128 GO TO 1096
1132 IOPADM = 5
1136 CALL SWAP (KOP(4),KOP(5))
1140 CALL SWAP (IOPQ(4),IOPQ(5))
1144 CALL SWAP (LABOP(4),LABOP(5))
1148 GO TO 1292
1152 CALL SWAP (KWF(3),KWF(5))
1156 CALL SWAP (IWFQ(3),IWFQ(5))
1160 CALL SWAP (LABWF(3),LABWF(5))
1164 GO TO 1292
1168 IOPADE = 4
1172 GO TO 1060
1176 CALL SWAP (KWF(2),KWF(3))
1180 CALL SWAP (IWFQ(2),IWFQ(3))
1184 CALL SWAP (LABWF(2),LABWF(3))
1188 GO TO 1292
1192 ITPADE = 2
1196 CALL SWAP (KOP(1),KOP(2))
1200 CALL SWAP (IOPQ(1),IOPQ(2))
1204 CALL SWAP (LABOP(1),LABOP(2))
1208 GO TO 1292
1212 IOPADE = 3
1216 GO TO 1060
1220 IOPADE = 2
1224 ITPADE = 1
1228 CALL SWAP (KWF(2),KWF(3))

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```
1232 CALL SWAP (IWFQ(2),IWFQ(3))
1236 CALL SWAP (LABWF(2),LABWF(3))
1240 CALL SWAP (KWF(4),KWF(5))
1244 CALL SWAP (IWFQ(4),IWFQ(5))
1248 CALL SWAP (LABWF(4),LABWF(5))
1252 CALL SWAP (KOP(1),KOP(2))
1256 CALL SWAP (IOPQ(1),IOPQ(2))
1260 CALL SWAP (LABOP(1),LABOP(2))
1264 GO TO 1096
1268 IOPADE = 3
1272 IOPADM = 4
1276 CALL SWAP (KOP(4),KOP(5))
1280 CALL SWAP (IOPQ(4),IOPQ(5))
1284 CALL SWAP (LABOP(4),LABOP(5))
1288 GO TO 1096
1292 GO TO (1296,1304,1304,1304,1312,1312,1312,1312,1312,1312,
11312,1312,1312). NIFR
1296 NMATEL = 3
1300 GO TO 1316
1304 NMATEL = 4
1308 GO TO 1316
1312 NMATEL = 5
1316 RETURN
1320 END
```

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      SUBROUTINE PROD(LUNONQ,NORNSQ,NALL,NSQALL,NUMMAT,NMATEL)
166 COMMON/GNOPRO/NRIP(12,12),IGP(12,12,4)
170 COMMON/TERPRO/KOP(5),KWF(5),IOPQ(5),IWFQ(5)
174 COMMON/SUBPRO/IOPQA(5),IWFQA(5),JDSLWF(4),JOSOP(4),JDSTWF(4),
      IMATELQ(5),NRIPS,IREPSB(9)
176 IF (NUMMAT - NMATEL) 180,192,178
178 CALL ERROR(47)
179 GO TO 192
180 IWFQP = IWFQ(NUMMAT + 1)
184 KWFP = KWF(NUMMAT + 1)
188 GO TO 200
192 IWFQP = IWFQ(1)
196 KWFP = KWF(1)
C
C   HERE THE SYMMETRY VALUE AND STATE OF KNOWLEDGE OF THE LEADING WAVE
C   FUNCTION OF THE NUMMAT MATRIX ELEMENT ARE STORED IN THE DUMMY
C   STORAGE SLOTS KWFP, IWFQP. IF NUMMAT=NMATEL, THEN THE NUMMAT+1
C   ELEMENT IS THE FIRST ELEMENT.
C
200 NSUM = IWFQP + IOPQ(NUMMAT) + IWFQ(NUMMAT) + 1
C
C   THE VALUES OF IWFQP, IOPQ(NUMMAT), IWFQ(NUMMAT) DESIGNATE
C   THE STATE OF KNOWLEDGE OF THE LEADING WAVE FUNCTION, THE OPERATOR,
C   AND THE TRAILING WAVE FUNCTION OF THE NUMMAT MATRIX ELEMENT. VALUES
C   OF 1 INDICATE KNOWLEDGE OF UNIT SYMMETRIES, OF 0 INDICATE LACK OF
C   KNOWLEDGE. THE VALUE OF NSUM-1 GIVES DIRECTLY THE NUMBER OF UNIT
C   SYMMETRIES KNOWN.
C
204 GO TO (408,408,268,208), NSUM
C
C   WE FOLLOW DIFFERENT PATHS FOR DIFFERENT NUMBERS OF UNIT SYMMETRIES
C   KNOWN
C
208 IDV = KOP(NUMMAT)
212 JDV = KWF(NUMMAT)
C
C   THIS PORTION IS FOR ALL THREE UNIT SYMMETRIES KNOWN. ITS FUNCTION
C   IS TO DETERMINE WHETHER THESE THREE SYMMETRIES ARE COMPATIBLE, THAT
C   IS WHETHER THE SYMMETRY OF OF ANY ONE IS CONTAINED IN THE GROUP
C   MULTIPLICATION PRODUCT OF THE OTHER TWO. THE SYMMETRIES OF THE
C   OPERATOR AND TRAILING WAVE FUNCTION ARE PLACED IN IDV AND JDV. THE
C   NUMBER OF IRREDUCIBLE REPRESENTATIONS RESULTING FROM THE GROUP
C   PRODUCT IDV X JDV ARE STORED IN NRIPS. EACH OF THESE REPRESENTATIONS
C   FOR COINCIDENCE. IF THERE ARE NO COINCIDENCES FOR ANY OF THE
C   PRODUCT REPRESENTATIONS, THEN THE MATRIX ELEMENT IS ZERO. IF THIS
C   IS THE CASE THEN NRIPS IS SET EQUAL TO ZERO IN ORDER TO SIGNAL
C   SECTION 3000 THAT IT MAKES NO SENSE TO COMPUTE ANY SUCCEEDING
C   MATRIX ELEMENTS FOR THIS DEGENERATE PERMUTATION AND TO SIGNAL
C   SECTION 4000 NOT TO STORE THIS PARTICULAR SET OF GROUP PRODUCT
C   TERMS.
C
216 NRIPS = NRIP(IDV,JDV)
220 INDALL = 0
C
C   THE VALUE OF INDALL LATER USED TO DETERMINE WHETHER TO SET NRIPS
C   EQUAL TO ZERO (IF INDALL SET EQUAL TO 1).
C

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224 DO 252 NRS = 1,NRIPS
228 KDV = IGP(IDV,JDV,NRS)
232 IF (KDV - KWFP) 252,236,252
236 JDSOP(1) = IDV
240 JDSLWF(1) = KDV
244 JDSTWF(1) = JDV
C
C   WE HAVE FOUND THAT ONE OF THE IRREDUCIBLE REPRESENTATIONS MATCHES
C   KWFP. THEREFORE THE UNIT SYMMETRIES ARE STORED IN THE APPROPRIATE
C   STORAGE SLOTS. SINCE KWFP WILL BE MATCHED BY ONLY ONE OF THE
C   IRREDUCIBLE REPRESENTATIONS, NRIPS=1 WHEN A MATCH IS MADE AND ZERO
C   WHEN ONE IS NOT. THIS DONE BY SETTING NRIPS=INDALL.
C
248 INDALL = 1
252 CONTINUE
256 NRIPS = INDALL
260 MATLQ(NUMMAT) = 1
C
C   HERE WE INDICATE THAT THE NUMMAT MATRIX ELEMENT HAS BEEN EVALUATED.
C
264 GO TO 516
268 IF (NSUM - IWFQ - 2) 270,324,272
270 CALL ERROR(48)
271 GO TO 324
C
C   IF THE LEADING WAVE FUNCTION IS KNOWN, THE ARGUEMENT IS ZERO, IF
C   UNKNOWN THE ARGUEMENT IS ONE.
C
272 IDV = KOP(NUMMAT)
276 JDV = KWF(NUMMAT)
280 NRIPS = NRIP(IDV,JDV)
284 DO 300 NRS = 1,NRIPS
288 JDSLWF(NRS) = IGP(IDV,JDV,NRS)
292 JDSOP(NRS) = IDV
296 JDSTWF(NRS) = JDV
C
C   THE LAST THREE STATEMENTS STORE THE TWO GIVEN AND ONE COMPUTED UNIT
C   SYMMETRIES IN THEIR DUMMY STORAGE SLOTS FOR EACH VALUE OF NRS.
C
300 CONTINUE
304 IF (NUMMAT - NMATL) 316,308,306
306 CALL ERROR(49)
308 IWFQ(1) = 1
312 GO TO 320
316 IWFQ(NUMMAT + 1) = 1
320 MATLQ(NUMMAT) = 1
322 GO TO 516
C
C   HERE WE HAVE INDICATED THAT THE LEADING WAVE FUNCTION IS KNOWN AND
C   THAT THE NUMMAT MATRIX ELEMENT HAS BEEN EVALUATED.
C
324 IF (IWFQ(NUMMAT)) 326,328,368
326 CALL ERROR(50)
C
C   STATEMENTS 272 TO 320 EVALUATE THE MATRIX ELEMENT IF OPERATOR AND
C   TRAILING WAVE FUNCTION UNIT SYMMETRIES ARE KNOWN AND THE LEADING
C   WAVE FUNCTION UNIT SYMMETRY UNKNOWN. IF IWFQ(NUMMAT)=1, THEN THE
C   THE TRAILING WAVE FUNCTION IS UNKNOWN. SINCE TWO UNIT SYMMETRIES

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C ARE KNOWN FOR THIS CASE, THIS MEANS THE OPERATOR AND LEADING WAVE
C FUNCTION ARE KNOWN. IF IWFQ(NUMMAT)=1, THE TRAILING WAVE FUNCTION
C IS KNOWN. SINCE THE LEADING WAVE FUNCTION IS KNOWN AND SINCE TWO
C UNIT SYMMETRIES ARE KNOWN THE OPERATOR IS UNKNOWN.
C
328 IDV = KOP(NUMMAT)
332 NRIPS = NRIP(IDV,KWFP)
336 DO 352 NRS = 1,NRIPS
340 JDSTWF(NRS) = IGP(IDV,KWFP,NRS)
344 JDSOP(NRS) = IDV
348 JDSLWF(NRS) = KWFP
352 CONTINUE
356 IWFQ(NUMMAT) = 1
C
C THIS INDICATES THE TRAILING WAVE FUNCTION OF THE NUMMAT MATRIX
C ELEMENT HAS BEEN DETERMINED.
C
360 MATELQ(NUMMAT) = 1
364 GO TO 516
368 IDV = KWF(NUMMAT)
372 NRIPS = NRIP(IDV,KWFP)
376 DO 392 NRS = 1,NRIPS
380 JDSOP(NRS) = IGP(IDV,KWFP,NRS)
384 JDSLWF(NRS) = KWFP
388 JDSTWF(NRS) = IDV
392 CONTINUE
396 IOPQ(NUMMAT) = 1
400 MATELQ(NUMMAT) = 1
404 GO TO 516
408 IF (LUNONQ) 410,412,420
410 CALL ERROR(51)
C
C IF LUNONQ IS ZERO THE PROGRAM DOES NOT HAVE TO DEAL WITH THE N OR
C N**2 ADDITIONAL SYMMETRIES FOR THIS TERM, AT LEAST NOT YET. IF
C LUNONQ IS GREATER THAN ZERO THE PROGRAM DEALS WITH THESE SYMMETRIES.
C
412 MATELQ(NUMMAT) = 0
416 GO TO 516
420 LUNONQ = 0
C
C LUNONQ IS RESET TO ZERO ONCE THE DECISION HAS BEEN MADE TO DO THE
C ADDITIONAL SYMMETRIES. THE DECISION IS MADE ONCE FOR THE N CASE.
C IT IS MADE TWICE FOR THE N**2 CASE. THE RESETTING IS NECESSARY
C EVERY TIME THE DECISION HAS BEEN MADE SO THAT IT CAN BE MADE AGAIN
C WHEN NECESSARY.
C
424 IF (IWFQ) 426,428,432
426 CALL ERROR(52)
C
C IN THE FOLLOWING BRANCHES WE ARE IN THE SITUATION WHERE WE KNOW
C EITHER ONE OR NONE OF THE UNIT SYMMETRIES OF THE MATRIX ELEMENT. IF
C NONE ARE KNOWN THE BRANCHES TAKE US OUT OF THE SUBROUTINE SO THAT
C WE CAN GO ON TO A MATRIX ELEMENT THAT DOES HAVE AT LEAST ONE UNIT
C SYMMETRY KNOWN. IF ONE SYMMETRY IS KNOWN THE BRANCHES DIRECT US SO
C THAT IF THE KNOWN UNIT SYMMETRY IS A WAVE FUNCTION, THE OPERATOR
C SYMMETRY IS SUPPLIED. IF THE KNOWN IS THE OPERATOR SYMMETRY, THE
C TRAILING WAVE FUNCTION SYMMETRY IS SUPPLIED. WE FIRST INVESTIGATE
C THE CASES WHERE EITHER OF THE WAVE FUNCTION SYMMETRIES ARE KNOWN

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C
428 IF (IWFQ(NUMMAT)) 430,468,432
430 CALL ERROR(53)
431 GO TO 468
432 IF (NORNSQ - 1) 434,436,452
434 CALL ERROR(54)
C
C   IF NORNSQ=1, WE MUST SUPPLY THE FIRST (N) SYMMETRY. IF NORNSQ=2,
C   WE MUST SUPPLY THE SECOND (N**2) SYMMETRY. THE PARTICULAR
C   REPRESENTATIONS SUPPLIED IS DETERMINED BY SECTION 8000. WHEN A UNIT
C   SYMMETRY IS SUPPLIED IOPQ(NUMMAT) (OR IWFQ(NUMMAT)) IS SET EQUAL TO
C   ONE INDICATING THE KNOWLEDGE OF THIS UNIT SYMMETRY FOR THIS
C   PARTICULAR GROUP TERM. ALSO IOPQA(NUMMAT) (OR IWFQA(NUMMAT)) IS SET
C   EQUAL TO ONE INDICATING THE KNOWLEDGE OF THIS UNIT SYMMETRY FOR
C   THIS SET OF GROUP TERMS.
C
436 KOP(NUMMAT) = IREPSB(NALL)
440 IOPQ(NUMMAT) = 1
444 IOPQA(NUMMAT) = 1
448 GO TO 200
452 KOP(NUMMAT) = IREPSB(NSQALL)
456 IOPQ(NUMMAT) = 1
460 IOPQA(NUMMAT) = 1
464 GO TO 200
468 IF (IOPQ(NUMMAT)) 470,472,480
470 CALL ERROR(55)
472 MATELQ(NUMMAT) = 0
C
C   NONE OF THE UNIT SYMMETRIES ARE KNOWN FOR THE NUMMAT MATRIX ELEMENT.
C
476 GO TO 516
480 IF (NORNSQ - 1) 482,484,500
482 CALL ERROR(56)
484 KWF(NUMMAT) = IREPSB(NALL)
488 IWFQ(NUMMAT) = 1
492 IWFQA(NUMMAT) = 1
496 GO TO 200
500 KWF(NUMMAT) = IREPSB(NSQALL)
504 IWFQ(NUMMAT) = 1
508 IWFQA(NUMMAT) = 1
512 GO TO 200
516 RETURN
520 END

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SUBROUTINE SEARCH(IMECCD,JUPN,JWFN,KWFN,KPOS)
192 COMPLEX COCOME,COUPCF,TEMCC
196 COMMON/SUBSER/IDEGRR(12),IPARTM(12),IRDEG(12),MEMRFP(10,1,4),
    1CUCOME(5,4,4),COUPCF(10,10,4),NNDREP,MATCH(4)
200 DIMENSION INDROW(2),LOCATE(2),MEMNUM(2),TEMCC(8)

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C
C SUBROUTINE SEARCH SEARCHES OUT ALL THE COUPLING COEFFICIENTS
C CORRESPONDING TO A (MATRIX ELEMENT) SET OF UNIT SYMMETRIES. THERE
C ARE THREE UNIT SYMMETRIES PER MATRIX ELEMENT AND IF TWO OR THREE
C OF THESE SYMMETRIES ARE DEGENERATE THEN, SINCE FOR EACH DOUBLY
C DEGENERATE REPRESENTATION THERE ARE TWO MEMBERS, THERE ARE 2**2
C OR 2**3 COMBINATIONS OF THESE UNIT SYMMETRY MEMBERS. FOR A
C NON-DEGENERATE REPRESENTATION THE MEMBER IS IDENTICAL TO THE
C SYMMETRY ITSELF. FOR EACH OF THESE COMBINATIONS THERE CORRESPONDS
C A COUPLING COEFFICIENT. THUS FOR A SET OF UNIT SYMMETRIES, TWO OF
C WHICH ARE DOUBLY DEGENERATE, THERE IS A SET OF 2**2=4 COUPLING
C COEFFICIENTS, SOME OF WHICH CAN BE ZERO. SIMILARLY IF ALL THREE OF
C THE UNIT SYMMETRIES ARE DOUBLY DEGENERATE, THERE IS A SET OF 2**3=8
C COUPLING COEFFICIENTS. THESE ARE INITIALLY STORED IN THE MAIN
C PROGRAM IN A THREE SUBSCRIPT ARRAY, EACH SUBSCRIPT CORRESPONDING
C TO A UNIT SYMMETRY AND BEING ONE OR TWO DIMENSIONAL DEPENDING ON
C WHETHER THE UNIT SYMMETRY IS NON-DEGENERATE OR DOUBLY DEGENERATE.
C MAIN PROGRAM STORAGE FOR THE COUPLING COEFFICIENTS IS IN THE ARRAY
C COUPCF(NSETCM,NCMSET,NUMROW), WHERE NSETCM IS THE INDEX OF THE SET
C OF COLUMNS AND CORRESPONDS TO THE OPERATOR UNIT SYMMETRY, NCMSET
C IS THE INDEX OF THE COLUMN IN THE SET NSETCM AND CORRESPONDS TO THE
C TRAILING WAVE FUNCTION UNIT SYMMETRY, AND NUMROW IS THE INDEX OF
C THE ROW AND CORRESPONDS TO THE LEADING WAVE FUNCTION UNIT SYMMETRY.
C ALTHOUGH THE RULE THAT A SUBSCRIPT IS TWO DIMENSIONAL FOR A DOUBLY
C DEGENERATE REPRESENTATION HOLDS, THIS IS SOMETIMES DISGUISED BY THE
C FACT THAT THE ARRAYS ARE STACKED AND THUS A PARTICULAR SUBSCRIPT
C MAY TAKE ON VALUES 3,4 OR 5,6 ETC. RATHER THAN 1,2. SUBROUTINE
C SEARCH, GIVEN ALL 3 UNIT SYMMETRIES, CHOSSES THE FIRST MEMBER OF
C EACH AND EXTRACTS FROM THE MAIN PROGRAM ARRAY NOT ONLY THE
C CORRESPONDING COUPLING COEFFICIENT (TERMED THE FIRST COUPLING
C COEFFICIENT) BUT ALL COUPLING COEFFICIENTS CORRESPONDING TO THIS
C SET OF UNIT SYMMETRIES. SUBROUTINE SEARCH STORES THIS SET OF
C COUPLING COEFFICIENTS IN THE TEMPORARY STORAGE ARRAY TEMCC(ITEMCC)
C WHERE THE ORDER OF STORAGE OF COUPCF(NSETCM,NCMSET,NUMROW) HAS
C NUMROW VARYING MOST RAPIDLY, NCMSET THE NEXT MOST RAPIDLY, AND
C NSETCM THE MOST SLOWLY. WE MUST NOT LOSE THE INFORMATION CONTAINED
C IN THE THREE SUBSCRIPTS HOWEVER, SINCE IF WE CHANGE THE MEMBER OF
C A DOUBLY DEGENERATE WAVE FUNCTION (FOR THE COMPLEMENTARY MEMBER)
C OF THE IMECCD MATRIX ELEMENT, THEN WE MUST ALSO CHANGE THE MEMBER
C OF THE TRAILING WAVE FUNCTION OF THE IMECCD+1 MATRIX ELEMENT (FOR
C LEADING WAVE FUNCTION OF IMECCD ELEMENT) OR OF THE LEADING WAVE
C FUNCTION OF THE IMECCD-1 ELEMENT (FOR TRAILING FUNCTION OF IMECCD
C ELEMENT). THUS WE MUST HAVE A CONTINUING RECORD OF THE MEMBERS
C CURRENTLY MAKING UP EACH MATRIX ELEMENT SO THAT WHEN WE DO MEMBER
C PERMUTATIONS OF THE UNIT SYMMETRIES WE CAN EXTRACT THE CORRECT
C COUPLING COEFFICIENTS. A PROBLEM ARISES IN THAT FORTRAN IV THERE
C IS ONLY PROVISION FOR 3 SUBSCRIPTS. SINCE IN STORING ALL THE
C COUPLING COEFFICIENTS WE NEED ONE SUBSCRIPT TO INDICATE WHICH
C (IMECCD) MATRIX ELEMENT THEY ARE FOR, THIS ONLY LEAVES TWO
C SUBSCRIPTS TO CARRY THE INFORMATION OF THE ORIGINAL 3, NSETCM,
C NCMSET, NUMROW. THIS DONE BY STACKING THE COUPLING COEFFICIENTS
C CORRESPONDING TO THE OPERATOR SECOND MEMBER ON THE COEFFICIENTS

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C   CORRESPONDING TO THE OPERATOR FIRST MEMBER (WHERE THE OPERATOR IS
C   DOUBLY DEGENERATE). THE STACKING IS FURTHER DESCRIBED IN SECTION
C   7000 OF THE MAIN PROGRAM. THUS THE LAST PART OF SUBROUTINE SEARCH
C   STACKS THE COEFFICIENTS IN TEMCC(ITEMCC) IN THE THREE DIMENSIONAL
C   ARRAY COCUME(IMECCD,NEWIA,NEWIB).
C
204 ICLK = 1
C
C   ICLK CLOCKS THE OPERATOR AND TRAILING WAVE FUNCTION INITIAL MEMBERS.
C
208 INMROW = 4
C
C   INMROW INDICATES THE NUMBER OF ROWS INDEXED BY LEADING WAVE FUNCTION
C   MEMBERS WHICH COULD CORRESPOND TO THE OPERATOR AND TRAILING WAVE
C   FUNCTION SYMMETRIES GIVEN. STATEMENT 208 IS AN INITIALIZATION AND
C   MAY BE CHANGED DEPENDING ON THE DEGENERACYS OF THE THREE UNIT
C   SYMMETRIES
C
212 NUMREP = JUPN
C
C   THE OPERATOR SYMMETRY IS PUT IN NUMREP FOR ICLK=1. FOR ICLK=2 THE
C   TRAILING WAVE FUNCTION SYMMETRY WILL BE PUT IN NUMREP. NUMREP IS
C   USED AS AN INDEX TO DETERMINE THE POSITIONS OF THE COUPLING
C   COEFFICIENTS IN THE MAIN PROGRAM ARRAY.
C
214 IRDGDV = IRDEG(NUMREP)
216 IF (IRDGDV - 1) 218,228,220
218 CALL ERROR(57)
219 GO TO 228
C
C   IRDEG(NUMREP) IS THE DEGENERACY OF THE SYMMETRY NUMREP.
C
220 LOCATE(ICLK) = NNDREP + IDEGRR(NUMREP)
C
C   NNDREP IS THE NUMBER OF NON-DEGENERATE REPRESENTATIONS.
C   IDEGRR(NUMREP) IS THE DEGENERATE REPRESENTATION RANKING FOR THE
C   NUMREP SYMMETRY. STATEMENT 220 IS USED WHEN NUMREP IS DOUBLY
C   DEGENERATE TO STORE IN LOCATE(ICLK) EITHER THE NUMBER OF THE SET
C   OF COLUMNS (FOR NUMREP=JOPN, ICLK=1) OR THE NUMBER OF THE COLUMN
C   IN THE SET (FOR NUMREP=JWFN, ICLK=2).
C
224 GO TO 248
228 INMROW = INMROW - 2
229 IF (KPOS) 232,232,230
230 NUMREP = MATCH(NUMREP)
C
C   IF NUMREP IS NON-DEGENERATE THEN THE VALUE OF INMROW MUST BE
C   REDUCED. IF BOTH JOPN AND JWFN ARE NON-DEGENERATE THEN THIS
C   STATEMENT IS DONE TWICE AND THE FINAL VALUE OF INMROW IS ONE.
C
232 IF (NUMREP - NNDREP) 244,244,236
C
C   FOR MOST GROUPS THE REPRESENTATIONS ARE ORDERED SO THAT THE
C   NON-DEGENERATE ONES COME FIRST FOLLOWED BY THE DOUBLY-DEGENERATE
C   ONES. HOWEVER FOR THE GROUPS C6, C3H THE REPRESENTATIONS ARE
C   ORDERED IN THE FOLLOWING MANNER. ONE NON-DEGENERATE, ONE DOUBLY
C   DEGENERATE, ONE NON-DEGENERATE, AND THE REMAINDER DOUBLY DEGENERATE.
C   THIS BRANCH POINT HANDLES THIS PROBLEM. IF NUMREP IS GREATER THAN

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C      NNDREP, THE NUMBER OF NON-DEGENERATE REPRESENTATIONS, THEN WE ARE
C      DEALING WITH C6 OR C3H. FOR THESE GROUPS THE FIRST NON-DEGENERATE
C      REPRESENTATION OTHER THAN THE TOTALLY SYMMETRIC ONE, IS THE THIRD
C      REPRESENTATION IN ORDER. AS THIS IS THE FIRST NON-DEGENERATE
C      REPRESENTATION WE SET LOCATE(ICLK)=1. FOR ALL OTHER GROUPS WE HAVE
C      NUMREP EQUAL TO OR LESS THAN NNDREP FOR THE NON-DEGENERATE
C      REPRESENTATIONS.
C
236 LOCATE(ICLK) = 2
240 GO TO 248
244 LOCATE(ICLK) = NUMREP
248 IF (ICLK - 1) 250,252,268
250 CALL ERROR(58)
C
C      IF ICLK=1 WE HAVE CHECKED ONLY THE OPERATOR SYMMETRY. IF ICLK=2
C      WE HAVE CHECKED BOTH OPERATOR AND TRAILING WAVE FUNCTION SYMMETRY
C      AND THEREFORE GO ON TO INVESTIGATE THE LEADING WAVE FUNCTION
C      AND THE RIW INDEX.
C
252 IDGOP = IRDGOV
C
C      HERE WE STORE THE OPERATOR DEGENERACY IN IDGOP. WE THEN ADVANCE THE
C      CLOCK ICLK AND CHECK THE TRAILING WAVE FUNCTION SYMMETRY
C
256 ICLK = 2
260 NUMREP = JWFN
264 GO TO 214
268 IDGTWF = IRDGOV
C
C      THE TRAILING WAVE FUNCTION DEGENERACY IS STORED IN IDGTWF.
C
272 IF (INMROW) 274,276,284
274 CALL ERROR(59)
C
C      FOR INMROW=0, ALL THREE UNIT SYMMETRIES ARE NON-DEGENERATE AND
C      THERE IS ONLY ONE COUPLING COEFFICIENT FOR THE IMECCD MATRIX
C      ELEMENT AND IT IS EQUAL TO 1. FOR INMROW GREATER THAN ZERO THE
C      COUPLING COEFFICIENT SET MUST BE CALCULATED.
C
276 COCDME(IMECCD,1,1) = (1.0,0.0)
280 GO TO 564
284 NSETCM = LOCATE(1)
288 NCMSET = LOCATE(2)
C
C      HERE THE OPERATOR AND TRAILING WAVE FUNCTION SYMMETRIES, THRU THE
C      SPECIFICATION OF LOCATE(1) AND LOCATE(2), DETERMINE THE SUBSCRIPTS
C      NSETCM AND NCMSET OF THE MAIN PROGRAM ARRAY STORING THE COUPLING
C      COEFFICIENTS COUPCF(NSETCM,NCMSET,NUMROW). THE SUBSCRIPT NUMROW IS
C      YET TO BE DETERMINED AND IS EVALUATED IN THE NEXT PORTION OF
C      THE SUBROUTINE.
C
292 IF ((IRDEG(KWFN) - 1) 294,295,308
294 CALL ERROR(60)
C
C      THIS BRANCH DETERMINES IF THE LEADING WAVE FUNCTION SYMMETRY IS
C      DOUBLY DEGENERATE OR NOT. THIS PORTION OF THE SUBROUTINE THEN SETS
C      THE LEADING WAVE FUNCTION IN MEMBER FORM. IF NON-DEGENERATE
C      (IRDEG(KWFN)-1), THERE IS ONE MEMBER AND IT IS STORED IN MEMNUM(1).

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C   IF DOUBLY DEGENERATE (IRDEG(KWFN)=2), THERE ARE TWO MEMBERS WHICH
C   ARE STORED IN MEMNUM(1) AND MEMNUM(2).
C
295 IF (KPOS) 296,296,298
296 KWFD = KWFN
297 GO TO 299
298 KWFD = MATCH(KWFN)
299 MEMNUM(1) = 1000 * KWFD
C
C   THIS IS THE FORMULA FOR CONVERTING NON-DEGENERATE REPRESENTATIONS
C   TO MEMBER FORM.
C
300 IDGLWF = 1
C
C   THE DEGENERACY OF THE LEADING WAVE FUNCTION IS STORED IN IDGLWF.
C
304 GO TO 332
308 MEMNUM(1) = 1000 * KWFD + 1
C
C   THIS IS THE FORMULA FOR CONVERTING DOUBLY DEGENERATE REPRESENTATIONS
C   TO MEMBER FORM
C
312 IDGLWF = 2
C
C   THE DEGENERACY OF THE LEADING WAVE FUNCTION IS STORED IN IDGLWF.
C
316 IF (IPARTM(KWFN)) 318,320,328
318 CALL ERROR(61)
C
C   DEGENERACYS DUE TO SPACIAL SYMMETRY ELEMENTS HAVE THEIR PARTNER
C   MEMBERS DETERMINED BY ADDING 1 TO THE FIRST MEMBER. THOSE WHOSE
C   DEGENERACYS ARE DUE TO TIME REVERSAL HAVE THEIR PARTNER MEMBERS
C   DETERMINED BY REFERENCE TO THE ARRAY IPARTM(KWFN). FOR ALL SPATIAL
C   SYMMETRY DEGENERACYS IPARTM(KWFN)=0 AND IS GREATER THAN ZERO FOR
C   ALL THOSE DUE TO TIME REVERSAL. THUS IPARTM(KWFN) FORMS THE BRANCH
C   BASIS.
C
320 MEMNUM(2) = MEMNUM(1) + 1
324 GO TO 332
328 MEMNUM(2) = IPARTM(KWFN)
C
C   THE FOLLOWING TWO LOOPS DECIDE WHICH ROWS (VALUES OF NUMROW) OF THE
C   ARRAY COUPCF(NSETCM,NCMSET,NUMROW) CORRESPOND TO THE MEMBER(S)
C   MEMNUM(1) (MEMNUM(2)). THE NUMBER OF ROWS TO CHOOSE FROM IS INMROW,
C   THE NUMBER OF MEMBERS TO CHOOSE FROM IS IDGLWF.
C
332 DO 348 INUMRO = 1,INMROW
336 DO 348 MEMCLK = 1,IDGLWF
340 IF (MEMREP(NSETCM,NCMSET,INUMRO) - MEMNUM(MEMCLK)) 348,344,348
C
C   STATEMENT 340 LOOKS FOR COINCIDENCES BETWEEN THE GIVEN MEMBERS
C   MEMNUM(MEMCLK) AND THE MEMBERS OF MEMREP(NSETCM,NCMSET,INUMRO)
C   (FOR ALL VALUES OF INUMRO=1,INMROW). WHEN A COINCIDENCE IS FOUND
C   THE VALUE OF INUMRO IS STORED IN INDROW(MEMCLK). SINCE THE VALUE
C   MEMCLK=1,IDGLWF THERE ARE IDGLWF VALUES OF INUMRO STORED. THE
C   ARRAY COUPCF(NSETCM,NCMSET,INUMRO) COMBINES WITH THE ARRAY
C   MEMREP(NSETCM,NCMSET,INUMRO) TO MAKE AVAILABLE FROM THE MAIN
C   PROGRAM NOT ONLY THE COUPLING COEFFICIENTS FOR EACH MEMBER

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C      COMBINATION BUT ALSO THE SPECIFICATION OF THE LEADING WAVE FUNCTION
C      MEMBER CORRESPONDING TO THIS COUPLING COEFFICIENT.
C
344 INDROW(MEMCLK) = INUMRO
348 CONTINUE
352 JREORD = 0
356 KREORD = 1
360 LREORD = 3
364 ITEMCC = 0
C
C      STATEMENTS 352 TO 364 ARE INITIALIZATION STATEMENTS. IN THE
C      FOLLOWING PORTION OF THE SUBROUTINE, HAVING DETERMINED THE INITIAL
C      VALUES OF NSETCM AND NCMSET, HAVING SPECIFIED THE PERTINENT ROW(S)
C      INDROW(MEMCLK), AND HAVING DETERMINED OPERATOR AND TRAILING WAVE
C      FUNCTION DEGENERACYS (IDGOP AND IDGTWF), THE COMPLETE SET OF
C      COUPLING COEFFICIENTS COUPCF(NSETCM,NCMSET,NUMROW) CORRESPONDING TO
C      THE UNIT SYMMETRY ASSIGNMENTS JOPN, JWFN, KWFN ARE EXTRACTED FROM
C      THE MAIN PROGRAM ARRAY AND ASSIGNED TO THE TEMPORARY STORAGE ARRAY
C      TEMCC(ITEMCC). DEPENDING ON THE DEGENERACYS OF THE UNIT SYMMETRIES
C      THE RANGE OF ITEMCC CAN BE AS SMALL AS 1 OR AS LITTLE AS 8. ITEMCC
C      IS INITIALIZED IN STATEMENT 364. THE VARIABLES JREORD, KREORD, AND
C      LREORD ARE USED AS DECISION VARIABLES IN THE FURTHER REORDERING OF
C      TEMCC(ITEMCC) TO THE FINAL MATRIX ELEMENT COUPLING COEFFICIENT
C      ARRAY COCUME(IMECCD,NEWIA,NEWIB).
C
368 DO 384 IMLWF = 1,IOGLWF
C
C      WE HAVE 2**NDEGUS (WHERE NDEGUS IS 0,1,2 DEPENDING ON HOW MANY OF
C      THE TWO UNIT SYMMETRIES, OPERATOR AND TRAILING WAVE FUNCTION, ARE
C      DEGENERATE, 0,1, OR 2) MEMBER PERMUTATIONS OF THE PRODUCT OF THE
C      OPERATOR AND TRAILING WAVE FUNCTION MEMBERS. FOR EACH OF THESE
C      PERMUTATIONS WE GO THROUGH THIS DO LOOP ONCE. SINCE FOR EACH TIME
C      THROUGH THE DO LOOP WE EXTRACT IOGLWF COUPLING COEFFICIENTS, THUS
C      THE NUMBER OF COUPLING COEFFICIENTS IN THE SET IS IOGLWF*(2**NDEGUS)
C      NOTE THAT NDEGUS APPEARS IN NO EXECUTABLE STATEMENT OR SPECIFICATION
C      STATEMENT IN THE MAIN PROGRAM OR ANY SUBROUTINE.
C
372 NUMROW = INDROW(IMLWF)
C
C      NUMROW IS DUMMY STORAGE FOR THE ROW INDEX.
C
376 ITEMCC = ITEMCC + 1
380 TEMCC(ITEMCC) = COUPCF(NSETCM,NCMSET,NUMROW)
384 CONTINUE
388 IF (IDGTWF - 1) 390,412,392
390 CALL ERROR(62)
391 GO TO 412
C
C      HERE WE CHECK IF THE TRAILING WAVE FUNCTION IS DEGENERATE OR NOT.
C      IF IT IS NOT (OR IF IDGTWF=1) WE GO ON TO CHECK THE OPERATOR. IF IT
C      IS (OR IF IDGTWF IS NOT EQUAL TO 1) THEN THE VALUE OF NCMSET IS
C      ADVANCED BY ONE AND IDGTWF SET EQUAL TO ONE.
C
392 JREORD = JREORD + 4
396 KREORD = 0
C
C      THESE TWO REORDER VALUES ARE SET TO NEW VALUES. THESE TWO AS WELL
C      AS LREORD COULD BE RESET AGAIN IN A LATER STATEMENT. THE VALUES OF

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C THESE THREE REORDER VARIABLES ARE DETERMINED BY THE DEGENERACYS
 C OF THE THREE UNIT SYMMETRIES. THERE ARE FIVE POSSIBLE CASES AND
 C THEY ARE LISTED BELOW. THERE IS NO CASE POSSIBLE THAT HAS ONLY
 C ONE UNIT SYMMETRY DOUBLY DEGENERATE.
 C

	IDGOP	IDGTWF	IDGLWF	JREORD	KREORD	LREORD
C	2	2	2	8	1	3,8
C	2	2	1	4	7	1,8
C	2	1	2	4	1	1,8
C	1	2	2	4	1	3
C	1	1	1	1	1	3

C FOR ALL CASES WHERE THE OPERATOR IS DOUBLY DEGENERATE THERE ARE TWO
 C VALUES FOR LREORD. THE SMALLER VALUE CORRESPONDS TO THE FIRST
 C OPERATOR MEMBER (SMALLER VALUE OF NSETCM) AND THE LARGER VALUE TO
 C THE SECOND MEMBER (LARGER VALUE OF NSETCM).
 C

```

400 NCMSET = NCMSET + 1
404 IDGTWF = 1
408 GO TO 368
412 IF (IDGOP - 1) 414,452,416
414 CALL ERROR(69)
415 GO TO 452
  
```

C
 C HERE WE CHECK IF THE OPERATOR IS DEGENERATE OR NOT. IF IT IS NOT
 C (OR IF IDGOP HAS BEEN RESET TO 1) THEN ALL COUPLING COEFFICIENTS
 C HAVE BEEN STORED IN TEMCC(ITEMCC). IF IT IS DEGENERATE AND IDGOP=2
 C THEN WE MUST ADVANCE NSETCM BY ONE AND SET IDGOP=1. THE LATTER IS
 C DONE SO THAT THIS PATH IS GONE THROUGH ONLY ONCE FOR DEGENERATE
 C OPERATORS. WHEN THIS PATH IS GONE THROUGH WE MUST CHECK TO SEE IF
 C THE TRAILING WAVE FUNCTION IS DEGENERATE. IF THE TRAILING WAVE
 C FUNCTION IS DEGENERATE, THEN AT THIS POINT KREORD=3. IF IT IS
 C NON-DEGENERATE KREORD=1. THUS KREORD ENABLES ONE TO TELL THE
 C DEGENERACY OF THE TRAILING WAVE FUNCTION. IF DEGENERATE WE MUST
 C RESET IDGTWF=2 AND RETURN NCMSET TO ITS INITIAL VALUE. THE
 C NECESSITY FOR ALL OF THIS IS THAT WHEN OPERATOR AND TRAILING WAVE
 C FUNCTION ARE DEGENERATE THEN FOR EACH OPERATOR MEMBER BOTH MEMBERS
 C OF THE TRAILING WAVE FUNCTION MUST BE CONSIDERED WHEN EXTRACTING
 C COUPLING COEFFICIENTS.
 C

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416 NSETCM = NSETCM + 1
420 IDGOP = 1
424 IF (KREORD) 426,440,428
426 CALL ERROR(64)
427 GO TO 440
428 JREORD = 4
432 LRFORD = 1
436 GO TO 368
440 NCMSET = NCMSET - 1
444 IDGTWF = 2
448 GO TO 368
  
```

C
 C THE NEXT PORTION OF THE SUBROUTINE SETS UP THE REMAINDER OF THE
 C REORDER VARIABLE SCHEDULE. FOR THE CASES WHERE LREORD HAS TWO
 C VALUES (FOR THE OPERATOR DEGENERATE) ONLY THE LOWEST VALUE HAS BEEN
 C OR WILL BE SET INITIALLY. THE HIGHER VALUE WILL BE USED LATER IN
 C THE REORDERING INTO THE ARRAY COCOME(IMECCD,NEWIA,NEWIB).
 C

```

452 IF (IDGLWF - 1) 454,456,468
454 CALL ERROR(65)
  
```

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456 JREORD = 4
460 LREORD = 1
464 GO TO 472
C
C   THIS IS THE CASE FOR OPERATOR AND TRAILING WAVE FUNCTION DEGENERATE
C   AND LEADING WAVE FUNCTION NON-DEGENERATE
C
468 KREORD = 1
C
C   THIS IS THE CASE FOR ALL TIMES THE LEADING WAVE FUNCTION IS
C   DEGENERATE
C   THE LAST PART OF SUBROUTINE SEARCH IS USED TO REORDER THE COUPLING
C   COEFFICIENTS STORED IN TEMCC(NUMCC) AND TO STORE THEM IN THE ARRAY
C   COCOME(IMECCD,NEWIA,NEWIB). IMECCD DENOTES THE NUMBER OF THE MATRIX
C   ELEMENT AND NEWIA, NEWIB INDEX THE STACKED SET OF COUPLING
C   COEFFICIENTS FOR THE IMECCD MATRIX ELEMENT. THE NEXT FOUR
C   STATEMENTS ARE INITIALIZATION ONES FOR THE INDICES NEWIA, NEWIB
C   AND FOR THE DECISION VARIABLES NEWAB, KLREOR.
C
472 NEWIA = 1
476 NEWIB = 1
480 NEWAB = 1
484 KLREOR = 0
488 DO 560 NUMCC = 1,JREORD
C
C   JREORD IS THE NUMBER OF COUPLING COEFFICIENTS IN THE SET. THUS BY
C   COMPLETING THIS DO LOOP WE REORDER ALL THE COEFFICIENTS FOR THE
C   IMECCD MATRIX ELEMENT AND STORE THEM IN THE THREE DIMENSIONAL ARRAY
C   COCOME(IMECCD,NEWIA,NEWIB)
C
492 COCOME(IMECCD,NEWIA,NEWIB) = TEMCC(NUMCC)
496 IF (IDGLWF - 1) 498,516,500
498 CALL ERROR(66)
499 GO TO 516
C
C   IF THE LEADING WAVE FUNCTION IS DEGENERATE THE COEFFICIENT NEWIB
C   IS VARIED BETWEEN 1 AND 2 FOR NON-DEGENERATE OPERATORS AND FOR THE
C   FIRST MEMBER OF A DEGENERATE OPERATOR. IT IS VARIED BETWEEN 3 AND 4
C   FOR THE SECOND MEMBER OF A DEGENERATE OPERATOR. IF THE LEADING WAVE
C   FUNCTION IS NON-DEGENERATE THE COEFFICIENT NEWIB IS KEPT CONSTANT
C   AT 1 OR 3 DEPENDING ON THE NATURE OF THE OPERATOR.
C
500 IF (NEWIB - NEWAB) 502,504,512
502 CALL ERROR(69)
504 NEWIB = NEWIB + 1
508 GO TO 516
512 NEWIB = NEWIB - 1
516 KLREOR = KLREOR + 1
C
C   KLREOR IS A DECISION VARIABLE USED IN THE VARIATION OF NEWIA. THE
C   VARIATION OF NEWIA IS RELATED TO THE TRAILING WAVE FUNCTION AND
C   OPERATOR IN THE SAME MANNER AS THE VARIATION OF NEWIB IS RELATED
C   TO THE LEADING WAVE FUNCTION AND OPERATOR.
C
520 IF (KLREOR - KREORD) 522,536,524
522 CALL ERROR(67)
523 GO TO 536
524 NEWIA = NEWIA + 1

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528 IF (KLREOR - KREORD - 1) 536,536,532
532 NEWIA = NEWIA - 1
536 IF (NUMCC - LREORD) 560,560,540

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C
C   THIS LAST BRANCH IS USED TO RESET THE VALUES OF KREORD, LREORD,
C   NEWIA, NEWIB, NEWAB AT THE PROPER POINT IN THE NUMCC DO LOOP. THIS
C   IS ONLY NEEDED IF THE OPERATOR IS DEGENERATE. FOR A NON-DEGENERATE
C   OPERATOR IT IS ONLY ON THE LAST PASS THROUGH THE NUMCC DO LOOP
C   (NUMCC=JREORD) THAT NUMCC IS GREATER THAN LREORD AND THE VALUES OF
C   THE ABOVE ARE RESET. HOWEVER FOR THIS CASE THESE NEW VALUES ARE
C   NEVER USED AND THE RESETTING IS MEANINGLESS. FOR DEGENERATE
C   OPERATORS THE RESET POINT IS ALWAYS HALFWAY THROUGH THE SET OF
C   COUPLING COEFFICIENTS AND THE RESULT IS SUCH THAT NEWIA, NEWIB HAVE
C   THE VALUES 3 OR 4 RATHER THAN 1 OR 2.
C

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540 KLREOR = 0
544 LREORD = 8
548 NEWIA = 3
552 NEWIB = 3
556 NEWAB = 3
560 CONTINUE
564 RETURN
568 END

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      SUBROUTINE SYMANA(MODEPI,NCOM)
180 COMMON/SUBSYM/ITECM(28),KAROP(28),KARWF(28),NIX(6),NIY(6,5),
      INADD(4),JVIB(28,90)
185 COMMON/1000/IVISB(6,50,35),TEXGD(6,50,35)
190 COMMON/3000/NDOP(6,50),NDWF(6,50,35)
194 DIMENSION NY(50),KIVS(4)
196 NINIT = 2
200 GO TO (204,204,212,220,220), MODEPI
204 NFITER = 18
206 NINIT = 1
208 GO TO 222
212 NFITER = 28
216 GO TO 222
220 NFITER = 14
222 DO 232 N = 1,50
224 NY(N) = 1
225 NDWF(NCOM,N,1) = 0
226 DO 232 K = 1,35
228 IVISB(NCOM,N,K) = 0
230 TEXGD(NCOM,N,K) = 0
232 CONTINUE
236 NTX = 1
240 NX = 0
244 NDOP(NCOM,1) = 0
246 NM = 0
248 DO 572 NTER = NINIT , NFITER
252 KNOP = KAROP(NTER)
256 KNWF = KARWF(NTER)
258 KTEC = ITECM(NTER)
259 IF (KTEC) 572,572,260
260 DO 572 ITECOM = 1,KTEC
264 CALL TRANS(NTER,ITECOM,NWFDMY,2,KNWF,LINDW,LROPW)
268 CALL TRANS(NTER,ITECOM,NOPDMY,1,KNOP,LINDO,LROPO)
269 LINDI = LINDO
270 LROPI = LROPO
272 DO 284 N = 1,NTX
276 NR = N
280 IF (NOPDMY - NDOP(NCOM,N)) 284,316,284
284 CONTINUE
288 NX = NX + 1
292 NTX = NX
296 NDOP(NCOM,NX) = NOPDMY
300 NDWF(NCOM,NX,1) = NWFDMY
308 NM = NX
312 GO TO 344
316 NTY = NY(NR)
320 DO 328 IY = 1,NTY
324 IF (NWFDMY - NDWF(NCOM,NR,IY)) 328,325,329
325 ND = IY
326 NM = NR
327 GO TO 348
328 CONTINUE
332 NDWF(NCOM,NR,NTY + 1) = NWFDMY
336 NY(NR) = NY(NR) + 1
340 NM = NR
344 ND = NY(NM)
348 KON = IVISB(NCOM,NM,ND)

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350 IVS = KON + 1111
352 IEG = IEXGD(NCOM,NM,ND) + 1
356 KIVS(4) = IVS/1000
360 KISU = IVS - 1000*KIVS(4)
364 KIVS(3) = KISU/100
368 KISU = KISU - 100*KIVS(3)
372 KIVS(2) = KISU/10
376 KIVS(1) = KISU - 10*KIVS(2)
378 GO TO (380,380,440,502,502), MODEPI
380 GO TO (396,384,396,384,408,408,384,396,396,384,408,408,
      1384,396,408,408,408), NTER
384 KAP = 4
386 GO TO (388,414,388,414,388,414,388,414), IEG
388 IEXGD(NCOM,NM,ND) = IEG
392 GO TO 414
396 KAP = 3
398 GO TO (400,400,414,414,400,400,414,414), IEG
400 IEXGD(NCOM,NM,ND) = IEG + 1
404 GO TO 414
408 KAP = 2
410 GO TO (412,412,412,412,414,414,414,414), IEG
412 IEXGD(NCOM,NM,ND) = IEG + 3
414 NDAX = KIVS(KAP)
416 GO TO (420,420,420,420,420,427,427,427,427,427,427,427,
      1427,427,427,427,427), NTER
420 GO TO (422,572,572,424), NDAX
422 IVISB(NCOM,NM,ND) = KON + NADD(KAP)
423 GO TO 572
424 IVISB(NCOM,NM,ND) = KON - NADD(KAP)
425 GO TO 572
427 IF (LINDI) 428,428,420
428 IF (JVIB(NTER,ITECOM) - 1) 429,435,429
429 IF (LR0PI - 1000) 430,420,435
430 GO TO (432,422,572,572), NUA
432 IVISB(NCOM,NM,ND) = KON + 3*NADD(KAP)
433 GO TO 572
435 GO TO (437,422,572,424), NDAX
437 IVISB(NCOM,NM,ND) = KON + 2*NADD(KAP)
438 GO TO 572
440 GO TO (444,484,448,448,460,460,484,460,484,448,472,448,484,448,
      1448,472,460,460,484,460,460,460,448,472,472,448,448,460), NTER
444 CALL ERROR(4)
448 KAP = 4
450 GO TO (452,492,452,492,452,492,452,492,452,492,452,452,
      1492,452,492), IEG
452 IEXGD(NCOM,NM,ND) = IEG
456 GO TO 492
460 KAP = 3
462 GO TO (464,464,492,492,464,464,492,492,464,464,492,492,464,
      1464,492,492), IEG
464 IEXGD(NCOM,NM,ND) = IEG + 1
468 GO TO 492
472 KAP = 2
474 GO TO (476,476,476,476,492,492,492,492,476,476,476,476,492,
      1492,492,492), IEG
476 IEXGD(NCOM,NM,ND) = IEG + 3
480 GO TO 492
484 KAP = 1

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486 GO TO (488,488,488,488,488,488,488,488,492,492,492,492,492,
      1492,492,492), IEG
488 IEXGD(NCOM,NM,ND) = IEG + 7
492 NDAX = KIVS(KAP)
494 GO TO (496,420,420,420,420,420,420,420,427,427,427,427,420,420,420,
      1420,420,420,420,420,420,420,427,427,427,427,427,427,427,427,427), NTER
496 CALL ERROR(2)
500 GO TO 420
502 GO TO (504,508,508,512,508,508,508,508,548,512,512,548,512,
      1508,548), NTER
504 CALL ERROR(5)
508 IF (NCOM - 3) 516,516,532
512 IF (NCOM - 3) 532,532,516
516 KAP = 4
520 GO TO (524,560,524,560,524,560,524,560), IEG
524 IEXGD(NCOM,NM,ND) = IEG
528 GO TO 560
532 KAP = 3
536 GO TO (540,540,560,560,560,540,540,560,560), IEG
540 IEXGD(NCOM,NM,ND) = IEG + 1
544 GO TO 560
548 KAP = 2
552 GO TO (556,556,556,556,560,560,560,560), IEG
556 IEXGD(NCOM,NM,ND) = IEG + 3
560 NDAX = KIVS(KAP)
562 GO TO (564,420,420,420,420,420,420,420,420,427,427,427,
      1420,420), NTER
564 CALL ERROR(3)
568 GO TO 420
572 CONTINUE
574 NIX(NCOM) = NX
578 NK = NX
582 DO 590 N = 1,NK
586 NIY(NCOM,N) = NY(N)
590 CONTINUE
594 RETURN
598 END

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Appendix XIISymmetry Pattern Data Sheets for the
Point Group C_{4v}

DATA SHEET FOR C_{4v}

349

$1 \rightarrow 1$ { GROUND STATE BORROWING
EXCITED STATE BORROWING

MODE & PERTURBATION COMPONENTS & SYMMETRIES →		1	11	22	33	44	55		
ABSORPTION	COMP 1 SUB SYM SUB/VIB SYM μ_1/μ_1						55		
	COMP 2 SUB SYM SUB/VIB SYM μ_2/μ_2	1	11	12	13	14	15		
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1 SUB SYM SUB/VIB SYM $\mu_2/\mu_1 m_1$						515, 555		
	COMP 2 SUB SYM SUB/VIB SYM $\mu_3/\mu_1 m_2$						525, 555		
	COMP 3 SUB SYM SUB/VIB SYM $\mu_4/\mu_2 m_3$	15	115, 515	125	135	145	515, 525, 535, 545		
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZEEMAN SPLITTING, "A" AND "C" TERMS	COMP 1 SUB SYM SUB/VIB SYM $\mu_2/\mu_2 m_2$						55		
	COMP 2 SUB SYM SUB/VIB SYM $\mu_3/\mu_1 m_2$								
	COMP 3 SUB SYM SUB/VIB SYM $\mu_4/\mu_2 m_3$								
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE ZEEMAN SPLITTING, "A" TERM	COMP 1 SUB SYM SUB/VIB SYM $\mu_2/\mu_1 m_1$						55		
	COMP 2 SUB SYM SUB/VIB SYM $\mu_3/\mu_1 m_2$								
	COMP 3 SUB SYM SUB/VIB SYM $\mu_4/\mu_2 m_3$								
MODE & PERTURBATION COMPONENTS & SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1 SUB SYM SUB/VIB SYM m_1/μ_1								525, 555
	COMP 2 SUB SYM SUB/VIB SYM m_2/μ_2	2	21, 22	23, 24	121, 122				
	COMP 3 SUB SYM SUB/VIB SYM $\mu_1 m_3$								525, 555
	COMP 4 SUB SYM SUB/VIB SYM $\mu_2 m_2$		21			122			

DATA SHEET FOR C_{4v} $2 \rightarrow 2$

GROUND STATE BORROWING
EXCITED STATE BORROWING

MODE # 1			PERTURBATION COMPONENTS		SYMMETRIES		1	11	22	33	44	55			
ABSORPTION	COMP 1	SUB SYM													
		SUB/VIB SYM									55				
	COMP 2	SUB SYM	2		21	24	23				25				
		SUB/VIB SYM		22											
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1	SUB SYM													
		SUB/VIB SYM									525, 555				
	COMP 2	SUB SYM													
		SUB/VIB SYM									515, 555				
	COMP 3	SUB SYM	25		215	245	235								
		SUB/VIB SYM		225, 525	515	545	535	515, 525, 535, 545							
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZEEMAN SPLITTING, "A" AND "C" TERMS	COMP 1	SUB SYM										55			
		SUB/VIB SYM													
	COMP 2	SUB SYM													
		SUB/VIB SYM													
	COMP 3	SUB SYM													
		SUB/VIB SYM													
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE ZEEMAN SPLITTING, "A" TERM	COMP 1	SUB SYM										55			
		SUB/VIB SYM													
	COMP 2	SUB SYM													
		SUB/VIB SYM													
	COMP 3	SUB SYM													
		SUB/VIB SYM													
MODE # 2			PERTURBATION COMPONENTS		SYMMETRIES		2	12	34	112	222	332	442	552	
NATURAL OPTICAL ACTIVITY	COMP 1	SUB SYM													
		SUB/VIB SYM												515, 555	
	COMP 2	SUB SYM	1	11, 12	13, 14										
		SUB/VIB SYM				211, 212									
	COMP 3	SUB SYM													
		SUB/VIB SYM													515, 555
COMP 4	SUB SYM		12												
	SUB/VIB SYM					211									

DATA SHEET FOR C_{4v}

351

3 → 3

{ GROUND STATE BORROWING
EXCITED STATE BORROWING

MODE & COMPONENTS		PERTURBATION SYMMETRIES →		1	11	22	33	44	55		
ABSORPTION	COMP 1 SUB SYM $\mu_1 \mu_1$ SUB/VIB SYM								55		
	COMP 2 SUB SYM $\mu_2 \mu_2$ SUB/VIB SYM	3		34		31		32	35		
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1 SUB SYM $\mu_1 \mu_1 m_1$ SUB/VIB SYM								535, 555		
	COMP 2 SUB SYM $\mu_1 \mu_1 m_2$ SUB/VIB SYM								545, 555		
	COMP 3 SUB SYM $\mu_1 \mu_1 m_3$ SUB/VIB SYM	35		345		315		325			
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A" AND "C" TERMS	COMP 1 SUB SYM $\mu_2 \mu_2 m_1$ SUB/VIB SYM								55		
	COMP 2 SUB SYM $\mu_2 \mu_2 m_2$ SUB/VIB SYM										
	COMP 3 SUB SYM $\mu_2 \mu_2 m_3$ SUB/VIB SYM										
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE, FEELMAN SPLITTING, "A" TERM	COMP 1 SUB SYM $\mu_2 \mu_2 m_1$ SUB/VIB SYM								55		
	COMP 2 SUB SYM $\mu_2 \mu_2 m_2$ SUB/VIB SYM										
	COMP 3 SUB SYM $\mu_2 \mu_2 m_3$ SUB/VIB SYM										
MODE & COMPONENTS		PERTURBATION SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1 SUB SYM $m_1 \mu_1$ SUB/VIB SYM										545, 555
	COMP 2 SUB SYM $m_2 \mu_2$ SUB/VIB SYM	4	43, 44	41, 42							
	COMP 3 SUB SYM $\mu_1 m_1$ SUB/VIB SYM				343, 344						545, 555
	COMP 4 SUB SYM $\mu_2 m_2$ SUB/VIB SYM		43				344				

DATA SHEET FOR C_{4v}
 $4 \rightarrow 4$ { GROUND STATE BORROWING
EXCITED STATE BORROWING

MODE 1		PERTURBATION SYMMETRIES $\rightarrow$		1	11	22	33	44	55
ABSORPTION	COMP 1	SUB SYM							
	μ_1/μ_1	SUB/VIB SYM							55
	COMP 2	SUB SYM	4		43	42	41		45
	μ_2/μ_2	SUB/VIB SYM		44					
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1	SUB SYM							
	μ_1/μ_1	SUB/VIB SYM							545, 555
	COMP 2	SUB SYM							
	μ_2/μ_2	SUB/VIB SYM							535, 555
	COMP 3	SUB SYM	45		435	425	415		
	μ_1/μ_2	SUB/VIB SYM		445, 545	535	525	515	515, 525, 535, 545	
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZEEMAN SPLITTING, "A" AND "C" TERMS	COMP 1	SUB SYM							55
	μ_1/μ_1	SUB/VIB SYM							
	COMP 2	SUB SYM							
	μ_2/μ_2	SUB/VIB SYM							
	COMP 3	SUB SYM							
	μ_1/μ_2	SUB/VIB SYM							
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE ZEEMAN SPLITTING, "A" TERM	COMP 1	SUB SYM							55
	μ_1/μ_1	SUB/VIB SYM							
	COMP 2	SUB SYM							
	μ_2/μ_2	SUB/VIB SYM							
	COMP 3	SUB SYM							
	μ_1/μ_2	SUB/VIB SYM							

MODE 2		PERTURBATION SYMMETRIES $\rightarrow$		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1	SUB SYM									
	m_1/μ_1	SUB/VIB SYM									535, 555
	COMP 2	SUB SYM	3	33, 34	31, 32						
	m_2/μ_2	SUB/VIB SYM				434, 433					
	COMP 3	SUB SYM									
	μ_1/m_1	SUB/VIB SYM									535, 555
	COMP 4	SUB SYM		34							
	μ_2/m_2	SUB/VIB SYM						433			

DATA SHEET FOR C_{4v}

2 → 1

GROUND STATE BORROWING

1 → 2

EXCITED STATE BORROWING

MODE & PERTURBATION COMPONENTS & SYMMETRIES →		1	11	22	33	44	55
ABSORPTION	COMP 1 SUB SYM 1 SUB/VIB SYM μ_1/μ_1						55
	COMP 2 SUB SYM μ_2/μ_2 SUB/VIB SYM			11			
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1 SUB SYM $\mu_2/\mu_1 m_1$ SUB/VIB SYM						525, 515, 555
	COMP 2 SUB SYM $\mu_1/\mu_1 m_2$ SUB/VIB SYM						515, 525, 555
	COMP 3 SUB SYM $\mu_1/\mu_2 m_2$ SUB/VIB SYM			115, 515			
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A" AND "C" TERMS	COMP 1 SUB SYM $\mu_2/\mu_2 m_2$ SUB/VIB SYM						
	COMP 2 SUB SYM $\mu_2/\mu_1 m_2$ SUB/VIB SYM						
	COMP 3 SUB SYM $\mu_1/\mu_2 m_2$ SUB/VIB SYM						
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A" TERM	COMP 1 SUB SYM $\mu_2/\mu_1 m_2$ SUB/VIB SYM						
	COMP 2 SUB SYM $\mu_2/\mu_1 m_2$ SUB/VIB SYM						
	COMP 3 SUB SYM $\mu_2/\mu_2 m_2$ SUB/VIB SYM						

MODE & PERTURBATION COMPONENTS & SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1 SUB SYM m_1/μ_1 SUB/VIB SYM								515, 555
	COMP 2 SUB SYM m_2/μ_2 SUB/VIB SYM		12			211			
	COMP 3 SUB SYM μ_1/μ_1 SUB/VIB SYM								515, 555
	COMP 4 SUB SYM μ_2/μ_2 SUB/VIB SYM	1	11, 12	13, 14					
					211, 212				

DATA SHEET FOR G_{IV}
 $1 \rightarrow 2$
 $2 \rightarrow 1$

GROUND STATE BORROWING
EXCITED STATE BORROWING

MODE #		PERTURBATION COMPONENTS & SYMMETRIES $\rightarrow$		1	11	22	33	44	55		
ABSORPTION	COMP 1	SUB SYM									
	μ_1/μ_1	SUB/VIB SYM							55		
	COMP 2	SUB SYM									
	μ_2/μ_2	SUB/VIB SYM			22						
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1	SUB SYM									
	$\mu_1/\mu_1 m_1$	SUB/VIB SYM							515, 525, 555		
	COMP 2	SUB SYM									
	$\mu_2/\mu_2 m_2$	SUB/VIB SYM							525, 515, 555		
	COMP 3	SUB SYM									
	$\mu_1/\mu_1 m_1$	SUB/VIB SYM			225, 525						
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A" AND "C" TERMS	COMP 1	SUB SYM									
	$\mu_2/\mu_2 m_2$	SUB/VIB SYM									
	COMP 2	SUB SYM									
	$\mu_3/\mu_3 m_3$	SUB/VIB SYM									
	COMP 3	SUB SYM									
	$\mu_1/\mu_1 m_1$	SUB/VIB SYM									
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A" TERM	COMP 1	SUB SYM									
	$\mu_2/\mu_2 m_2$	SUB/VIB SYM									
	COMP 2	SUB SYM									
	$\mu_3/\mu_3 m_3$	SUB/VIB SYM									
	COMP 3	SUB SYM									
	$\mu_1/\mu_1 m_1$	SUB/VIB SYM									
MODE #		PERTURBATION COMPONENTS & SYMMETRIES $\rightarrow$		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1	SUB SYM									
	m_1/μ_1	SUB/VIB SYM									525, 555
	COMP 2	SUB SYM		21							
	m_2/μ_2	SUB/VIB SYM					122				
	COMP 3	SUB SYM									
	$\mu_1 m_1$	SUB/VIB SYM									525, 555
	COMP 4	SUB SYM	2	21, 22	23, 24						
	$\mu_2 m_2$	SUB/VIB SYM				121, 122					

DATA SHEET FOR C_{4v}

4 → 3

GROUND STATE BORROWING

3 → 4

EXCITED STATE BORROWING

MODE #		PERTURBATION COMPONENTS		SYMMETRIES →		1	11	22	33	44	55		
ABSORPTION	COMP 1	SUB SYM											
	μ_1/μ_1	SUB/VIB SYM									55		
	COMP 2	SUB SYM											
	μ_2/μ_2	SUB/VIB SYM			33								
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1	SUB SYM											
	$\mu_2/\mu_1 m_1$	SUB/VIB SYM								545, 535, 555			
	COMP 2	SUB SYM											
	$\mu_1/\mu_1 m_2$	SUB/VIB SYM								535, 545, 555			
	COMP 3	SUB SYM											
	$\mu_1/\mu_2 m_2$	SUB/VIB SYM			335, 535								
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZEEMAN SPLITTING, "A AND C" TERMS	COMP 1	SUB SYM											
	$\mu_2/\mu_1 m_1$	SUB/VIB SYM											
	COMP 2	SUB SYM											
	$\mu_1/\mu_1 m_2$	SUB/VIB SYM											
	COMP 3	SUB SYM											
	$\mu_1/\mu_2 m_2$	SUB/VIB SYM											
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE ZEEMAN SPLITTING, "A TERM"	COMP 1	SUB SYM											
	$\mu_2/\mu_1 m_1$	SUB/VIB SYM											
	COMP 2	SUB SYM											
	$\mu_1/\mu_1 m_2$	SUB/VIB SYM											
	COMP 3	SUB SYM											
	$\mu_1/\mu_2 m_2$	SUB/VIB SYM											
MODE #		PERTURBATION COMPONENTS		SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1	SUB SYM											
	m_1/μ_1	SUB/VIB SYM											535, 555
	COMP 2	SUB SYM		34									
	m_2/μ_2	SUB/VIB SYM						433					
	COMP 3	SUB SYM											535, 555
	$\mu_1 m_1$	SUB/VIB SYM											
	COMP 4	SUB SYM	9	34, 33	32, 31								
	$\mu_2 m_2$	SUB/VIB SYM			434, 433								

DATA SHEET FOR C_{IV}

3 → 4 GROUND STATE BORROWING
 4 → 3 EXCITED STATE BORROWING

MODE 1 PERTURBATION COMPONENTS SYMMETRIES →		1	11	22	33	44	55		
ABSORPTION	COMP 1 SUB SYM μ_1/μ_1 SUB/VIB SYM						55		
	COMP 2 SUB SYM μ_2/μ_2 SUB/VIB SYM			44					
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1 SUB SYM $\mu_2/\mu_1 m_1$ SUB/VIB SYM						535, 545, 555		
	COMP 2 SUB SYM $\mu_1/\mu_2 m_2$ SUB/VIB SYM						545, 535, 555		
	COMP 3 SUB SYM $\mu_1/\mu_2 m_2$ SUB/VIB SYM			445, 545					
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZEEMAN SPLITTING, "A AND C" TERMS	COMP 1 SUB SYM $\mu_2/\mu_2 m_2$ SUB/VIB SYM								
	COMP 2 SUB SYM $\mu_2/\mu_1 m_2$ SUB/VIB SYM								
	COMP 3 SUB SYM $\mu_1/\mu_2 m_2$ SUB/VIB SYM								
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE, FINEMAN SPLITTING, "A" TERM	COMP 1 SUB SYM $\mu_2/\mu_2 m_2$ SUB/VIB SYM								
	COMP 2 SUB SYM $\mu_2/\mu_1 m_2$ SUB/VIB SYM								
	COMP 3 SUB SYM $\mu_1/\mu_2 m_2$ SUB/VIB SYM								
MODE 2 PERTURBATION COMPONENTS SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1 SUB SYM m_1/μ_1 SUB/VIB SYM								545, 555
	COMP 2 SUB SYM m_2/μ_2 SUB/VIB SYM		43			344			
	COMP 3 SUB SYM $\mu_1 m_2$ SUB/VIB SYM								545, 555
	COMP 4 SUB SYM $\mu_2 m_2$ SUB/VIB SYM	4	43, 44	41, 42					
					343, 344				

DATA SHEET FOR C_{4v}

$3 \rightarrow 1$ GROUND STATE BORROWING
 $1 \rightarrow 3$ EXCITED STATE BORROWING

MODE & PERTURBATION COMPONENTS & SYMMETRIES →		1	11	22	33	44	55		
ABSORPTION	COMP 1 SUB SYM 1 SUB/VIB SYM μ_1/μ_1						55		
	COMP 2 SUB SYM μ_2/μ_2 SUB/VIB SYM				11				
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1 SUB SYM $\mu_2/\mu_1 m_1$ SUB/VIB SYM						535, 515, 555		
	COMP 2 SUB SYM $\mu_1/\mu_2 m_2$ SUB/VIB SYM						545, 525, 555		
	COMP 3 SUB SYM $\mu_1/\mu_2 m_1$ SUB/VIB SYM				115, 515				
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZEEMAN SPLITTING, "A" AND "C" TERMS	COMP 1 SUB SYM $\mu_2/\mu_1 m_2$ SUB/VIB SYM								
	COMP 2 SUB SYM $\mu_2/\mu_1 m_2$ SUB/VIB SYM								
	COMP 3 SUB SYM $\mu_1/\mu_2 m_1$ SUB/VIB SYM								
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE ZEEMAN SPLITTING, "A" TERM	COMP 1 SUB SYM $\mu_2/\mu_1 m_1$ SUB/VIB SYM								
	COMP 2 SUB SYM $\mu_2/\mu_1 m_2$ SUB/VIB SYM								
	COMP 3 SUB SYM $\mu_1/\mu_2 m_1$ SUB/VIB SYM								
MODE & PERTURBATION COMPONENTS & SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1 SUB SYM m_1/μ_1 SUB/VIB SYM								545, 555
	COMP 2 SUB SYM m_2/μ_2 SUB/VIB SYM			21			121, 124		
	COMP 3 SUB SYM $\mu_1 m_1$ SUB/VIB SYM								545, 555
	COMP 4 SUB SYM $\mu_2 m_2$ SUB/VIB SYM			21				124, 122	

4 → 2
2 → 4

GROUND STATE BORROWING
EXCITED STATE BORROWING

MODE & PERTURBATION COMPONENTS & SYMMETRIES →		1	11	22	33	44	55		
ABSORPTION	COMP 1 SUB SYM SUB/VIB μ_3/μ_1 SYM						55		
	COMP 2 SUB SYM SUB/VIB μ_2/μ_1 SYM			22					
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1 SUB SYM SUB/VIB $\mu_2/\mu_1 m_1$ SYM						545, 525, 555		
	COMP 2 SUB SYM SUB/VIB $\mu_1/\mu_1 m_1$ SYM						535, 515, 555		
	COMP 3 SUB SYM SUB/VIB $\mu_1/\mu_1 m_1$ SYM			225, 525					
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A" AND "C" TERMS GROUND STATE ZEEMAN SPLITTING, "A" AND "C" TERMS	COMP 1 SUB SYM SUB/VIB $\mu_2/\mu_1 m_1$ SYM								
	COMP 2 SUB SYM SUB/VIB $\mu_2/\mu_1 m_2$ SYM								
	COMP 3 SUB SYM SUB/VIB $\mu_1/\mu_1 m_1$ SYM								
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A" TERM EXCITED STATE ZEEMAN SPLITTING, "A" TERM	COMP 1 SUB SYM SUB/VIB $\mu_2/\mu_1 m_1$ SYM								
	COMP 2 SUB SYM SUB/VIB $\mu_2/\mu_1 m_2$ SYM								
	COMP 3 SUB SYM SUB/VIB $\mu_1/\mu_1 m_1$ SYM								
MODE & PERTURBATION COMPONENTS & SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1 SUB SYM SUB/VIB m_1/μ_1 SYM								535, 555
	COMP 2 SUB SYM SUB/VIB m_2/μ_2 SYM			12			212, 213		
	COMP 3 SUB SYM SUB/VIB μ_1/m_1 SYM								535, 555
	COMP 4 SUB SYM SUB/VIB μ_2/m_2 SYM			12				213, 211	

DATA SHEET FOR C_{4v}
 $1 \rightarrow 3$
 $3 \rightarrow 1$

GROUND STATE BORROWING
EXCITED STATE BORROWING

MODE 1 PERTURBATION COMPONENTS & SYMMETRIES →		1	11	22	33	44	55		
ABSORPTION	COMP 1 μ_4/μ_1 SUB SYM SUB/VIB SYM						55		
	COMP 2 μ_2/μ_2 SUB SYM SUB/VIB SYM				33				
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1 $\mu_2/\mu_1 m_1$ SUB SYM SUB/VIB SYM						515, 535, 555		
	COMP 2 $\mu_3/\mu_2 m_2$ SUB SYM SUB/VIB SYM						525, 545, 555		
	COMP 3 $\mu_1/\mu_2 m_2$ SUB SYM SUB/VIB SYM				335, 535				
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZEEMAN SPLITTING, "A" AND "C" TERMS	COMP 1 $\mu_2/\mu_2 m_2$ SUB SYM SUB/VIB SYM								
	COMP 2 $\mu_3/\mu_1 m_2$ SUB SYM SUB/VIB SYM								
	COMP 3 $\mu_1/\mu_2 m_2$ SUB SYM SUB/VIB SYM								
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE ZEEMAN SPLITTING, "A" TERM	COMP 1 $\mu_2/\mu_2 m_2$ SUB SYM SUB/VIB SYM								
	COMP 2 $\mu_3/\mu_1 m_2$ SUB SYM SUB/VIB SYM								
	COMP 3 $\mu_1/\mu_2 m_2$ SUB SYM SUB/VIB SYM								
MODE 2 PERTURBATION COMPONENTS & SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1 m_3/μ_1 SUB SYM SUB/VIB SYM								525, 555
	COMP 2 m_2/μ_2 SUB SYM SUB/VIB SYM			43			343, 342		
	COMP 3 $\mu_1 m_1$ SUB SYM SUB/VIB SYM								525, 555
	COMP 4 $\mu_2 m_2$ SUB SYM SUB/VIB SYM			43				342, 344	

DATA SHEET FOR C_{4v}

$$\begin{array}{l} 2 \rightarrow 4 \\ 4 \rightarrow 2 \end{array}$$

GROUND STATE BORROWING
EXCITED STATE BORROWING

MODE #		PERTURBATION SYMMETRIES →		1	11	22	33	44	55		
ABSORPTION	COMP 1 SUB SYM SUB/VIB SYM $\mu_1 \mu_1$								55		
	COMP 2 SUB SYM SUB/VIB SYM $\mu_2 \mu_2$						44				
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1 SUB SYM SUB/VIB SYM $\mu_1 \mu_1 m_1$								525, 545, 555		
	COMP 2 SUB SYM SUB/VIB SYM $\mu_1 \mu_1 m_2$								515, 535, 555		
	COMP 3 SUB SYM SUB/VIB SYM $\mu_1 \mu_2 m_2$						445, 545				
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZEEMAN SPLITTING, "A" AND "C" TERMS	COMP 1 SUB SYM SUB/VIB SYM $\mu_2 \mu_2 m_2$										
	COMP 2 SUB SYM SUB/VIB SYM $\mu_1 \mu_1 m_2$										
	COMP 3 SUB SYM SUB/VIB SYM $\mu_1 \mu_2 m_2$										
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE ZEEMAN SPLITTING, "A" TERM	COMP 1 SUB SYM SUB/VIB SYM $\mu_2 \mu_2 m_1$										
	COMP 2 SUB SYM SUB/VIB SYM $\mu_1 \mu_1 m_2$										
	COMP 3 SUB SYM SUB/VIB SYM $\mu_1 \mu_2 m_2$										
MODE #		PERTURBATION SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1 SUB SYM SUB/VIB SYM $m_1 \mu_1$										515, 555
	COMP 2 SUB SYM SUB/VIB SYM $m_2 \mu_2$			34					434, 431		
	COMP 3 SUB SYM SUB/VIB SYM $\mu_1 m_1$										515, 555
	COMP 4 SUB SYM SUB/VIB SYM $\mu_2 m_2$			34						431, 433	

DATA SHEET FOR C_{4v}

$4 \rightarrow 1$ GROUND STATE BORROWING
 $1 \rightarrow 4$ EXCITED STATE BORROWING

MODE #		PERTURBATION COMPONENTS & SYMMETRIES →		1	11	22	33	44	55		
ABSORPTION	COMP 1	SUB SYM									
	μ_1/μ_1	SUB/VIB SYM							55		
	COMP 2	SUB SYM									
	μ_2/μ_2	SUB/VIB SYM					11				
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1	SUB SYM									
	μ_2/μ_1	SUB/VIB SYM							545, 515, 555		
	COMP 2	SUB SYM									
	μ_1/μ_2	SUB/VIB SYM							535, 525, 555		
	COMP 3	SUB SYM									
	μ_1/μ_2	SUB/VIB SYM					115, 515				
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZEEMAN SPLITTING, "A" AND "C" TERMS	COMP 1	SUB SYM									
	μ_2/μ_2	SUB/VIB SYM									
	COMP 2	SUB SYM									
	μ_2/μ_1	SUB/VIB SYM									
	COMP 3	SUB SYM									
	μ_1/μ_2	SUB/VIB SYM									
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE ZEEMAN SPLITTING, "A" TERM	COMP 1	SUB SYM									
	μ_2/μ_1	SUB/VIB SYM									
	COMP 2	SUB SYM									
	μ_2/μ_2	SUB/VIB SYM									
	COMP 3	SUB SYM									
	μ_1/μ_2	SUB/VIB SYM									
MODE #		PERTURBATION COMPONENTS & SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1	SUB SYM									
	m_1/μ_1	SUB/VIB SYM									535, 555
	COMP 2	SUB SYM			21						
	m_2/μ_2	SUB/VIB SYM								121, 123	
	COMP 3	SUB SYM									
	μ_1/m_1	SUB/VIB SYM									535, 555
	COMP 4	SUB SYM			21						
	μ_2/m_2	SUB/VIB SYM							123, 122		

DATA SHEET FOR C_{4v}

3 → 2 GROUND STATE BORROWING
 2 → 3 EXCITED STATE BORROWING

MODE #	PERTURBATION COMPONENTS	SYMMETRIES	1	11	22	33	44	55		
ABSORPTION	COMP 1	SUB SYM								
	μ_3/μ_1	SUB/VIB SYM						55		
	COMP 2	SUB SYM								
	μ_2/μ_2	SUB/VIB SYM					22			
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1	SUB SYM								
	$\mu_3/\mu_1 m_1$	SUB/VIB SYM						535, 525, 555		
	COMP 2	SUB SYM								
	$\mu_3/\mu_1 m_2$	SUB/VIB SYM						545, 515, 555		
	COMP 3	SUB SYM								
	$\mu_1/\mu_2 m_2$	SUB/VIB SYM					225, 525			
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZEEMAN SPLITTING, "A" AND "C" TERMS	COMP 1	SUB SYM								
	$\mu_3/\mu_1 m_1$	SUB/VIB SYM								
	COMP 2	SUB SYM								
	$\mu_3/\mu_1 m_2$	SUB/VIB SYM								
	COMP 3	SUB SYM								
	$\mu_1/\mu_2 m_2$	SUB/VIB SYM								
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE BORROWING SPLITTING, "A" TERM	COMP 1	SUB SYM								
	$\mu_3/\mu_1 m_1$	SUB/VIB SYM								
	COMP 2	SUB SYM								
	$\mu_3/\mu_1 m_2$	SUB/VIB SYM								
	COMP 3	SUB SYM								
	$\mu_1/\mu_2 m_2$	SUB/VIB SYM								
MODE #	PERTURBATION COMPONENTS	SYMMETRIES	2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1	SUB SYM								
	m_3/μ_1	SUB/VIB SYM								545, 555
	COMP 2	SUB SYM			12					
	m_2/μ_2	SUB/VIB SYM							214, 212	
	COMP 3	SUB SYM								
	$\mu_1 m_1$	SUB/VIB SYM								545, 555
	COMP 4	SUB SYM			12					
	$\mu_2 m_2$	SUB/VIB SYM						211, 214		

DATA SHEET FOR C_{4v}

2 → 3

GROUND STATE BORROWING

3 → 2

EXCITED STATE BORROWING

MODE & PERTURBATION COMPONENTS SYMMETRIES →		1	11	22	33	44	55
ABSORPTION	COMP SUB 1 SYM SUB/VIB μ_1/μ_1 SYM						55
	COMP SUB 2 SYM SUB/VIB μ_2/μ_2 SYM					33	
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP SUB 1 SYM SUB/VIB $\mu_2/\mu_1 m_1$ SYM						525, 535, 555
	COMP SUB 2 SYM SUB/VIB $\mu_1/\mu_1 m_2$ SYM						515, 545, 555
	COMP SUB 3 SYM SUB/VIB $\mu_1/\mu_2 m_2$ SYM					335, 535	
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A" AND "C" TERMS GROUND STATE REEMAN SPLITTING	COMP SUB 1 SYM SUB/VIB $\mu_2/\mu_2 m_1$ SYM						
	COMP SUB 2 SYM SUB/VIB $\mu_2/\mu_1 m_2$ SYM						
	COMP SUB 3 SYM SUB/VIB $\mu_1/\mu_2 m_1$ SYM						
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM EXCITED STATE REEMAN SPLITTING	COMP SUB 1 SYM SUB/VIB $\mu_2/\mu_1 m_1$ SYM						
	COMP SUB 2 SYM SUB/VIB $\mu_2/\mu_1 m_2$ SYM						
	COMP SUB 3 SYM SUB/VIB $\mu_1/\mu_2 m_2$ SYM						

MODE & PERTURBATION COMPONENTS SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP SUB 1 SYM SUB/VIB m_1/μ_1 SYM								515, 555
	COMP SUB 2 SYM SUB/VIB m_2/μ_2 SYM			43				343, 341	
	COMP SUB 3 SYM SUB/VIB $\mu_1 m_1$ SYM								515, 555
	COMP SUB 4 SYM SUB/VIB $\mu_2 m_2$ SYM			43			341, 344		

DATA SHEET FOR C_{4v}
 $1 \rightarrow 4$
 $4 \rightarrow 1$

 GROUND STATE BORROWING
 EXCITED STATE BORROWING

MODE 1: PERTURBATION COMPONENTS $\downarrow$ SYMMETRIES $\rightarrow$		1	11	22	33	44	55		
ABSORPTION	COMP 1 SUB SYM μ_1/μ_2 SUB/VIB SYM						55		
	COMP 2 SUB SYM μ_2/μ_2 SUB/VIB SYM					44			
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1 SUB SYM $\mu_2/\mu_1 m_1$ SUB/VIB SYM						515, 545, 555		
	COMP 2 SUB SYM $\mu_1/\mu_2 m_2$ SUB/VIB SYM						525, 535, 555		
	COMP 3 SUB SYM $\mu_1/\mu_2 m_2$ SUB/VIB SYM					445, 545			
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A AND C" TERMS	COMP 1 SUB SYM $\mu_2/\mu_1 m_1$ SUB/VIB SYM								
	COMP 2 SUB SYM $\mu_2/\mu_1 m_2$ SUB/VIB SYM								
	COMP 3 SUB SYM $\mu_1/\mu_2 m_2$ SUB/VIB SYM								
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "EXCITED STATE BORROWING SPLITTING" A TERM	COMP 1 SUB SYM $\mu_2/\mu_1 m_1$ SUB/VIB SYM								
	COMP 2 SUB SYM $\mu_2/\mu_1 m_2$ SUB/VIB SYM								
	COMP 3 SUB SYM $\mu_1/\mu_2 m_2$ SUB/VIB SYM								
MODE 2: PERTURBATION COMPONENTS $\downarrow$ SYMMETRIES $\rightarrow$		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1 SUB SYM m_1/μ_1 SUB/VIB SYM								525, 555
	COMP 2 SUB SYM m_2/μ_2 SUB/VIB SYM			34				434, 432	
	COMP 3 SUB SYM $\mu_1 m_1$ SUB/VIB SYM								525, 555
	COMP 4 SUB SYM $\mu_2 m_2$ SUB/VIB SYM			34					
							432, 433		

DATA SHEET FOR C_{4y}

1 → 5

GROUND STATE BORROWING

$$5 \rightarrow 1$$

EXCITED STATE BORROWING

MODE & PERTURBATION COMPONENTS & SYMMETRIES →		1	11	22	33	44	55
ABSORPTION	COMP 1 SUB SYM 1/1 ₁ /1 ₁ SUB/VIB SYM	1		12	13	14	15
	COMP 2 SUB SYM 1/2 ₁ /1 ₂ SUB/VIB SYM		11	22	33	44	55
MAGNETICALLY-INDUCED "B" TERM	COMP 1 SUB SYM 1/2 ₁ /1 ₁ SUB/VIB SYM	11, 15		121, 125 111 115, 515	131, 135 133, 333 335, 535	141, 145 144, 444 445, 545	115 515, 525, 535, 545
	COMP 2 SUB SYM 1/2 ₁ /1 ₂ SUB/VIB SYM	12, 15		125 122 225, 525	132, 135 432, 433 335, 535	142, 145 342, 344 445, 545	125 515, 525, 535, 545
	COMP 3 SUB SYM 1/2 ₁ /1 ₂ SUB/VIB SYM						515, 525, 535, 545
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZERO-QUANTUM SPLITTING, "A" AND "C" TERMS	COMP 1 SUB SYM 1/2 ₁ /1 ₁ SUB/VIB SYM						
	COMP 2 SUB SYM 1/2 ₁ /1 ₂ SUB/VIB SYM	1					
	COMP 3 SUB SYM 1/2 ₁ /1 ₂ SUB/VIB SYM		11	22	33	44	55
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE, Raman SPLITTING, "A" TERM	COMP 1 SUB SYM 1/2 ₁ /1 ₁ SUB/VIB SYM						
	COMP 2 SUB SYM 1/2 ₁ /1 ₂ SUB/VIB SYM	1					
	COMP 3 SUB SYM 1/2 ₁ /1 ₂ SUB/VIB SYM		11	22	33	44	55
NATURAL OPTICAL ACTIVITY	COMP 1 SUB SYM 1/2 ₁ /1 ₁ SUB/VIB SYM						
	COMP 2 SUB SYM 1/2 ₁ /1 ₂ SUB/VIB SYM	1					
	COMP 3 SUB SYM 1/2 ₁ /1 ₂ SUB/VIB SYM		11	22	33	44	55

DATA SHEET FOR CIV

3 → 5 GROUND STATE BORROWING
5 → 3 EXCITED STATE BORROWING

MODE 1		PERTURBATION COMPONENTS & SYMMETRIES →					
		1	11	22	33	44	55
ABSORPTION	COMP 1 SUB SYM 1 μ ₁ μ ₁ SUB/VIB SYM	3		34	31	32	35
	COMP 2 SUB SYM μ ₂ μ ₂ SUB/VIB SYM		33	44	11	22	
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1 SUB SYM μ ₂ μ ₁ m ₁ SUB/VIB SYM	33, 35		343, 345	313, 315	323, 325	335
	COMP 2 SUB SYM μ ₁ μ ₁ m ₂ SUB/VIB SYM	34, 35		345	314, 315	324, 325	345
	COMP 3 SUB SYM μ ₁ μ ₂ m ₃ SUB/VIB SYM						
							515, 525, 535, 545
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "A" AND "C" TERMS GROUND STATE SPLITTING	COMP 1 SUB SYM μ ₂ μ ₂ m ₃ SUB/VIB SYM						
	COMP 2 SUB SYM μ ₁ μ ₁ m ₂ SUB/VIB SYM	3					
	COMP 3 SUB SYM μ ₁ μ ₂ m ₁ SUB/VIB SYM		33	44	11	22	
							55
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM EXCITED STATE SPLITTING	COMP 1 SUB SYM μ ₂ μ ₁ m ₁ SUB/VIB SYM						
	COMP 2 SUB SYM μ ₁ μ ₁ m ₂ SUB/VIB SYM	3					
	COMP 3 SUB SYM μ ₁ μ ₂ m ₃ SUB/VIB SYM		33	44	11	22	
							55

DATA SHEET FOR C₄y

5 → 2 GROUND STATE BORROWING
2 → 5 EXCITED STATE BORROWING

[illegible]

DATA SHEET FOR C₄v

 $5 \rightarrow 3$

GROUND STATE BORROWING

3 → 5

EXCITED STATE BORROWING

[illegible]

DATA SHEET FOR C₁y

$$\begin{array}{l} 5 \rightarrow 4 \\ 4 \rightarrow 5 \end{array}$$

GROUND STATE BORROWING
EXCITED STATE BORROWING

[illegible]

DATA SHEET FOR C_{4v}
 $5 \rightarrow 5$ { GROUND STATE BORROWING
EXCITED STATE BORROWING

MODE # PERTURBATION COMPONENTS SYMMETRIES →		1	11	22	33	44	55		
ABSORPTION	COMP 1 SUB SYM μ_1/μ_1 SUB/VIB SYM						11, 22, 33, 44		
	COMP 2 SUB SYM μ_2/μ_2 SUB/VIB SYM	5					51, 52, 53, 54		
MAGNETICALLY-INDUCED OPTICAL ACTIVITY "B" TERM	COMP 1 SUB SYM $\mu_2/\mu_1 m_1$ SUB/VIB SYM						111, 222, 333, 444, 511, 522, 533, 544, 512, 513, 514, 523, 524, 534		
	COMP 2 SUB SYM $\mu_3/\mu_1 m_2$ SUB/VIB SYM						121, 122, 343, 344, 511, 522, 533, 544, 512, 513, 514, 523, 524, 534		
	COMP 3 SUB SYM $\mu_3/\mu_2 m_2$ SUB/VIB SYM	51, 52 53, 54					512, 513, 514, 523, 524, 534, 511, 522, 533, 544		
	COMP 4 SUB SYM $\mu_3/\mu_2 m_3$ SUB/VIB SYM			511, 522, 533, 544, 512, 513, 514, 523, 524, 534	524, 512, 515, 525, 535, 545	523, 514, 515, 525, 535, 545	512, 513, 514, 523, 524, 534, 511, 522, 533, 544		
MAGNETICALLY-INDUCED OPTICAL ACTIVITY GROUND STATE ZEEMAN SPLITTING, "A" AND "C" TERMS	COMP 1 SUB SYM $\mu_2/\mu_1 m_3$ SUB/VIB SYM						11, 22, 33, 44		
	COMP 2 SUB SYM $\mu_3/\mu_1 m_2$ SUB/VIB SYM						11, 22, 33, 44 12, 34		
	COMP 3 SUB SYM $\mu_3/\mu_2 m_3$ SUB/VIB SYM								
MAGNETICALLY-INDUCED OPTICAL ACTIVITY EXCITED STATE ZEEMAN SPLITTING, "A" TERM	COMP 1 SUB SYM $\mu_2/\mu_1 m_1$ SUB/VIB SYM						11, 22, 33, 44		
	COMP 2 SUB SYM $\mu_3/\mu_1 m_2$ SUB/VIB SYM						11, 22, 33, 44 12, 34		
	COMP 3 SUB SYM $\mu_3/\mu_2 m_3$ SUB/VIB SYM								
MODE # PERTURBATION COMPONENTS SYMMETRIES →		2	12	34	112	222	332	442	552
NATURAL OPTICAL ACTIVITY	COMP 1 SUB SYM m_3/μ_1 SUB/VIB SYM								121, 122, 343, 344, 512, 534
	COMP 2 SUB SYM m_2/μ_2 SUB/VIB SYM	5	55	55					
	COMP 3 SUB SYM μ_1/m_3 SUB/VIB SYM				555	555	555	555	
	COMP 4 SUB SYM μ_2/m_2 SUB/VIB SYM	5	55	55					121, 122, 343, 344, 512, 534

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