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OSCILLATOR STRENGTHS IN MAGNESIUM PORPHIN
(Thesis)

L. D. Johnson
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Submitted by L. D. Johnson as a dissertation to the Graduate School of the University of Tennessee in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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L. D. Johnson and H. C. Schweinler

Submitted by L. D. Johnson as a dissertation to the
Graduate School of The University of Tennessee
in partial fulfillment of the requirements
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Doctor of Philosophy

OCTOBER 1967

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ABSTRACT

Molecular orbitals were written as linear combinations of atomic orbitals for magnesium porphin, a chlorophyll prototype. Oscillator strengths for the allowed electronic transitions were calculated.

An atomic orbital basis set of orthonormalized, real Slater orbitals was used. All electrons outside closed atomic shells were considered. Magnesium porphin has D_{4h} symmetry. Symmetry orbitals were obtained by applying group theoretical projection operators to the atomic orbitals. The symmetry orbitals were orthonormalized by diagonalizing their overlap matrix.

The Hartree-Fock molecular orbitals were formally written as linear combinations of the set of orthonormalized symmetry orbitals. The resulting eigenvalue equation was separated into two parts using the property that each of the atomic orbitals is an approximate solution to an atomic Hartree-Fock equation, and an approximate solution was obtained by perturbation methods. The result was a set of molecular orbitals which were energy weighted according to the atomic orbitals involved.

Oscillator strengths for every electronic transition which is allowed by symmetry were calculated using this set of molecular orbitals. The results indicate that all major electronic transitions occur under the influence of light polarized in the plane of the molecule. The Soret band is attributed to transitions involving orbitals belonging to the two dimensional

irreducible representation whose simple polynomial basis function is $x^2 - y^2$.

(This polynomial has nodal surfaces at the nitrogen positions.) A strong absorption band in the region of 3,200 Å is predicted.

CHAPTER I

INTRODUCTION

I. PORPHYRINS

Among the class of compounds known as porphyrins are a number of substances of great biological importance. Each member of this class of compounds may be derived formally from the basic porphin skeleton shown in Figure 1. Porphin is formed from four five-membered heterocyclic rings known as pyrrole rings. (Pyrrole is the stable heterocyclic molecule, NC_4H_5 .) The pyrrole rings are tied together by four CH groups or methene bridges.

The naturally occurring porphyrins are based on porphin modified in several ways. Various side chains may be attached to the outer carbon atoms or to the methene bridge carbon atoms. There may be a metal atom in the central position replacing the two hydrogen atoms in porphin. If there are substitutions on the outer carbon atoms or the methene carbons, the compound is called a porphyrin. If the carbon atoms are unsubstituted but a metal atom appears in the central position, then the compound is properly called a metal porphin.

The porphin skeleton is essentially planar. X-ray crystallographic analysis has revealed some deviation from planarity in certain nickel and copper porphyrins (Fleischer, 1963). The maximum deviations are of the order of 0.25 Å. out of the plane.

FIGURE 1
FREE BASE PORPHIN

II. ABSORPTION SPECTRA OF PORPHINS

Stern and his coworkers, in the period from 1934 to 1937, investigated the absorption spectra of some forty naturally occurring free-base porphins. He found that all these compounds have a four-banded visible spectrum of moderate intensity in the region 6,600 Å. to 5,000 Å. and an extremely strong band at 4,000 Å. A typical absorption spectrum of a free base porphin is shown in Figure 2.

When a free base porphin is converted to a metal salt, the four visible bands collapse into two. This part of the spectrum of magnesium tetraphenyl porphin is shown in Figure 3. (Dorough, et al, 1951 and 1952). The intense absorption band at 4,000 Å. persists in the metal salts.

The 4,000 Å. absorption band is, in fact, common to all cyclic tetrapyrrole structures except for the porphyrinogens, in which all four nitrogen atoms are hydrogenated. It is commonly ten to twenty times as intense as the strongest of the visible bands and is usually referred to as the Soret band after its discoverer (Soret, 1883).

III. PREVIOUS THEORETICAL INVESTIGATIONS

The first attempt at a theoretical interpretation of the absorption spectrum of porphin was reported by Simpson in 1949. Simpson approximated the porphin structure by an eighteen membered cyclic polyene and applied the free electron theory. The first molecular orbital treatment of porphin was by Longuet-Higgins, Rector, and Platt

FIGURE 2

ABSORPTION SPECTRUM FOR FREE BASE PORPHIN

FIGURE 3

ABSORPTION SPECTRUM FOR MAGNESIUM TETRAPHENYL PORPHYRIN

in 1950. Their calculation was a straightforward Huckel theory calculation, using a perturbation to account for the nitrogen atoms. The results of these calculations did not differ greatly. Quantitative agreement with experimental data was poor in both cases. Both calculations predict that degenerate states are involved in both the 4,000 Å. and 6,000 Å. transitions, and neither accounts satisfactorily for the observed difference in intensity of optical and ultraviolet absorption. Platt, in 1956, using the free electron model and relating the porphyrin structure to a twenty-membered cyclic polyene, was able to qualitatively account for the observed difference in intensities of the absorption bands, but again, quantitative agreement was quite poor. Gouterman, in work reported in 1959, 1961, and 1963, attempted to improve the Huckel model calculations by adding an approximate configuration interaction, but found that it was still necessary to assume accidental degeneracy in the two highest filled one-electron states and that quantitative accuracy was still lacking.

CHAPTER II

MOLECULAR ORBITAL THEORY

I. SELF-CONSISTENT FIELD M.O.-L.C.A.O. THEORY

The nonrelativistic Hamiltonian operator for a system consisting of N_a atomic nuclei and N electrons is,

$$H = \sum_{\alpha=1}^{N_a} \left[-\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 \right] + \sum_{v=1}^N \left[-\frac{\hbar^2}{2m_0} \nabla_v^2 \right] + V_{nn} + V_{ne} + V_{ee}, \quad (1)$$

where

$$V_{nn} = \frac{1}{2} \sum_{\alpha=1}^{N_a} \sum_{\alpha'=1}^{N_a} \frac{(Z_\alpha e)(Z_{\alpha'} e)}{|\vec{R}_\alpha - \vec{R}_{\alpha'}|},$$

$$V_{ne} = \sum_{\alpha=1}^{N_a} \sum_{v=1}^N \frac{(Z_\alpha e)(-e)}{|\vec{r}_v - \vec{R}_\alpha|},$$

$$V_{ee} = \frac{1}{2} \sum_{v=1}^N \sum_{\mu=1}^N \frac{(-e)(-e)}{|\vec{r}_v - \vec{r}_\mu|}.$$

M_α and m_0 denote, respectively, the mass of the α th atomic nucleus and the rest mass of an electron; $\vec{R}_\alpha$ and $\vec{r}_v$ denote the coordinates of the α th nucleus and the v th electron; and Z_α is the atomic number of the α th nucleus. A prime on a double summation indicates that terms

involving equal values of the summation variables are to be omitted.

The total wave function for the system is determined by the solutions of the eigenvalue equation,

$$H \left(\{\vec{R}_\alpha\}, \{\vec{r}_\nu\} \right) \Psi \left(\{\vec{R}_\alpha\}, \{\vec{r}_\nu\} \right) = W \Psi \left(\{\vec{R}_\alpha\}, \{\vec{r}_\nu\} \right). \quad (2)$$

The notation $\{\vec{R}_\alpha\}$ means the set of all nuclear coordinates, and $\{\vec{r}_\nu\}$ means the set of all electronic coordinates.

In the Born-Oppenheimer approximation, the nuclear and electronic motion may be separated. The equation for the electronic wave function is

$$\left(\sum_{\nu=1}^N \left[-\frac{\hbar^2}{2m_0} \nabla_\nu^2 \right] + V_{ne} + V_{ee} \right) \Psi \left(\{\vec{R}_\alpha\}, \{\vec{r}_\nu\} \right) = E(\{\vec{R}_\alpha\}) \Psi \left(\{\vec{R}_\alpha\}, \{\vec{r}_\nu\} \right). \quad (3)$$

The electronic wave function and energy depend parametrically upon the nuclear coordinates. The electronic energy enters the equation for the nuclear part of the wave function as an added term in the potential energy.

Rewriting equation (3) in atomic units,

$$\left(\sum_{\nu=1}^N \left[\frac{1}{2} \nabla_\nu^2 \right] - \sum_{\alpha=1}^N \sum_{\nu=1}^N \frac{Z_\alpha}{|\vec{r}_\nu - \vec{R}_\alpha|} + \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1}^N \frac{1}{|\vec{r}_\nu - \vec{r}_\mu|} \right) \Psi \left(\{\vec{r}_\nu\} \right) = E \Psi \left(\{\vec{r}_\nu\} \right). \quad (4)$$

One atomic unit of length is a_0 , the Bohr radius, or 0.529172 Å. One atomic unit of energy is 27.2098 e.v., or 627.51 kcal./mole. This system of units will be used throughout the remainder of this report, unless otherwise specifically noted. In equation (4) the arguments indicating the dependence of ψ and E on the nuclear coordinates have been suppressed.

Molecular orbital theory is concerned with finding solutions to equation (4). The basic concept of molecular orbital theory is to find approximate electronic wave functions by assigning each electron to a one-electron wave function which, in general, extends over the entire molecule. Such a one-electron wave function which depends only on the spatial coordinates of the electron is called a molecular orbital. When the dependence is on space and spin coordinates, the function is called a molecular spin orbital.

The simplest total electronic wave function which can be constructed from one-electron functions and which takes into proper account the symmetry under exchange of electronic space and spin coordinates is a single anti-symmetrized product, or Slater determinant.

$$\Psi(\{\vec{r}_v\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_N(2) \\ \dots & \dots & \dots & \dots \\ \psi_1(N) & \psi_2(N) & \dots & \psi_N(N) \end{vmatrix} \quad (5)$$

$\psi_i(v)$ is the i th molecular spin orbital, normalized to unity, a function of the space and spin coordinates of the v th electron. A function such

as (5) cannot be an exact eigenfunction of equation (4) because it does not adequately take into account the correlation of the electronic motion. The error in energy which persists when the best possible molecular spin orbitals have been determined is called the correlation energy. Although correlation energies are commonly quite large (about one e.v. per electron), molecular properties which are determined by expectation values of one-electron operators are quite accurately predicted by self-consistent field wave functions of the form of (5) (Parr, 1963).

Rewriting (4) in schematic form,

$$H \Psi = E \Psi, \quad (6)$$

and taking the inner product with Ψ (which is assumed to be normalized) on either side, the energy is obtained as a functional of Ψ

$$E = (\Psi, H \Psi). \quad (7)$$

Applying the variational principle, the best possible ground state wave function is that Ψ for which E is an absolute minimum. Taking Ψ to be of the form of (5), minimizing E , and performing a unitary transformation on the molecular orbitals leads to the Hartree-Fock integro-differential equations for the molecular spin orbitals (Roothaan, 1951).

In what has come to be called the M.O.-L.C.A.O. method, molecular orbitals are approximated as linear combinations of atomic orbitals. The extension of the Hartree-Fock self-consistent field method to the calculation of molecular wave functions was first developed by Roothaan (1951).

His work provided a logical and mathematically rigorous scheme for determining the proper linear combinations of atomic orbitals.

Roothaan's original molecular orbital theory work dealt with molecules having closed shell structure. An electron shell is defined as a set of molecular spin orbitals in which every molecular orbital occurs twice, once with either spin, and in which, if there is degeneracy due to molecular symmetry, the molecular orbitals form a complete degenerate set. If the anti-symmetrized product (5) represents a closed shell structure, the molecular spin orbitals are given by

$$\begin{aligned}\psi_{2i-1} &= \varphi_i \alpha, \\ \psi_{2i} &= \varphi_i \beta,\end{aligned}\tag{8}$$

where i ranges from 1 to $N/2$ and where α and β are spin functions corresponding to spin $+1/2$ and $-1/2$, respectively, and where φ_i represents the i th molecular orbital. In this case the Hartree-Fock integro-differential equations are

$$F \varphi_i(\vec{r}) = \epsilon_i \varphi_i(\vec{r}); \quad i = 1, 2, \dots, N/2.\tag{9}$$

$$F = T + V + C - A.\tag{10}$$

F is the Hartree-Fock Hamiltonian operator and is made up of four terms which are called, respectively, the kinetic energy, potential energy, Coulomb, and exchange terms.

$$T = -\frac{1}{2} \nabla^2.$$

$$V = - \sum_{\alpha=1}^N \frac{Z_{\alpha}}{|\vec{r} - \vec{R}_{\alpha}|}$$

$$C = 2 \sum_{j=1}^{N/2} \int \frac{\varphi_j(\vec{r}')^* \varphi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} dv' \quad (11)$$

$$A\varphi_i(\vec{r}) = \sum_{j=1}^{N/2} \left\{ \int \frac{\varphi_j(\vec{r}')^* \varphi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} dv' \varphi_j(\vec{r}) \right\}.$$

The factor of two in the Coulomb term is a result of the sum over spins having already been carried out. The notation dv indicates that the integration involves space coordinates only. When the spin sum is also implied, the differential d will be used.

Expressing each molecular orbital as a linear combination of the atomic orbitals,

$$\varphi_i = \sum_p \chi_p C_{pi} \quad (12)$$

χ_p represents the p th atomic orbital and the C 's are coefficients to be determined. Substituting equation (12) in equation (9) and taking the inner product on both sides with χ_p , leads to a set of $N/2$ equations for the C 's,

$$\sum_p C_{pi} (F_{p,p} - \epsilon_i S_{p,p}) = 0, \quad (13)$$

where

$$F_{p'p} = (\chi_{p'}, F\chi_p),$$

$$S_{p'p} = (\chi_{p'}, \chi_p).$$

The equations (13) would be a set of linear, homogeneous equations were it not for the implicit dependence of the Hartree-Fock Hamiltonian on the final molecular orbitals. The Coulomb and exchange terms of F , in terms of the atomic orbitals, are

$$C = 2 \sum_q \sum_{q'} \sum_{j=1}^{N/2} C_{qj}^* C_{q'j} \int \frac{\chi_q(\vec{r}')^* \chi_{q'}(\vec{r}')}{|\vec{r} - \vec{r}'|} dv',$$

$$A\chi_p(\vec{r}) = \sum_q \sum_{q'} \sum_{j=1}^{N/2} C_{qj}^* C_{q'j} \int \frac{\chi_q(\vec{r}')^* \chi_p(\vec{r}')}{|\vec{r} - \vec{r}'|} dv' \chi_{q'}(\vec{r}).$$

Equations (13) must be solved by a method of trial and error. One assumes a set of coefficients for equation (12), calculates F , then solves (13) for a new set of coefficients. The secular equation,

$$|F_{p'p} - \epsilon_i S_{p'p}| = 0, \quad (15)$$

determines a set of ϵ 's. Then the coefficients C_{pi} are uniquely determined to within a phase factor by equations (13) and the requirement that the molecular orbitals be normalized. If the calculated coefficients do not agree well with those assumed, a new set of coefficients is

assumed and the process repeated until the molecular orbitals are self-consistent.

II. SIMPLER MOLECULAR ORBITAL THEORIES

Two simpler molecular orbital theories have been applied to porphyrins in earlier investigations, and therefore, are mentioned briefly here. Both the Hückel theory and the free-electron theory of molecular structure are intended primarily for application to conjugated hydrocarbons. Good discussions of these theories and fairly complete sets of references may be found in the recent book by Salem (1966).

Both theories assume that only a few of the electrons in a molecule are delocalized and that only these electrons need be considered. The Hückel model assigns these delocalized electrons (called pi-electrons) to molecular orbitals which are made up of linear combinations of atomic orbitals having a common nodal plane. The free-electron theory assigns the delocalized electrons to molecular orbitals which are solutions to the wave equation for a one-dimensional square well.

Free-electron theory applies only to a molecule whose structure is at least approximately that of a linear or cyclic polyene. The one-electron eigenfunctions and eigenvalues are

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n \pi x}{L},$$

$$E_n = \frac{n^2 h^2}{8m_o L^2},$$

where L is the length of the molecule.

In the Hückel theory a secular equation, of the form of (15), must be solved for the orbital energies. The form of the one-electron effective Hamiltonian operator is not specified. Matrix elements of the Hamiltonian between atomic orbitals on neighboring atoms are assumed to be all equal and are assigned an empirical value. The diagonal matrix elements are also assumed to be all equal and are assigned a second empirical value. Overlap integrals are neglected. Atoms other than carbon are accounted for by changing the values of the parameters.

CHAPTER III

USE OF GROUP THEORY IN MOLECULAR ORBITAL THEORY

I. DEFINITIONS

A group is defined as a set of objects, called elements, among which one kind of operation, called multiplication, is defined. A group must exhibit closure under multiplication, the associative law must hold, there must be one and only one unit element, and every element must have a reciprocal. These properties are an essential part of the definition of a group. The number of elements in the group is called the order of the group.

Abstract group theory is concerned only with the way in which the group elements combine under multiplication and has nothing at all to say about specific properties of the individual elements. A group made up of elements which are defined, whether the definitions are verbal or analytic, is a realization of an abstract group.

For certain pairs of groups, a correspondence may be established such that for each element in one of the groups there is one and only one corresponding element in the second group and each element of the second group corresponds to at least one element of the first and such that the product of two elements in one group corresponds to the product of the corresponding elements in the other group. In this case, it is said that the first group is homomorphic onto the second group. If the

two groups are of the same order, there must be a unique one-to-one correspondence between their elements and they are said to be isomorphic.

A representation is a group of square matrices onto which the group to be represented is homomorphic. The number of rows or columns of one of the matrices is called the dimension of the representation. If each element of a representation is transformed by the same similarity transformation, the result is an equivalent representation. Usually, it is possible to find a similarity transformation which will block diagonalize, or reduce, each element of a given representation. If this is not possible, the representation is said to be irreducible. Every abstract group has a uniquely determined number of irreducible representations each of which is uniquely determined to within a similarity transformation.

II. THE GROUP OF THE SCHROEDINGER EQUATION

Consider a physical system whose state vectors satisfy the Schroedinger equation.

$$H\psi = E\psi. \quad (16)$$

Let R represent a real orthogonal transformation in configuration space.

$$x'_i = \sum_{j=1}^n R_{ij} x_j; \quad i = 1, 2, \dots, n. \quad (17)$$

In general, there will be a set of such transformations under which Equation (16) is invariant. This set of transformations forms a group and is called the group of the Schroedinger equation. The group itself

is called the symmetry group of configuration space. The functional substitution operator corresponding to element R of the group is denoted by P_R and is defined as follows. If f is a function in configuration space, then $P_R f$ is a new function such that

$$P_R f(x'_1, x'_2, \dots, x'_n) = f(x_1, x_2, \dots, x_n). \quad (18)$$

The x 's and x' 's are related by Equation (17). In order to emphasize the fundamental importance of the symmetry element R over the transformation matrix R , Equation (18) may be written,

$$P_R f(R\{x_i\}) = f(\{x_i\}),$$

or

$$P_R f(\{x_i\}) = f(R^{-1}\{x_i\}).$$

The functional substitution operators are linear and unitary (Wigner, 1959).

The functional substitution operators commute with the Hamiltonian operator of Equation (16). Therefore, if the eigenvectors, $\psi_1, \psi_2, \dots, \psi_{\mathcal{L}}$, all belong to a single eigenvalue E , then

$$P_R \psi_{\nu} = \sum_{k=1}^{\mathcal{L}} D(R)_{k\nu} \psi_k. \quad (19)$$

The set of $\mathcal{L}$ by $\mathcal{L}$ matrices, $D(R)$, forms a representation of the symmetry group of configuration space. This may be seen by operating on (19) with P_S .

$$P_S P_R \psi_\nu = P_{SR} \psi_\nu = \sum_{\lambda=1}^{\mathcal{L}} \sum_{k=1}^{\mathcal{L}} D(S)_{\lambda k} D(R)_{k\nu} \psi_\lambda.$$

From (19),

$$P_{SR} \psi_\nu = \sum_{\lambda=1}^{\mathcal{L}} D(SR)_{\lambda\nu} \psi_\lambda.$$

Equating coefficients,

$$D(SR)_{\lambda\nu} = \sum_{k=1}^{\mathcal{L}} D(S)_{\lambda k} D(R)_{k\nu}.$$

The set of matrices $D(R)$ forms a group onto which the symmetry group is homomorphic and, therefore, comprises a representation of the symmetry group. If the $\mathcal{L}$ eigenvectors are mutually orthogonal, the representation is by unitary matrices (Wigner, 1959).

III. BASIS FUNCTIONS AND PROJECTION OPERATORS

Suppose the set of matrices, $D^{(j)}(R)$, is the j th irreducible representation, of dimension $\mathcal{L}_j$, of a symmetry group of configuration space and $f_1^{(j)}, f_2^{(j)}, \dots, f_{\mathcal{L}_j}^{(j)}$ are functions in configuration space. If

$$P_R f_\mu^{(j)} = \sum_{\lambda=1}^{\mathcal{L}_j} D^{(j)}(R)_{\lambda\mu} f_\lambda^{(j)}; \mu = 1, 2, \dots, \mathcal{L}_j, \quad (20)$$

then $f_k^{(j)}$ is said to belong to the k th row of the irreducible representation j and the other $\mathcal{L}_j - 1$ functions are called its partner functions (Wigner, 1959). The functions are also called basis functions for the irreducible representation, j .

Two functions which belong to two different irreducible representations or to different rows of the same irreducible representation are orthogonal. Consider the scalar product of the functions $f_{\mu}^{(j)}$ and $g_{\mu'}^{(j')}$. Using the unitary property of the functional substitution operators and Equation (20),

$$\left(f_{\mu}^{(j)}, g_{\mu'}^{(j')} \right) = \left(P_R f_{\mu}^{(j)}, P_R g_{\mu'}^{(j')} \right) = \sum_{\lambda=1}^{\ell_j} \sum_{\lambda'=1}^{\ell_{j'}} D^{(j)}(R)^*_{\lambda\mu} D^{(j')}(R)_{\lambda'\mu'} \left(f_{\lambda}^{(j)}, g_{\lambda'}^{(j')} \right). \quad (21)$$

For a group of order h , a fundamental theorem of group theory is

$$\sum_R D^{(j)}(R)^*_{\lambda\mu} D^{(j')}(R)_{\lambda'\mu'} = \frac{h}{\ell_j} \delta_{jj'} \delta_{\lambda\lambda'} \delta_{\mu\mu'}. \quad (22)$$

Summing (21) over all the group elements and using (22),

$$\left(f_{\mu}^{(j)}, g_{\mu'}^{(j')} \right) = \frac{1}{\ell_j} \delta_{jj'} \delta_{\mu\mu'} \sum_{\lambda=1}^{\ell_j} \left(f_{\lambda}^{(j)}, g_{\lambda}^{(j)} \right).$$

An operator S which commutes with each of the functional substitution operators is called a symmetric operator. The Hamiltonian operator of Equation (16) is a symmetric operator. If S is a symmetric operator and $g_{\mu}^{(j)}$ belongs to the μ th row of irreducible representation j , then $Sg_{\mu}^{(j)}$ also belongs to the μ th row of irreducible representation j . Therefore,

$$\left(f_{\mu}^{(j)}, Sg_{\mu'}^{(j')} \right) = \frac{1}{\ell_j} \delta_{jj'} \delta_{\mu\mu'} \sum_{\lambda=1}^{\ell_j} \left(f_{\lambda}^{(j)}, Sg_{\lambda}^{(j)} \right) \quad (23)$$

(Wigner, 1959).

For a group of order h whose irreducible representations are known, a set of operators, called projection operators, may be defined as follows.

$$P_{k\lambda}^{(j)} = \sqrt{\frac{h_j}{h}} \sum_R D^{(j)}(R^{-1})_{k\lambda} P_R. \quad (24)$$

The summation is over all elements of the group. The projection operator, $P_{k\lambda}^{(j)}$, operating on an arbitrary function in configuration space, produces a function which belongs to the λ th row of the j th irreducible representation. This may be shown as follows.

$$P_{k\lambda}^{(j)} F = \sqrt{\frac{h_j}{h}} \sum_R D^{(j)}(R^{-1})_{k\lambda} P_R F,$$

where F is an arbitrary function in configuration space. Operating with P_Q ,

$$P_Q P_{k\lambda}^{(j)} F = \sqrt{\frac{h_j}{h}} \sum_R D^{(j)}(R^{-1})_{k\lambda} P_Q P_R F. \quad (25)$$

Using the group closure property,

$$QR = S,$$

another group element, and

$$P_Q P_R = P_S.$$

The rearrangement theorem says that, if the set of elements $(E, A_2, A_3, \dots, A_h)$ comprise a group and if Q is an element of the group, then the

set of elements $(Q E, QA_2, QA_3, \dots, QA_h)$ contains each element of the group once and only once. Therefore, as R ranges over all the group elements, $S = QR$ also ranges over the entire group and Equation (25) may be written,

$$P_Q P_{k\lambda}^{(j)} F = \sqrt{\frac{\ell_j}{h}} \sum_S D^{(j)}(S^{-1}Q)_{k\lambda} P_S F, \quad (26)$$

since

$$R^{-1} = S^{-1} Q.$$

$$D^{(j)}(S^{-1}Q)_{k\lambda} = \sum_{\mu=1}^{\ell_j} D^{(j)}(S^{-1})_{k\mu} D^{(j)}(Q)_{\mu\lambda}.$$

Substituting in (26) and rearranging terms,

$$P_Q [P_{k\lambda}^{(j)} F] = \sum_{\mu=1}^j D^{(j)}(Q)_{\mu\lambda} \sqrt{\frac{\ell_j}{h}} \sum_S D^{(j)}(S^{-1})_{k\mu} P_S F,$$

or, from (24),

$$P_Q [P_{k\lambda}^{(j)} F] = \sum_{\mu=1}^{\ell_j} D^{(j)}(Q)_{\mu\lambda} [P_{k\mu}^{(j)} F].$$

Therefore, the set of functions $P_{k\lambda}^{(j)} F$, for $\lambda = 1, 2, \dots, \ell_j$, is a set of partners for the j th irreducible representation. In general, from a single function F , ℓ_j such sets of partners may be formed, corresponding to $k = 1, 2, \dots, \ell_j$.

If S is a symmetric operator and F and G are arbitrary functions in configuration space, then applying Equation (23),

$$\left(P_{k\lambda}^{(j)} F, S P_{k'\lambda'}^{(j')} G \right) = \delta_{jj'} \delta_{\lambda\lambda'} \frac{1}{\ell_j} \sum_{\lambda=1}^{\ell_j} \left(P_{k\lambda}^{(j)} F, S P_{k'\lambda}^{(j)} G \right).$$

Using Equation (24) and the unitary property of the functional substitution operators and choosing unitary matrices for the irreducible representation,

$$\left(P_{k\lambda}^{(j)} F, S P_{k'\lambda'}^{(j')} G \right) = \frac{1}{h} \sum_Q \sum_R D^{(j)}(R^{-1})_{k'\lambda} D^{(j)}(Q)_{\lambda k} \left(F, S P_{Q^{-1}R}^{(j)} G \right).$$

Substituting this in the equation above, using the definition of matrix multiplication and the rearrangement theorem, gives the following useful formula.

$$\left(P_{k\lambda}^{(j)} F, S P_{k'\lambda'}^{(j')} G \right) = \delta_{jj'} \delta_{\lambda\lambda'} \sqrt{\frac{h}{\ell_j}} \left(F, S P_{k'k}^{(j)} G \right). \quad (27)$$

IV. SYMMETRY ORBITALS

Most molecules of theoretical interest have symmetry. The complete and nonredundant set of symmetry operations, each of which results in a different but physically indistinguishable configuration form a group. The set of coordinate transformations corresponding to this set of symmetry operations forms the group of the Schroedinger equation for

the molecule. Equations (2), (3), and (4) are invariant under these coordinate transformations.

Having determined the symmetry group of configuration space for the molecule being considered, projection operators can be formed from Equation (24). Applying the projection operators to the atomic orbitals centered on each of the nuclei which make up the framework of the molecule results in a set of functions each of which is a linear combination of atomic orbitals and each of which belongs to one of the irreducible representations of the symmetry group. These functions are called symmetry orbitals.

In practice it is not always necessary to apply the projection operators to every atomic orbital on every nucleus. Often it is possible to obtain a complete set of symmetry orbitals by projecting on atomic orbitals centered on a restricted set of nuclei. This restricted set of nuclei is called the basic domain of the molecule.

Roothaan(1951) showed that the Hartree-Fock self-consistent field molecular orbitals may be chosen as sets of partner functions belonging to the irreducible representations of the symmetry group and that the Hartree-Fock Hamiltonian operator is a symmetric operator under the functional substitution operators. Hence a molecular orbital may be expanded in terms of symmetry orbitals which belong to the same row of the same irreducible representation. This gives, in place of Equation (12),

$$\varphi_{i\lambda}^{(j)} = \sum_p \chi_{p\lambda}^{(j)} c_{pi}^{(j)} .$$

where $\varphi_{i\lambda}^{(j)}$ is the ith molecular orbital belonging to row λ of the jth irreducible representation and $\chi_{p\lambda}^{(j)}$ is the pth symmetry orbital belonging to the same row of the same irreducible representation. Using the orthogonal properties of basis functions for the irreducible representation (23), the set of $N/2$ Equations (13) is replaced with a number of sets of equations of smaller order.

$$\sum_p c_{pi}^{(j)} [F_{p'p}^{(j)} - \epsilon_i^{(j)} S_{p'p}^{(j)}] = 0. \quad (28)$$

There is a set of equations like (28) for each row of each irreducible representation. The number of equations in each set is the number of different molecular orbitals belonging to row λ of irreducible representation j . The secular equation for the one-electron energies is similarly reduced.

$$|F_{p'p}^{(j)} - \epsilon_i^{(j)} S_{p'p}^{(j)}| = 0.$$

CHAPTER IV

THEORY OF OPTICAL SPECTRA

I. TRANSITION PROBABILITIES

The theory of the interaction of radiation and matter is discussed in many of the standard texts on quantum mechanics. An excellent treatment of this subject may be found in Chapters I and VI and Appendix 12 of J. C. Slater's Quantum Theory of Atomic Structure, Volume I (1960). The formulas below are quoted directly from Slater. The Gaussian system of units is used in this chapter. Certain important formulas will be rewritten in atomic units at the conclusion of the chapter.

When an atomic system in a stationary state n (with energy E_n and wave function Ψ_n) interacts with an external electromagnetic field, the probability per second of transition to a lower state m (with energy E_m and wave function Ψ_m), with emission of a photon of frequency given by Bohr's frequency condition is

$$\text{Probability of emission} = A + B\rho_\nu,$$

where ρ_ν is the energy density of external isotropic radiation of frequency ν . The probability per second of transition to a higher energy level with absorption of a photon is

$$\text{Probability of absorption} = B\rho_\nu.$$

It was established by Einstein (1917) that the multipliers of ρ_ν were the same in the emission and absorption equations. A and B are often called the Einstein A and B coefficients.

In 1926, Dirac showed that the interaction of an electromagnetic field with an atomic system could be explained if the field, as well as the atomic system, were treated quantum mechanically. Dirac calculated the Einstein coefficients with the following results for transitions between stationary states m and n of the atomic system.

$$A = \frac{8\pi h \nu^3}{c^3} \frac{8\pi^3 |M_{nm}|^2}{3h^2}, \quad (29)$$

$$B = \frac{8\pi^3 |M_{nm}|^2}{3h^2}. \quad (30)$$

The factor $|M_{nm}|^2$ is the absolute square of the matrix element of the dipole moment operator.

$$\vec{M}_{nm} = (\psi_n, \sum_j (-e) \vec{r}_j \psi_m)$$

$\vec{r}_j$ is the coordinate vector of electron j and the summation is over all electrons in the atomic system.

$$|M_{nm}|^2 = \vec{M}_{nm}^* \cdot \vec{M}_{nm}.$$

Equations (29) and (30) apply to atomic systems with randomly oriented dipole moments interacting with unpolarized electromagnetic fields. The factor of 1/3 which appears in these equations results

from averaging over the square of the cosine of the angle between the dipole moment of the atom and the electric vector of the field. If an atomic system is oriented with its dipole moment in a definite direction and if this system interacts with linearly polarized light, the coefficients A and B will vanish in the case that the direction of polarization is perpendicular to the dipole moment. However, if the dipole moment and the direction of polarization are parallel, both in the x direction, for example, then

$$A = \frac{8\pi h \nu^3}{c^3} \frac{8\pi^3 |(M_x)_{nm}|^2}{h^2}, \quad (31)$$

and

$$B = \frac{8\pi^3 |(M_x)_{nm}|^2}{h^2}. \quad (32)$$

The formulas and discussion above hold for atoms and, when nuclear motion is neglected, for molecules whose center of charge is at the origin.

II. OSCILLATOR STRENGTHS

The oscillator strengths are important because they provide a convenient set of dimensionless quantities proportional to the Einstein coefficients and because of an important theorem called the Kuhn-Thomas sum rule or f sum rule. The following is a convenient definition for the oscillator strength of a transition between stationary states m and n.

$$f_{nm}^{(\alpha\alpha)} = \frac{2m_0}{\hbar^2} (E_n - E_m) \left| \left(\psi_n, \sum_j x_j^\alpha \psi_m \right) \right|^2. \quad (33)$$

The sum is over all electrons. For $\alpha = 1, 2, 3$, x_j^α is respectively the x, y, and z coordinate of electron j; m_0 is the mass of an electron (Schweinler, 1965). In terms of the matrix elements of the dipole moment operator,

$$f_{nm}^{(\alpha\alpha)} = \frac{2m_0}{e^2 \hbar^2} (E_n - E_m) \left| (M^\alpha)_{nm} \right|^2.$$

Equations (30) and (32) may be written as a single equation.

$$B = \frac{\pi e^2 f_{nm}}{m_0 (E_n - E_m)}. \quad (34)$$

If the dipole moment is in the x direction and the incident radiation is linearly polarized in the x direction, then

$$f_{nm} = f_{nm}^{(xx)}.$$

For unpolarized light, or random orientation of dipole moments,

$$f_{nm} = \frac{1}{3} \sum_{\alpha=1}^3 f_{nm}^{(\alpha\alpha)}.$$

The f sum rule mentioned above states that

$$\sum_n f_{nm}^{(\alpha\alpha)} = N,$$

where N is the number of electrons in the atom or molecule and where the sum over n is over all final states n corresponding to the initial state m . This rule follows directly from the commutation relations for coordinates and momenta and is exactly true for any system when the potential energy commutes with the coordinate operators. The derivation of the f sum rule is given in Appendix II of Slater's Quantum Theory of Atomic Structure, Volume I (1960).

If all quantities are expressed in atomic units,

$$f_{nm}^{(\alpha\alpha)} = 2 (E_n - E_m) \left| \left(\Psi_n, \sum_j x_j^\alpha \Psi_m \right) \right|^2. \quad (35)$$

III. EVALUATION OF MATRIX ELEMENTS

To calculate oscillator strengths in a molecule, it is necessary to evaluate the matrix elements of

$$\sum_j x_j^\alpha$$

between determinantal wave functions. The wave functions, Ψ_n and Ψ_m , which appear in equation (35), are of the form shown in equation (5). The matrix element in equation (35) will vanish unless the one-electron functions $\Psi_\mu(i)$ which appear in column μ of Ψ_n are replaced by $\Psi'_\mu(i)$ in column μ of Ψ_m and unless the one-electron functions which appear in every other column of Ψ_m are identical to those in the corresponding column of Ψ_n . The functions $\Psi_\mu(i)$ and $\Psi'_\mu(i)$ are molecular spin orbitals and are products of molecular orbitals with spin functions, as

shown in equation (8). If the matrix element does not vanish, it may be written

$$\left(\psi_n, \sum_j x_j^\alpha \psi_m \right) = \left(\varphi_\mu^{(i)}, x_i^\alpha \varphi'_\mu^{(i)} \right),$$

where $\varphi_\mu^{(i)}$ and $\varphi'_\mu^{(i)}$ are the molecular orbitals appearing in column μ of ψ_n and ψ_m , respectively. This is shown by Slater in section 12-5 of the work cited earlier.

Analyzing the dipole moment matrix elements using group theory leads to a form which is very useful for picking our selection rules for the transitions. For practically any molecule with symmetry, with a reasonable choice for the coordinate system, the simple functions x , y , and z , or some simple linear combinations of these, will belong to certain of the irreducible representations of the symmetry group of the molecule. Let $f_\lambda^{(j)}$ denote the simple polynomial basis function belonging to row λ of irreducible representation j , and let $\varphi_{n\lambda}^{(j)}$ be the n th molecular orbital belonging to row λ of irreducible representation j . The dipole moment matrix elements are integrals of the form

$$\left(\varphi_{n_1 \lambda_1}^{(j_1)}, f_\lambda^{(j)} \varphi_{n_2 \lambda_2}^{(j_2)} \right).$$

Using the functional substitution operators defined in equation (18),

$$\left(\varphi_{n_1 \lambda_1}^{(j_1)}, F_\lambda^{(j)} \varphi_{n_2 \lambda_2}^{(j_2)} \right) = \frac{1}{h} \sum_R \left(P_R \varphi_{n_1 \lambda_1}^{(j_1)}, P_R [f_\lambda^{(j)} \varphi_{n_2 \lambda_2}^{(j_2)}] \right),$$

where h is the order of the group. From equation (18), it is obvious that

$$P_R(fg) = (P_R f) (P_R g).$$

Using this relation and equation (20)

$$\begin{aligned} & \left(\varphi_{n_1}^{(j_1)}_{\lambda_1}, f_{\lambda}^{(j)} \varphi_{n_2}^{(j_2)}_{\lambda_2} \right) \\ &= \frac{1}{h} \sum_R \sum_{\mu_1=1}^{\ell_{j_1}} \sum_{\mu=1}^{\ell_j} \sum_{\mu_2=1}^{\ell_{j_2}} D^{(j_1)}_{\mu_1 \lambda_1}(R)^* D^{(j)}_{\mu \lambda}(R) D^{(j_2)}_{\mu_2 \lambda_2}(R) \\ & \left(\varphi_{n_1}^{(j_1)}_{\mu_1}, f_{\mu}^{(j)} \varphi_{n_2}^{(j_2)}_{\mu_2} \right). \end{aligned} \quad (36)$$

Before proceeding with this derivation it is necessary to make some remarks about direct products of matrices. Let A be an n_1 by n_2 matrix, let R be an n_1 by n_2 matrix, and let C be the matrix which is the direct product of A with B . The direct product is denoted

$$C = A \times B.$$

The definition of the direct product is

$$C_{ik;j\ell} = A_{ij} B_{k\ell}.$$

The matrix C is an $n_1 n_1$ by $n_2 n_2$ matrix whose rows and columns are denoted by doubled index sets taken in lexicographical order.

Now consider $D^{(j)}(R)$, the matrix corresponding to group element R in irreducible representation j of a group, and $D^{(j_2)}(R)$, the matrix corresponding to element R in irreducible representation j_2 of the same group. Denote the direct product of these two matrices by a matrix $\Delta^{(jj_2)}(R)$.

$$\Delta^{(jj_2)}(R)_{\mu\mu_2; \lambda\lambda_2} = D^{(j)}(R)_{\mu\lambda} D^{(j_2)}(R)_{\mu_2\lambda_2}. \quad (37)$$

The set of matrices, $\Delta^{(jj_2)}(R)$, for all group elements R forms a representation of the group which is, in general reducible by a similarity transformation. Let $S^{(jj_2)}$ denote the unitary matrix which reduces the direct product representation.

$$\begin{aligned} \sum_{\mu\mu_2} \sum_{\lambda\lambda_2} S^{(jj_2)}_{JM; \mu\mu_2} \Delta^{(jj_2)}(R)_{\mu\mu_2; \lambda\lambda_2} S^{(jj_2)*}_{JM'; \lambda\lambda_2} \\ = \delta_{jj'} D^{(J)}(R)_{mm'}. \end{aligned}$$

The elements, $S^{(jj_2)}_{JM; \mu\mu_2}$, of the unitary matrix which reduces the direct product representation are called the Wigner coupling coefficients.

$$\Delta^{(jj_2)}(R)_{\mu\mu_2; \lambda\lambda_2} = \sum_{J=1}^c \sum_{M=1}^{\ell_J} \sum_{M'=1}^{\ell_J} S^{(jj_2)}_{JM; \mu\mu_2} D^{(J)}(R)_{mm'} S^{(jj_2)}_{JM'; \lambda\lambda_2}, \quad (38)$$

where c is the number of inequivalent irreducible representations in the group and ℓ_J is the dimensionality of irreducible representation J .

Now equation (37) and (38) are used to substitute for

$D_{\mu\lambda}^{(j)}(R) D_{\mu_2\lambda_2}^{(j_2)}(R)$ in equation (36). Then the sum over R may be carried out using equation (22). After a little simplification the result is

$$\begin{aligned} & \left(\varphi_{n_1 \lambda_1}^{(j_1)}, f_{\lambda}^{(j)} \varphi_{n_2 \lambda_2}^{(j_2)} \right) \\ &= s_{j_1 \lambda_1; \lambda \lambda_2}^{(jj_2)} \sum_{\mu_1=1}^{\ell_{j_1}} \left(\varphi_{n_1 \mu_1}^{(j_1)}, \sum_{\mu=1}^{\ell_j} \sum_{\mu_2=1}^{\ell_{j_2}} D_{j_1 \mu_1, \mu \mu_2}^{(jj_2)*} f_{\mu}^{(j)} \varphi_{n_2 \mu_2}^{(j_2)} \right). \end{aligned}$$

The post-factor of the inner product in the above equation belongs to row μ_1 of irreducible representation j_1 , and, therefore, the inner product is independent of μ_1 according to equation (23). Any convenient value may be selected for μ_1 and the equation written as follows.

$$\left(\varphi_{n_1 \lambda_1}^{(j_1)}, f_{\lambda}^{(j)} \varphi_{n_2 \lambda_2}^{(j_2)} \right) = s_{j_1 \lambda_1; \lambda \lambda_2}^{(jj_2)} \langle \langle n_1(j_1) || f^{(j)} || n_2(j_2) \rangle \rangle, \quad (39)$$

where

$$\langle \langle n_1(j_1) || f^{(j)} || n_2(j_2) \rangle \rangle = \left(\varphi_{n_1 \mu_1}^{(j_1)}, \sum_{\mu=1}^{\ell_j} \sum_{\mu_2=1}^{\ell_{j_2}} s_{j_1 \mu_1; \mu \mu_2}^{(jj_2)*} f_{\mu}^{(j)} \varphi_{n_2 \mu_2}^{(j_2)} \right). \quad (40)$$

The quantities defined in equation (40) are called reduced matrix elements. The form of equation (39) emphasizes the point that much of

the symmetry dependence of the dipole matrix elements is revealed by the Wigner coefficients. It will be noted that this equation is very similar to the Wigner-Eckart theorem which applies to matrix elements of tensor operators in the rotation group (Wigner, 1959).

CHAPTER V

DETAILS OF THE CALCULATIONS

I. STRUCTURE AND SYMMETRY

The model chosen for the magnesium porphin structure is shown in Figure 4. The internuclear distances between nearest neighbor carbon atoms and between each nitrogen atom and its nearest neighbor carbon atoms were assumed to be equal all around the ring. Similarly each hydrogen atom was assumed to be at an equal distance from its nearest neighbor carbon atom. The following values were selected for these internuclear distances.

$$\text{C-C distance} = \text{C-N distance} = 1.4 \text{ \AA} = 2.64564 \text{ a.u.}$$

$$\text{C-H distance} = 1.1 \text{ \AA} = 2.07872 \text{ a.u.}$$

The angle between the lines of centers from C_1 to C_2 and from C_1 to C_{20} was chosen to be 126° . Each hydrogen atom was assumed to be located symmetrically with respect to its two second neighbor carbon atoms. These choices, together with the assumptions of planarity and four-fold symmetry, define the structure of the model. Table I gives the nuclear coordinates of atoms in the first quadrant.

No experimental data on the structure of magnesium porphin is available at the present time. However, data which is available on other metalloporphyrins and free base porphyrins indicates that this model should be a good approximation to the actual structure of

FIGURE 4
MAGNESIUM PORPHIN

TABLE I

NUCLEAR COORDINATES IN ATOMIC UNITS OF ATOMS IN THE FIRST QUADRANT

Atom	x	y
H ₁	8.66404	0.
H ₃	8.63845	5.03975
H ₄	5.03975	8.63845
C ₁	6.58532	0.
C ₂	5.38422	2.35728
C ₃	6.58532	4.71457
C ₄	4.71457	6.58532
C ₅	2.35728	5.38422
N ₁	2.77115	2.77115
M _g	0.	0.

magnesium porphin (Fleischer, 1963; Hoard, Hamor, and Hamor, 1963).

The molecule, with the coordinate axes oriented as in Figure 4, page 37, has the following symmetry elements. The z axis is a four-fold rotation axis. The x axis, the y axis, and the two lines defined by $y = x, z = 0$, and $y = -x, z = 0$ are two-fold rotation axes. The xy plane, the xz plane, the yz plane, and the planes defined by $y = x$ and $y = -x$ are reflection planes.

The point symmetry group which consists of the identity, rotations about a four-fold axis, and reflections in four different planes each of which contains the rotation axis is conventionally given the name C_{4v} . The symmetry group of configuration space for magnesium porphin is the product of C_{4v} with C_s , the group of order two which consists of the identity and reflection in a single plane. This group is isomorphic with the symmetry group D_{4h} . In the remainder of this paper, this group will be called D_{4h} , although the scheme for labeling the irreducible representations is not the one conventionally used for D_{4h} . The irreducible representations have been labeled with a single or a double prime to indicate the behavior of their basis functions under reflection in the plane of the molecule. The conventional labeling scheme gives precedence to the parity operator, but it was felt that in such a large molecule the parity of the wave function might be the less significant property. The character table for D_{4h} is shown in Table II. In calculations, it is convenient to number the irreducible representations. The numbering of the representations is also indicated in Table II.

TABLE II

CHARACTER TABLE FOR D_{4h} SHOWING MODIFIED LABELING OF IRREDUCIBLE
REPRESENTATIONS AND SIMPLE POLYNOMIAL BASIS FUNCTIONS

	D_{4h}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	σ_h	$2S_4$	i	$2C'_2$	$2C''_2$	Basis
1	A'_1	1	1	1	1	1	1	1	1	1	1	1
2	A'_2	1	1	1	-1	-1	1	1	1	-1	-1	$xy(x^2-y^2)$
3	B'_1	1	-1	1	1	-1	1	-1	1	1	-1	x^2-y^2
4	B'_2	1	-1	1	-1	1	1	-1	1	-1	1	xy
5	E'	2	0	-2	0	0	2	0	-2	0	0	(x,y)
6	A''_1	1	1	1	1	1	-1	-1	-1	-1	-1	z
7	A''_2	1	1	1	-1	-1	-1	-1	-1	1	1	$xyz(x^2-y^2)$
8	B''_1	1	-1	1	1	-1	-1	1	-1	-1	1	$z(x^2-y^2)$
9	B''_2	1	-1	1	-1	1	-1	1	-1	1	-1	xyz
10	E''	2	0	-2	0	0	-2	0	2	0	0	(xz, yz)

The definitions of the elements of the symmetry group of magnesium porphin are given below.

E = the identity element.

C_4^m = rotation about the z axis through an angle $\frac{2\pi m}{4}$.

σ_v = reflection in the xz plane.

σ_v' = reflection in the yz plane.

σ_d = reflection in the plane defined by $y = x$.

σ_d' = reflection in the plane defined by $y = -x$.

These elements comprise the group C_{4v} . The remainder of D_{4h} is obtained by taking the product of each of these elements with σ_h .

σ_h = reflection in the xy plane.

$S_4 = C_4 \sigma_h$ = rotary-reflection operator.

$S_4^3 = C_4^3 \sigma_h$ = inversion or parity operator.

$C_2' = \sigma_v \sigma_h$ = rotation through π about the x axis.

$\bar{C}_2' = \sigma_v' \sigma_h$ = rotation through π about the y axis.

$C_2'' = \sigma_d \sigma_h$ = rotation through π about the axis $y = x, z = 0$.

$\bar{C}_2'' = \sigma_d' \sigma_h$ = rotation through π about the axis $y = -x, z = 0$.

The following relations also hold between elements of the group.

$$\sigma_v' = C_4^2 \sigma_v.$$

$$\sigma_d = C_4 \sigma_v.$$

$$\sigma_d' = C_4^3 \sigma_v.$$

Hence, every other element of the group may be written in terms of the elements E , C_4 , σ_v , and σ_h .

The one dimensional irreducible representations may be read directly from the character table. The matrices corresponding to the four basic elements of the group in the two dimensional irreducible representations are given in Table III. The relations between the group elements, given above, allow the projection operators, defined in equation (24), to be written in the relatively simple forms given in Table IV.

The Wigner coupling coefficients were found in the straightforward way by reducing the direct product representations. The coupling coefficients necessary in the calculations are given in Table V.

II. BASIS FUNCTIONS

Magnesium porphin has a total of 172 electrons. In this calculation it was assumed that closed shell electron structures were essentially unaffected by formation of the molecule. Assigning two electrons to the K shell of each carbon and each nitrogen atom and ten electrons to the K and L shells of the magnesium atom accounts for 58 electrons.

The atomic orbital basis set consists of 1s atomic orbitals centered on the hydrogen atoms, 2s and 2p atomic orbitals centered on the carbon and nitrogen atoms, and 3s and 3p atomic orbitals centered on the magnesium atom. The real orthonormalized Slater orbitals were

TABLE III
TWO DIMENSIONAL IRREDUCIBLE REPRESENTATIONS OF D_{4h}

	E	C_4	σ_v	σ_h
E'	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
E''	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$

TABLE IV
PROJECTION OPERATORS FOR D_{4h}

$$P_{11}^{(1)} = \frac{1}{4} \sum_{m=1}^4 P_{C_4}^m (P_E + P_{\sigma_v}) (P_E + P_{\sigma_h})$$

$$P_{11}^{(2)} = \frac{1}{4} \sum_{m=1}^4 P_{C_4}^m (P_E - P_{\sigma_v}) (P_E + P_{\sigma_h})$$

$$P_{11}^{(3)} = \frac{1}{4} \sum_{m=1}^4 (-1)^m P_{C_4}^m (P_E + P_{\sigma_v}) (P_E + P_{\sigma_h})$$

$$P_{11}^{(4)} = \frac{1}{4} \sum_{m=1}^4 (-1)^m P_{C_4}^m (P_E - P_{\sigma_v}) (P_E + P_{\sigma_h})$$

$$P_{11}^{(5)} = \frac{1}{8} \sum_{m=1}^4 \cos \frac{m\pi}{2} P_{C_4}^m (P_E + P_{\sigma_v}) (P_E + P_{\sigma_h})$$

$$P_{12}^{(5)} = \frac{1}{8} \sum_{m=1}^4 \sin \frac{m\pi}{2} P_{C_4}^m (P_E + P_{\sigma_v}) (P_E + P_{\sigma_h})$$

$$P_{21}^{(5)} = \frac{1}{8} \sum_{m=1}^4 (-\sin \frac{m\pi}{2}) P_{C_4}^m (P_E - P_{\sigma_v}) (P_E + P_{\sigma_h})$$

$$P_{22}^{(5)} = \frac{1}{8} \sum_{m=1}^4 \cos \frac{m\pi}{2} P_{C_4}^m (P_E - P_{\sigma_v}) (P_E + P_{\sigma_h})$$

TABLE IV (continued)

$$p_{11}^{(6)} = \frac{1}{4} \sum_{m=1}^4 P_{c_4}^m (P_E + P_{\sigma_v}) (P_E - P_{\sigma_h})$$

$$p_{11}^{(7)} = \frac{1}{4} \sum_{m=1}^4 P_{c_4}^m (P_E - P_{\sigma_v}) (P_E - P_{\sigma_h})$$

$$p_{11}^{(8)} = \frac{1}{4} \sum_{m=1}^4 (-1)^m P_{c_4}^m (P_E + P_{\sigma_v}) (P_E - P_{\sigma_h})$$

$$p_{11}^{(9)} = \frac{1}{4} \sum_{m=1}^4 (-1)^m P_{c_4}^m (P_E - P_{\sigma_v}) (P_E - P_{\sigma_h})$$

$$p_{11}^{(10)} = \frac{1}{8} \sum_{m=1}^4 \cos \frac{m\pi}{2} P_{c_4}^m (P_E + P_{\sigma_v}) (P_E - P_{\sigma_h})$$

$$p_{12}^{(10)} = \frac{1}{8} \sum_{m=1}^4 \sin \frac{m\pi}{2} P_{c_4}^m (P_E + P_{\sigma_v}) (P_E - P_{\sigma_h})$$

$$p_{21}^{(10)} = \frac{1}{8} \sum_{m=1}^4 (-\sin \frac{m\pi}{2}) P_{c_4}^m (P_E - P_{\sigma_v}) (P_E - P_{\sigma_h})$$

$$p_{22}^{(10)} = \frac{1}{8} \sum_{m=1}^4 \cos \frac{m\pi}{2} P_{c_4}^m (P_E - P_{\sigma_v}) (P_E - P_{\sigma_h})$$

TABLE V
WIGNER COUPLING COEFFICIENTS FOR D_{4h}

J	j	$\begin{matrix} (Jj) \\ S_{j'm';Mm} \end{matrix}$
5	1	$\delta_{j'5} \delta_{m'M}$
5	2	$\delta_{j'5} (-1)^{m'} (1 - \delta_{m'M})$
5	3	$\delta_{j'5} (-1)^{m' + 1} \delta_{m'M}$
5	4	$\delta_{j'5} (1 - \delta_{m'M})$
5	5	$\frac{1}{2} \{ (\delta_{j'1} + \delta_{j'3}) \delta_{Mm} + [(-1)^m \delta_{j'2} + \delta_{j'4}] (1 - \delta_{Mm}) \}$
5	6	$\delta_{j'10} \delta_{m'M}$
5	7	$\delta_{j'10} (-1)^{m'} (1 - \delta_{m'M})$
5	8	$\delta_{j'10} (-1)^{m' + 1} \delta_{m'M}$
5	9	$\delta_{j'10} (1 - \delta_{m'M})$
5	10	$\frac{1}{2} \{ (\delta_{j'6} + \delta_{j'8}) \delta_{Mm} + [(-1)^m \delta_{j'7} + \delta_{j'9}] (1 - \delta_{Mm}) \}$
6	$j \leq 5$	$\delta_{j', j+5} \delta_{m'm}$
6	$j \geq 6$	$\delta_{j', j-5} \delta_{m'm}$

used to represent the atomic orbitals. The single-term Slater orbitals have the following form,

$$\chi_{n\ell m}^{(\mu)}(r, \theta, \varphi) = N(n\ell |m| \mu) r^{n-1} e^{-\mu r} P_{\ell}^{|m|}(\cos \theta) \Phi_m(\varphi), \quad (41)$$

where,

$$N(n\ell |m| \mu) = \frac{(2\mu)^{n + \frac{1}{2}}}{\sqrt{(2n)!}} \cdot \sqrt{\frac{2\ell + 1}{2\pi(1 + \delta_{m0})} \frac{(\ell - |m|)!}{(\ell + |m|)!}},$$

and

$$\Phi_m(\varphi) = \begin{cases} \cos m \varphi & \text{if } m > 0 \\ 1 & \text{if } m = 0 \\ \sin |m| \varphi & \text{if } m < 0 \end{cases}.$$

The exponential coefficient μ depends upon the quantum numbers n and ℓ as well as the atomic species. The exponential coefficients used in this calculation were determined according to the set of rules given by Slater (1930). The values used are listed in Table VI.

For each atomic species, a set of orthonormal atomic orbitals was generated by using the Schmidt orthogonalization method on the single-term Slater orbitals for that species. The orthonormalized Slater orbitals are denoted by the chemical symbol for the atomic species with subscripts for the quantum numbers. Magnetic quantum numbers 1, -1, and 0 are denoted by the subscripts x, y, and z, respectively, when the orbital angular momentum quantum number is 1(p). The orthonormalized Slater orbitals are given in Table VII.

TABLE VI
EXPONENTIAL COEFFICIENTS FOR SLATER ORBITALS

Atomic Species	Orbital	μ
H	1 s	1.000
C	1 s	5.700
C	2 s	1.625
C	2 p	1.625
N	1 s	6.700
N	2 s	1.950
N	2 p	1.950
Mg	1 s	11.70
Mg	2 s	3.925
Mg	2 p	3.925
Mg	3 s	0.950
Mg	3 p	0.950

TABLE VII
ORTHONORMALIZED REAL SLATER ORBITALS

$$H_{1s} = \chi_{100}^{(1.000)}$$

$$C_{2s} = 11.0252 \chi_{200}^{(1.625)} - 0.2260 \chi_{100}^{(5.700)}$$

$$C_{2p} = \chi_{21\ m}^{(1.625)}$$

$$N_{2s} = 1.0270 \chi_{200}^{(1.950)} - 0.2341 \chi_{100}^{(6.700)}$$

$$N_{2p} = \chi_{21\ m}^{(1.950)}$$

$$M_{g_{3s}} = 1.0067 \chi_{300}^{(0.950)} - 0.1209 \chi_{200}^{(3.925)} + 0.0322 \chi_{100}^{(11.70)}$$

$$M_{g_{3p}} = 1.0062 \chi_{31\ m}^{(0.950)} - 0.1103 \chi_{21\ m}^{(3.925)}$$

A basis set of symmetry orbitals was formed from the set of atomic orbitals by applying the projection operations given in Table IV, page 44, to the members of the atomic orbital basis set which are centered on nuclei in the basic domain. The basic domain of magnesium porphyrin consists of hydrogen atoms one and three, carbon atoms one, two, and three, nitrogen atom one, and the magnesium atom. A symmetry orbital is denoted by $\psi_{n\lambda}^{(j)}$, where n is an ordinal label and j and λ indicate the irreducible representation and the row to which the function belongs. The symmetry orbitals are given in Table VIII.

The symmetry orbital basis set was orthonormalized by diagonalizing the matrix of overlap integrals between members of the set. The overlap matrix is block-diagonal due to the orthogonality properties given in equation (23). In evaluating overlap integrals between functions belonging to one of the two-dimensional representations, only those functions belonging to a particular row of the representation need be considered since, according to equation (23), the overlap integral does not depend on the partner label. Hence the overlap matrix may be diagonalized by diagonalizing separately the ten smaller matrices each of which is obtained by calculating the overlap integrals between functions belonging to a particular irreducible representation.

$$S_{n'n}^{(j)} = (\psi_{n'\lambda}^{(j)}, \psi_{n\lambda}^{(j)}).$$

The elements of the matrices $S^{(j)}$ were evaluated using equations (27) and (24) and the programs described in Appendices A and C. The eigenvectors

TABLE VIII
SYMMETRY ORBITALS

Irreducible Representation	Orbital Number	k	Atomic Orbital
1 (A'_1)	1	1	H ₁ ;1s
	2	1	H ₃ ;1s
	3	1	C ₁ ;2s
	4	1	C ₁ ;2px
	5	1	C ₂ ;2s
	6	1	C ₂ ;2px
	7	1	C ₂ ;2py
	8	1	C ₃ ;2s
	9	1	C ₃ ;2px
	10	1	C ₃ ;2py
	11	1	N ₁ ;2s
	12	1	N ₁ ;2px
	13*		Mg ₃ s
2 (A'_2)	1	1	H ₃ ;1s
	2	1	C ₁ ;2py
	3	1	C ₂ ;2s
	4	1	C ₂ ;2px
	5	1	C ₂ ;2py
	6	1	C ₃ ;2s
	7	1	C ₃ ;2px
	8	1	C ₃ ;2py
	9	1	N ₁ ;2px
3 (B'_1)	1	1	H ₁ ;1s
	2	1	H ₃ ;1s

TABLE VIII (continued)

Irreducible Representation	Orbital Number	k	Atomic Orbital
	3	1	C ₁ ;2s
	4	1	C ₁ ;2px
	5	1	C ₂ ;2s
	6	1	C ₂ ;2px
	7	1	C ₂ ;2py
	8	1	C ₃ ;2s
	9	1	C ₃ ;2px
	10	1	C ₃ ;2py
	11	1	N ₁ ;2px
4 (B' ₂)	1	1	H ₃ ;1s
	2	1	C ₁ ;2py
	3	1	C ₂ ;2s
	4	1	C ₂ ;2px
	5	1	C ₂ ;2py
	6	1	C ₃ ;2s
	7	1	C ₃ ;2px
	8	1	C ₃ ;2py
	9	1	N ₁ ;2s
	10	1	N ₁ ;2px
5 (E')	1	1	H ₁ ;1s
	2	1	H ₃ ;1s
	3	2	H ₃ ;1s
	4	1	C ₁ ;2s
	5	1	C ₁ ;2px
	6	2	C ₁ ;2py
	7	1	C ₂ ;2s

TABLE VIII (continued)

Irreducible Representation	Orbital Number	k	Atomic Orbital
	8	2	C ₂ ;2s
	9	1	C ₂ ;2px
	10	2	C ₂ ;2px
	11	1	C ₂ ;2py
	12	2	C ₂ ;2py
	13	1	C ₃ ;2s
	14	2	C ₃ ;2s
	15	1	C ₃ ;2px
	16	2	C ₃ ;2px
	17	1	C ₃ ;2py
	18	2	C ₃ ;2py
	19	1	N ₁ ;2s
	20	1	N ₁ ;2px
	21	2	N ₁ ;2px
	22*		Mg _{2px} if $\lambda = 1$ Mg _{2py} if $\lambda = 2$
6 (A'' ₁)	1	1	C ₁ ;2pz
	2	1	C ₂ ;2pz
	3	1	C ₃ ;2pz
	4	1	N ₁ ;2pz
	5*		Mg _{2pz}
7 (A'' ₂)	1	1	C ₂ ;2pz
	2	1	C ₃ ;2pz

TABLE VIII (continued)

Irreducible Representation	Orbital Number	k	Atomic Orbital
8 (B''_1)	1	1	$C_{1;2pz}$
	2	1	$C_{2;2pz}$
	3	1	$C_{3;2pz}$
9 (B''_2)	1	1	$C_{2;2pz}$
	2	1	$C_{3;2pz}$
	3	1	$N_{1;2pz}$
10 (E'')	1	1	$C_{1;2pz}$
	2	1	$C_{2;2pz}$
	3	2	$C_{2;2pz}$
	4	1	$C_{3;2pz}$
	5	2	$C_{3;2pz}$
	6	1	$N_{1;2pz}$

NOTE: This table should be read as follows: The first symmetry orbital, belonging to row λ of irreducible representation E' , is obtained by operating with $p^{(5)}_{1\lambda}$ on the 1s atomic orbital centered on hydrogen atom number one.

*These symmetry orbitals do not involve projection operators, but are simply atomic orbitals on the magnesium atom.

and eigenvalues of the overlap matrices were calculated using the program SYMAS listed in Appendix C.

$$\sum_{n=1}^{N_j} S_{n'n}^{(j)} C_{np}^{(j)} = \sigma_p^{(j)} C_{n'p}^{(j)}.$$

In the equation above, N_j denotes the number of sets of partners in the symmetry orbital basis set belonging to irreducible representation j .

Then a set of orthonormalized functions was formed as follows.

$$\psi_{p\lambda}^{(j)} = \frac{1}{\sqrt{\sigma_p^{(j)}}} \sum_{n=1}^{N_j} C_{np}^{(j)} \psi_{n\lambda}^{(j)}. \quad (42)$$

III. SOLUTION FOR THE MOLECULAR ORBITALS

The final molecular orbitals were written as linear combinations of the functions defined in equation (42).

$$\varphi_{m\lambda}^{(j)} = \sum_{p=1}^{N_j} Q_{pm}^{(j)} \psi_{p\lambda}^{(j)}. \quad (43)$$

These functions must satisfy the Hartree-Fock equations.

$$F \varphi_{m\lambda}^{(j)} = E_m^{(j)} \varphi_{m\lambda}^{(j)}. \quad (44)$$

The operator F is the Hartree-Fock Hamiltonian defined by equations (10) and (11). Using equations (42), (43), and (44),

$$\sum_{p=1}^{N_j} F_{p'p}^{(j)} Q_{p'm}^{(j)} = E_m^{(j)} Q_{p'm}^{(j)}, \quad (45)$$

where,

$$\begin{aligned} F_{p'p}^{(j)} &= (\Psi_{p'\lambda}^{(j)}, F \Psi_{p\lambda}^{(j)}) \\ &= \frac{1}{\sqrt{\sigma_{p'}^{(j)}}} \cdot \frac{1}{\sqrt{\sigma_p^{(j)}}} \sum_{n'=1}^{N_j} \sum_{n=1}^{n_j} C_{n'p'}^{(j)} C_{np}^{(j)} (\Psi_{n'\lambda}^{(j)}, F \Psi_{n\lambda}^{(j)}). \end{aligned} \quad (46)$$

The coefficients $Q_{p'm}^{(j)}$ and the one-electron energies $E_m^{(j)}$ may be found by solving the eigenvalue equation (45). However, the operator F depends implicitly on the final molecular orbitals, and, therefore, an approximation method must be used to solve for the matrix elements $F_{p'p}^{(j)}$. The approximation used is described in the following paragraphs.

The symmetry orbitals $\Psi_{n'\lambda}^{(j)}$ and $\Psi_{n\lambda}^{(j)}$ are formed by applying projection operators to certain orthonormalized Slater orbitals centered on atoms in the basic domain.

$$\begin{aligned} \Psi_{n'\lambda}^{(j)} &= p_{k'\lambda}^{(j)} A_{r'q'} \\ \Psi_{n\lambda}^{(j)} &= p_{k\lambda}^{(j)} A_{rq} \end{aligned} \quad (47)$$

The notation A_{rq} denotes an atomic orbital of atomic species A (A may be H, C, N, or Mg) centered on the r th atom of the species, where the atoms are labeled as shown in Figure 4, page 37. The subscript q

stands for the atomic orbital quantum numbers n , ℓ , and m . The Hartree-Fock Hamiltonian F is a symmetric operator under D_{4h} and commutes with the projection operators. Therefore, the matrix elements of F which appear in equation (46) may be written as follows.

$$(\psi_{n'\lambda}^{(j)}, F \psi_{n\lambda}^{(j)}) = (p_{k'\lambda}^{(j)} A_{r'q'}, p_{k\lambda}^{(j)} F A_{rq}). \quad (48)$$

The orthonormalized Slater orbitals approximate the solutions of an atomic Hartree-Fock equation.

$$[T + v(A_{rq}) + c(A_{rq}) - a(A_{rq})] A_{rq} = \epsilon(A_{rq}) A_{rq}. \quad (49)$$

The kinetic energy term T is the same as in equation (11). The potential energy, Coulomb, and exchange terms are similar to those in equation (11) but involve the other atomic orbitals on the same center. The eigenvalue $\epsilon(A_{rq})$ is the one-electron energy of the atomic orbital A_{rq} . Using equations (10) and (49),

$$F A_{rq} = \epsilon(A_{rq}) A_{rq} + \left\{ V + C - A - [v(A_{rq}) + c(A_{rq}) - a(A_{rq})] \right\} A_{rq}. \quad (50)$$

The matrix element of F as written in equation (48) may be rewritten using equations (47) and (50).

$$\begin{aligned} & (\psi_{n'\lambda}^{(j)}, F \psi_{n\lambda}^{(j)}) = \epsilon_n^{(j)} (\psi_{n'\lambda}^{(j)}, \psi_{n\lambda}^{(j)}) \\ & + (\psi_{n'\lambda}^{(j)}, p_{k\lambda}^{(j)} \{V + C - A - [v(A_{rq}) + c(A_{rq}) - a(A_{rq})]\} A_{rq}). \end{aligned} \quad (51)$$

The one-electron energy $\epsilon(A_{rq})$ of the atomic orbital A_{rq} has been specified here by labeling it with n and j , the ordinal and irreducible representation labels of the symmetry orbital which is formed by projecting on A_{rq} . Since F is a Hermitian operator, and since the basis functions are all real,

$$\begin{aligned}
 (\Psi_{n'\lambda}^{(j)}, F \Psi_n^{(j)}) &= (\Psi_n^{(j)}, F \Psi_{n'\lambda}^{(j)}) \\
 &= \epsilon_{n'}^{(j)} (\Psi_{n'\lambda}^{(j)}, \Psi_n^{(j)}) \\
 &+ (\Psi_n^{(j)}, P_{k'\lambda}^{(j)} \{V + C - A - [v(A'_{r'q'}) \\
 &+ c(A'_{r'q'}) - a(A'_{r'q'})]\} A'_{r'q'}). \quad (52)
 \end{aligned}$$

Taking one-half the sum of equations (51) and (52),

$$(\Psi_{n'\lambda}^{(j)}, F \Psi_n^{(j)}) = \frac{1}{2} [\epsilon_n^{(j)} + \epsilon_{n'}^{(j)}] S_{n'n}^{(j)} + W_{n'n}^{(j)}, \quad (53)$$

where,

$$S_{n'n}^{(j)} = (\Psi_{n'\lambda}^{(j)}, \Psi_n^{(j)}), \quad (54)$$

and,

$$\begin{aligned}
 W_{n'n}^{(j)} &= \frac{1}{2} (\Psi_{n'\lambda}^{(j)}, P_{k'\lambda}^{(j)} \{V + C - A - [v(A_{rq}) + c(A_{rq}) - a(A_{rq})]\} A_{rq}) \\
 &+ \frac{1}{2} (\Psi_n^{(j)}, P_{k'\lambda}^{(j)} \{V + C - A - [v(A'_{r'q'}) + c(A'_{r'q'}) - a(A'_{r'q'})]\} A'_{r'q'}). \quad (55)
 \end{aligned}$$

When equation (53) is substituted in equation (46) the following expression is obtained.

$$F_{p'p}^{(j)} = F_{p'p}^{o(j)} + R_{p'p}^{(j)}, \quad (56)$$

where,

$$F_{p'p}^{o(j)} = \frac{1}{2} \cdot \frac{1}{\sqrt{\sigma_{p'}^{(j)}}} \frac{1}{\sqrt{\sigma_p^{(j)}}} \sum_{n'=1}^{N_j} \sum_{m=1}^{N_j} C_{n'p'}^{(j)} C_{np}^{(j)} [\epsilon_{n'}^{(j)} + \epsilon_n^{(j)}] S_{n'n}^{(j)}, \quad (57)$$

$$R_{p'p}^{(j)} = \frac{1}{\sqrt{\sigma_{p'}^{(j)}}} \frac{1}{\sqrt{\sigma_p^{(j)}}} \sum_{n'=1}^{N_j} \sum_{n=1}^{N_j} C_{n'p'}^{(j)} C_{np}^{(j)} W_{n'n}^{(j)}. \quad (58)$$

Using equation (56), equation (45) may be rewritten as follows.

$$\sum_{p=1}^{N_j} [F_{p'p}^{o(j)} + R_{p'p}^{(j)}] Q_{pm}^{(j)} = E_m^{(j)} Q_{p'm}^{(j)}. \quad (59)$$

In matrix notation,

$$[F^{o(j)} + R^{(j)}] Q_m^{(j)} = E_m^{(j)} Q_m^{(j)}. \quad (60)$$

The operators V, C, and A are symmetric operators under D_{4h} .

Using this property and equation (47) the first term on the right hand side of equation (55) may be written,

$$\frac{1}{2} (\Psi_{n'\lambda}^{(j)}, [V + C - A] \Psi_{n\lambda}^{(j)}) - \frac{1}{2} (\Psi_{n'\lambda}^{(j)}, P_k \lambda^{(j)} [v(A_{rq}) + c(A_{rq}) - a(A_{rq})] A_{rq}).$$

This term has the form of a difference between a matrix element of an operator which represents a part of the total energy of an electron which may be found in widely differing parts of the molecule and a sum of matrix elements of operators which represent the same part of the total energy of an electron when the electron is near certain atomic centers equally spaced around the molecule. The second term on the right hand side of equation (55) is of the same form. It is reasonable to expect, therefore, that the term $W_{n'n}^{(j)}$ in equation (53) would make an appreciably smaller contribution to the matrix element of F between the symmetry orbitals than would the first term on the right-hand side of equation (53). If this is the case, then $F_{p'p}^{o(j)}$ should be the dominant term in equation (56) and equation (59), and the eigenvalue equation (60) should be soluble by means of perturbation theory.

According to perturbation theory, the first approximation to the solutions of equation (60) is obtained by solving the following equation.

$$F^{o(j)} Q_m^{o(j)} = E_m^{o(j)} Q_m^{o(j)}. \quad (61)$$

From equations (42) and (43), the approximate molecular orbitals in terms of the symmetry orbitals are the following.

$$\varphi_{n\lambda}^{o(j)} = \sum_{n=1}^{N_j} B_{nm}^{(j)} \psi_{n\lambda}^{(j)}, \quad (62)$$

where,

$$B_{nm}^{(j)} = \sum_{p=1}^{N_j} \frac{1}{\sqrt{\sigma_p^{(j)}}} C_{np}^{(j)} Q_{pm}^{o(j)}. \quad (63)$$

The values used for the atomic one-electron energies were those calculated by Herman and Skillman (1960). These values are listed in Table IX. Using these values and equation (57), the matrix elements $F_{p'p}^{(j)}$ were calculated. Equation (61) was solved using the program SYMAS, and the coefficients $B_{nm}^{(j)}$ of equation (63) were calculated. These values are presented in Table X. The eigenvalues of equation (61) are given in Table XI, and shown in Figure 5.

The first-order correction to the eigenvalues would be given by

$$E_n^{(1)}(j) = Q_m^{(j)+} R^{(j)} Q_m^{(j)},$$

where $Q_m^{(j)+}$ is the Hermitian conjugate of $Q_m^{(j)}$. The first-order correction to the eigenvectors is

$$Q_m^{(1)}(j) = \sum_{\substack{n \\ (n \neq m)}} (E_m^{(0)}(j) - E_n^{(0)}(j))^{-1} Q_n^{(j)+} R^{(j)} Q_m^{(j)} Q_n^{(j)}.$$

IV. CALCULATION OF MATRIX ELEMENTS AND OSCILLATOR STRENGTHS

Using equation (40) and Table V, page 46, the following specific formulas are obtained.

$$\begin{aligned} \langle\langle n' (5) || f^{(5)} || n (1) \rangle\rangle &= (\varphi_{n'1}^{(5)}, x \varphi_n^{(1)}) \\ &= (\varphi_{n'2}^{(5)}, y \varphi_n^{(1)}) , \end{aligned}$$

TABLE IX
ATOMIC ONE ELECTRON ENERGIES

A_{rq}	$\epsilon(A_{rq})$
H_{1s}	-0.50000 a.u.
C_{2s}	-0.64475
C_{2p}	-0.33015
N_{2s}	-0.84795
N_{2p}	-0.42225
Mg_{3s}	-0.25255
Mg_{3p}	-0.09285

TABLE X

COEFFICIENTS OF SYMMETRY ORBITALS IN THE APPROXIMATE
MOLECULAR ORBITALS

j	m	n	$B_{nm}^{o(j)}$	j	m	n	$B_{nm}^{o(j)}$	j	m	n	$B_{nm}^{o(j)}$
1	1	1	0.0082	3	9	9	0.2300	5	11	2	0.0280
1	1	2	-0.0026	3	9	10	0.0340	5	11	3	0.0298
1	1	3	-0.0570	3	9	11	-0.0574	5	11	4	-0.5951
1	1	4	-0.0146	3	10	1	0.0485	5	11	5	0.0736
1	1	5	-0.0980	3	10	2	0.0840	5	11	6	0.0048
1	1	6	0.2531	3	10	3	-0.0239	5	11	7	1.0239
1	1	7	-0.0649	3	10	4	-0.2222	5	11	8	-0.0473
1	1	8	-0.0085	3	10	5	0.0306	5	11	9	0.1182
1	1	9	-0.0172	3	10	6	0.7978	5	11	10	0.0011
1	1	10	0.0288	3	10	7	0.3477	5	11	11	-0.0655
1	1	11	0.6759	3	10	8	-0.0478	5	11	12	-0.0100
1	1	12	0.0557	3	10	9	-0.3567	5	11	13	-0.6248
1	1	13	-0.2882	3	10	10	0.5671	5	11	14	0.1731
1	2	1	-0.1066	3	10	11	0.1682	5	11	15	0.0987
1	2	2	-0.1680	3	11	1	0.0022	5	11	16	-0.0904
1	2	3	-0.0712	3	11	2	-0.0158	5	11	17	0.1076
1	2	4	0.3863	3	11	3	0.0422	5	11	18	0.0416
1	2	5	0.3213	3	11	4	0.0161	5	11	19	-0.1598
1	2	6	0.0813	3	11	5	-0.1988	5	11	20	-0.0645
1	2	7	-0.0281	3	11	6	0.2367	5	11	21	0.0115
1	2	8	-0.0360	3	11	7	0.0988	5	11	22	-0.0411
1	2	9	0.4223	3	11	8	0.0608	5	12	1	-0.0805
1	2	10	0.4316	3	11	9	0.0108	5	12	2	0.1513
1	2	11	-0.0446	3	11	10	0.2147	5	12	3	0.1166
1	2	12	-0.0357	3	11	11	0.8285	5	12	4	-0.0596
1	2	13	0.3042	4	1	1	0.0449	5	12	5	0.3309
1	3	1	0.1071	4	1	2	0.4362	5	12	6	0.0438
1	3	2	-0.1627	4	1	3	-0.2640	5	12	7	0.0513
1	3	3	-0.5247	4	1	4	-0.8150	5	12	8	0.0720
1	3	4	0.0405	4	1	5	0.1185	5	12	9	0.0442
1	3	5	-0.1726	4	1	6	0.1284	5	12	10	-0.4160
1	3	6	0.0010	4	1	7	-0.1084	5	12	11	-0.3267
1	3	7	-0.3854	4	1	8	-0.3516	5	12	12	0.2609
1	3	8	0.6800	4	1	9	-0.1631	5	12	13	-0.0924
1	3	9	-0.0139	4	1	10	-0.1259	5	12	14	-0.0623
1	3	10	-0.1828	4	2	1	-0.3171	5	12	15	-0.3254
1	3	11	0.0249	4	2	2	-0.0589	5	12	16	-0.2601
1	3	12	0.0991	4	2	3	-0.1699	5	12	17	-0.1489

TABLE X (continued)

j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$
1	3	13	0.0733	4	2	4	-0.0946	5	12	18	0.2128
1	4	1	0.0063	4	2	5	-0.2556	5	12	19	-0.0934
1	4	2	0.0227	4	2	6	0.9173	5	12	20	0.0077
1	4	3	0.0391	4	2	7	0.0996	5	12	21	-0.1169
1	4	4	-0.0155	4	2	8	-0.1647	5	12	22	-0.1316
1	4	5	-0.1179	4	2	9	0.0022	5	13	1	-0.0790
1	4	6	-0.3033	4	2	10	0.0198	5	13	2	-0.2418
1	4	7	0.0600	4	3	1	-0.2319	5	13	3	-0.1559
1	4	8	0.0340	4	3	2	-0.3318	5	13	4	0.0353
1	4	9	-0.0360	4	3	3	0.1956	5	13	5	0.0848
1	4	10	-0.1188	4	3	4	-0.3518	5	13	6	-0.0148
1	4	11	-0.2262	4	3	5	-0.5045	5	13	7	0.4364
1	4	12	0.0634	4	3	6	0.2605	5	13	8	-0.0660
1	4	13	1.0801	4	3	7	0.3526	5	13	9	-0.1499
1	5	1	0.1425	4	3	8	-0.1546	5	13	10	-0.0734
1	5	2	0.2996	4	3	9	-0.0887	5	13	11	-0.0829
1	5	3	-0.2989	4	3	10	-0.0666	5	13	12	0.0927
1	5	4	-0.0777	4	4	1	0.8961	5	13	13	0.6104
1	5	5	-0.2894	4	4	2	-0.0837	5	13	14	0.2840
1	5	6	0.1584	4	4	3	0.0675	5	13	15	0.0861
1	5	7	-0.0138	4	4	4	-0.0085	5	13	16	0.1033
1	5	8	-0.5250	4	4	5	-0.1981	5	13	17	0.0519
1	5	9	-0.1783	4	4	6	-0.2524	5	13	18	-0.1435
1	5	10	0.0021	4	4	7	-0.2102	5	13	19	-0.1633
1	5	11	0.0890	4	4	8	-0.1228	5	13	20	-0.1273
1	5	12	0.1378	4	4	9	-0.0103	5	13	21	-0.0396
1	5	13	0.2167	4	4	10	0.0007	5	13	22	-0.1982
1	6	1	0.0446	4	5	1	0.0006	5	14	1	0.0002
1	6	2	0.1727	4	5	2	0.0791	5	14	2	-0.1243
1	6	3	-0.0495	4	5	3	0.1410	5	14	3	-0.0209
1	6	4	-0.1466	4	5	4	-0.3234	5	14	4	-0.0310
1	6	5	-0.0215	4	5	5	0.0769	5	14	5	0.0373
1	6	6	0.7599	4	5	6	0.0248	5	14	6	0.0299
1	6	7	0.2396	4	5	7	0.0219	5	14	7	-0.0353
1	6	8	-0.2697	4	5	8	-0.0334	5	14	8	-0.1555
1	6	9	-0.2606	4	5	9	-0.6549	5	14	9	-0.1306
1	6	10	0.3209	4	5	10	-0.1354	5	14	10	-0.3810
1	6	11	0.1035	4	6	1	-0.0931	5	14	11	-0.1921
1	6	12	0.1621	4	6	2	-0.2304	5	14	12	-0.5233
1	6	13	0.5138	4	6	3	1.1265	5	14	13	-0.0005

TABLE X (continued)

j	m	n	$B_{nm}^{o(j)}$	j	m	n	$B_{nm}^{o(j)}$	j	m	n	$B_{nm}^{o(j)}$
1	7	1	0.3441	4	6	4	0.1450	5	14	14	0.4070
1	7	2	0.6949	4	6	5	-0.0286	5	14	15	0.4214
1	7	3	-0.1570	4	6	6	-0.2510	5	14	16	-0.3745
1	7	4	-0.0750	4	6	7	0.1135	5	14	17	-0.4344
1	7	5	0.1339	4	6	8	0.1838	5	14	18	-0.1984
1	7	6	-0.0889	4	6	9	-0.1843	5	14	19	-0.0471
1	7	7	-0.0305	4	6	10	-0.0681	5	14	20	0.0409
1	7	8	-0.2268	4	7	1	-0.0010	5	14	21	-0.0150
1	7	9	-0.1260	4	7	2	-0.2077	5	14	22	-0.1280
1	7	10	-0.0679	4	7	3	0.0002	5	15	1	-0.0311
1	7	11	-0.0295	4	7	4	0.0644	5	15	2	-0.0929
1	7	12	-0.1205	4	7	5	0.3701	5	15	3	0.0039
1	7	13	-0.1615	4	7	6	0.0026	5	15	4	0.0093
1	8	1	-0.0209	4	7	7	0.1337	5	15	5	0.1245
1	8	2	-0.0003	4	7	8	-0.4064	5	15	6	0.1794
1	8	3	0.5544	4	7	9	0.0024	5	15	7	-0.0490
1	8	4	-0.0942	4	7	10	-0.0367	5	15	8	-0.0028
1	8	5	-1.1219	4	8	1	0.0425	5	15	9	-0.3513
1	8	6	-0.1114	4	8	2	-0.0600	5	15	10	0.2464
1	8	7	0.0640	4	8	3	0.3258	5	15	11	-0.1920
1	8	8	0.4071	4	8	4	-0.2978	5	15	12	0.6553
1	8	9	-0.0494	4	8	5	0.5899	5	15	13	0.0363
1	8	10	-0.1722	4	8	6	-0.2452	5	15	14	-0.0228
1	8	11	0.1797	4	8	7	0.1364	5	15	15	0.3838
1	8	12	0.0758	4	8	8	0.5076	5	15	16	-0.0244
1	8	13	0.0940	4	8	9	-0.1374	5	15	17	-0.5105
1	9	1	0.5888	4	8	10	-0.2091	5	15	18	0.3833
1	9	2	-0.5629	4	9	1	-0.2428	5	15	19	-0.0091
1	9	3	-0.1768	4	9	2	0.3656	5	15	20	-0.0712
1	9	4	-0.1891	4	9	3	-0.0495	5	15	21	0.0585
1	9	5	0.0331	4	9	4	-0.0366	5	15	22	-0.0684
1	9	6	0.0036	4	9	5	0.4630	5	16	1	-0.0597
1	9	7	0.1956	4	9	6	0.0507	5	16	2	0.0497
1	9	8	0.1217	4	9	7	0.6959	5	16	3	-0.1983
1	9	9	0.1549	4	9	8	0.1642	5	16	4	0.0244
1	9	10	0.1044	4	9	9	0.0091	5	16	5	0.1064
1	9	11	-0.0065	4	9	10	0.0074	5	16	6	0.3085
1	9	12	-0.0316	4	10	1	0.0048	5	16	7	-0.0197
1	9	13	-0.0285	4	10	2	-0.0728	5	16	8	-0.0346
1	10	1	-0.0118	4	10	3	-0.1234	5	16	9	0.3214

TABLE X (continued)

j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$
1	10	2	-0.0354	4	10	4	0.0653	5	16	10	-0.2673
1	10	3	-0.0284	4	10	5	-0.1135	5	16	11	0.1794
1	10	4	-0.0337	4	10	6	0.0146	5	16	12	0.1452
1	10	5	0.1346	4	10	7	0.0105	5	16	13	-0.0563
1	10	6	-0.0731	4	10	8	0.0188	5	16	14	0.0860
1	10	7	0.0609	4	10	9	0.0418	5	16	15	-0.0882
1	10	8	0.0051	4	10	10	0.7715	5	16	16	0.5503
1	10	9	-0.0451	5	1	1	0.4124	5	16	17	-0.1633
1	10	10	-0.0491	5	1	2	-0.7445	5	16	18	0.2040
1	10	11	-0.0409	5	1	3	0.4498	5	16	19	0.0246
1	10	12	-0.7729	5	1	4	-0.1133	5	16	20	0.0788
1	10	13	-0.1829	5	1	5	-0.1331	5	16	21	-0.0695
1	11	1	0.0507	5	1	6	-0.0150	5	16	22	0.0710
1	11	2	-0.0542	5	1	7	-0.0105	5	17	1	-0.3108
1	11	3	-0.2672	5	1	8	0.0333	5	17	2	-0.6085
1	11	4	0.1207	5	1	9	-0.0045	5	17	3	-0.4472
1	11	5	-0.0874	5	1	10	0.0067	5	17	4	0.1389
1	11	6	0.2837	5	1	11	0.1404	5	17	5	0.0784
1	11	7	-0.8581	5	1	12	-0.0307	5	17	6	0.0336
1	11	8	0.2424	5	1	13	0.2504	5	17	7	-0.0936
1	11	9	-0.1225	5	1	14	-0.1916	5	17	8	-0.0395
1	11	10	-0.3256	5	1	15	0.2578	5	17	9	0.0865
1	11	11	0.0800	5	1	16	-0.1759	5	17	10	0.0406
1	11	12	0.2045	5	1	17	0.0440	5	17	11	0.0183
1	11	13	0.2097	5	1	18	0.0131	5	17	12	0.1040
1	12	1	0.1038	5	1	19	-0.0050	5	17	13	0.2070
1	12	2	0.0650	5	1	20	-0.0085	5	17	14	0.1139
1	12	3	-0.0929	5	1	21	-0.0139	5	17	15	0.1433
1	12	4	-0.1502	5	1	22	-0.0121	5	17	16	0.0853
1	12	5	0.1098	5	2	1	0.4522	5	17	17	0.0387
1	12	6	-0.1742	5	2	2	0.0827	5	17	18	0.0960
1	12	7	-0.2887	5	2	3	-0.7261	5	17	19	0.0424
1	12	8	-0.0581	5	2	4	-0.1560	5	17	20	0.0836
1	12	9	-0.2535	5	2	5	-0.1398	5	17	21	0.0966
1	12	10	0.4109	5	2	6	0.0397	5	17	22	0.1397
1	12	11	-0.0415	5	2	7	0.0729	5	18	1	-0.1429
1	12	12	-0.0362	5	2	8	-0.0541	5	18	2	0.1086
1	12	13	-0.1779	5	2	9	-0.0169	5	18	3	0.0205
1	13	1	-0.1468	5	2	10	0.0019	5	18	4	0.0952
1	13	2	0.2290	5	2	11	0.1227	5	18	5	0.3374

TABLE X (continued)

j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$
1	13	3	0.0051	5	2	12	0.0913	5	18	6	-0.2035
1	13	4	0.4723	5	2	13	-0.1098	5	18	7	-0.0375
1	13	5	0.0427	5	2	14	0.2602	5	18	8	-0.0244
1	13	6	-0.1325	5	2	15	-0.0642	5	18	9	-0.2377
1	13	7	-0.2577	5	2	16	0.2365	5	18	10	0.4964
1	13	8	-0.0766	5	2	17	0.0928	5	18	11	0.0632
1	13	9	-0.5679	5	2	18	0.0177	5	18	12	-0.4173
1	13	10	-0.1212	5	2	19	-0.0091	5	18	13	0.0002
1	13	11	-0.0232	5	2	20	-0.0419	5	18	14	0.0272
1	13	12	-0.0447	5	2	21	-0.0098	5	18	15	-0.2809
1	13	13	-0.0839	5	2	22	-0.0310	5	18	16	-0.1143
2	1	1	1.0255	5	3	1	0.0542	5	18	17	-0.2599
2	1	2	-0.0402	5	3	2	0.0009	5	18	18	-0.1113
2	1	3	0.0778	5	3	3	-0.0757	5	18	19	0.0594
2	1	4	0.0058	5	3	4	-0.2524	5	18	20	-0.0405
2	1	5	-0.0883	5	3	5	0.0968	5	18	21	0.0885
2	1	6	-0.4126	5	3	6	-0.1953	5	18	22	0.1212
2	1	7	-0.3771	5	3	7	-0.0716	5	19	1	-0.1031
2	1	8	0.0141	5	3	8	0.1146	5	19	2	-0.1677
2	1	9	-0.0161	5	3	9	0.3402	5	19	3	0.0052
2	2	1	-0.1221	5	3	10	0.2727	5	19	4	-0.0776
2	2	2	-0.1907	5	3	11	-0.7854	5	19	5	0.3791
2	2	3	0.8328	5	3	12	-0.0905	5	19	6	0.0027
2	2	4	0.0315	5	3	13	0.2210	5	19	7	0.3432
2	2	5	-0.1234	5	3	14	-0.0423	5	19	8	-0.0250
2	2	6	0.5601	5	3	15	-0.2747	5	19	9	0.1423
2	2	7	-0.0684	5	3	16	0.2124	5	19	10	0.0569
2	2	8	0.2835	5	3	17	-0.1958	5	19	11	-0.0373
2	2	9	-0.1458	5	3	18	0.0420	5	19	12	-0.0500
2	3	1	0.0427	5	3	19	0.1495	5	19	13	-0.0497
2	3	2	-0.0891	5	3	20	0.1529	5	19	14	0.0120
2	3	3	0.8077	5	3	21	0.0774	5	19	15	0.4722
2	3	4	0.0967	5	3	22	0.1144	5	19	16	-0.0746
2	3	5	0.1716	5	4	1	0.0028	5	19	17	0.5066
2	3	6	-1.2120	5	4	2	-0.0079	5	19	18	-0.0672
2	3	7	0.2905	5	4	3	-0.0054	5	19	19	-0.0030
2	3	8	0.0120	5	4	4	0.0198	5	19	20	-0.0733
2	3	9	-0.0590	5	4	5	-0.0161	5	19	21	0.0375
2	4	1	-0.0878	5	4	6	-0.0472	5	19	22	0.1863
2	4	2	0.0843	5	4	7	0.1271	5	20	1	0.0031

TABLE X (continued)

j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$
2	4	3	-0.0398	5	4	8	0.0659	5	20	2	0.0005
2	4	4	0.6532	5	4	9	0.0242	5	20	3	0.0161
2	4	5	-0.3305	5	4	10	0.0866	5	20	4	0.0374
2	4	6	0.0701	5	4	11	-0.0342	5	20	5	0.0217
2	4	7	0.0979	5	4	12	-0.0236	5	20	6	0.0272
2	4	8	0.3985	5	4	13	0.0025	5	20	7	-0.1685
2	4	9	0.1526	5	4	14	-0.0024	5	20	8	0.0520
2	5	1	0.0253	5	4	15	0.0148	5	20	9	0.1616
2	5	2	0.4433	5	4	16	0.0051	5	20	10	-0.1304
2	5	3	-0.3499	5	4	17	0.0370	5	20	11	0.0318
2	5	4	-0.0987	5	4	18	0.0205	5	20	12	-0.0720
2	5	5	0.3225	5	4	19	0.3132	5	20	13	0.0356
2	5	6	-0.2634	5	4	20	-0.0635	5	20	14	-0.0311
2	5	7	0.3021	5	4	21	-0.1443	5	20	15	0.0223
2	5	8	-0.6568	5	4	22	-1.3278	5	20	16	0.0126
2	5	9	0.1427	5	5	1	-0.0074	5	20	17	0.1420
2	6	1	-0.0143	5	5	2	0.0041	5	20	18	-0.1035
2	6	2	-0.1139	5	5	3	0.0031	5	20	19	0.0310
2	6	3	-0.1570	5	5	4	0.0128	5	20	20	0.7875
2	6	4	0.2910	5	5	5	0.0166	5	20	21	-0.2145
2	6	5	0.0054	5	5	6	0.0529	5	20	22	0.0216
2	6	6	0.0548	5	5	7	-0.0190	5	21	1	-0.0251
2	6	7	0.0004	5	5	8	0.0110	5	21	2	-0.0301
2	6	8	0.1492	5	5	9	-0.1360	5	21	3	0.0225
2	6	9	0.8430	5	5	10	-0.1781	5	21	4	0.0265
2	7	1	-0.1583	5	5	11	0.0532	5	21	5	-0.0044
2	7	2	-0.2404	5	5	12	0.0438	5	21	6	-0.2263
2	7	3	0.3269	5	5	13	-0.0056	5	21	7	-0.0258
2	7	4	0.2734	5	5	14	0.0071	5	21	8	0.0118
2	7	5	0.3991	5	5	15	0.0071	5	21	9	0.3158
2	7	6	-0.3835	5	5	16	0.0089	5	21	10	-0.1407
2	7	7	0.8921	5	5	17	-0.0212	5	21	11	0.2173
2	7	8	0.1312	5	5	18	-0.0224	5	21	12	0.1614
2	7	9	-0.0282	5	5	19	-0.9633	5	21	13	0.0297
2	8	1	-0.0000	5	5	20	-0.0196	5	21	14	-0.0194
2	8	2	0.4256	5	5	21	0.0317	5	21	15	0.0887
2	8	3	0.0000	5	5	22	0.4311	5	21	16	0.0747
2	8	4	-0.1009	5	6	1	-0.0086	5	21	17	0.0404
2	8	5	0.8378	5	6	2	0.0104	5	21	18	-0.5206
2	8	6	0.0000	5	6	3	0.0213	5	21	19	0.0227

TABLE X (continued)

j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$
2	8	7	-0.0800	5	6	4	-0.0555	5	21	20	0.0477
2	8	8	0.7721	5	6	5	0.1093	5	21	21	-0.0823
2	8	9	-0.0000	5	6	6	0.4196	5	21	22	0.0788
2	9	1	-0.1940	5	6	7	0.0203	5	22	1	0.0208
2	9	2	0.2404	5	6	8	-0.3437	5	22	2	0.0559
2	9	3	-0.0242	5	6	9	-0.1554	5	22	3	0.0219
2	9	4	-0.6708	5	6	10	-0.2634	5	22	4	-0.0009
2	9	5	-0.1938	5	6	11	-0.3278	5	22	5	0.0213
2	9	6	0.1129	5	6	12	0.1725	5	22	6	-0.1260
2	9	7	0.5561	5	6	13	0.2680	5	22	7	0.0243
2	9	8	0.0252	5	6	14	-0.0961	5	22	8	-0.1227
2	9	9	-0.1453	5	6	15	-0.3205	5	22	9	-0.0014
3	1	1	-0.1002	5	6	16	0.1506	5	22	10	0.2289
3	1	2	-0.1422	5	6	17	0.1522	5	22	11	-0.0185
3	1	3	0.0618	5	6	18	-0.5780	5	22	12	-0.1225
3	1	4	0.0961	5	6	19	-0.0227	5	22	13	-0.0462
3	1	5	0.5150	5	6	20	-0.0687	5	22	14	0.0221
3	1	6	-0.1046	5	6	21	0.0833	5	22	15	0.0128
3	1	7	-0.0173	5	6	22	-0.1463	5	22	16	0.0170
3	1	8	0.8022	5	7	1	-0.0062	5	22	17	0.0058
3	1	9	-0.1040	5	7	2	0.0077	5	22	18	0.0403
3	1	10	0.2889	5	7	3	0.1641	5	22	19	0.0637
3	1	11	-0.1564	5	7	4	-0.0593	5	22	20	0.1598
3	2	1	0.1034	5	7	5	0.0250	5	22	21	0.8096
3	2	2	0.0309	5	7	6	0.1848	5	22	22	0.2373
3	2	3	-0.0771	5	7	7	0.1241	6	1	1	0.0212
3	2	4	-0.2363	5	7	8	-0.7622	6	1	2	-0.0812
3	2	5	-0.2254	5	7	9	-0.0027	6	1	3	0.0107
3	2	6	0.2916	5	7	10	-0.0185	6	1	4	0.5239
3	2	7	-0.1951	5	7	11	-0.0300	6	1	5	-0.1347
3	2	8	-0.2166	5	7	12	0.1400	6	2	1	-0.3123
3	2	9	0.2377	5	7	13	0.3222	6	2	2	0.7426
3	2	10	-0.7844	5	7	14	-0.5288	6	2	3	-0.1256
3	2	11	0.1879	5	7	15	-0.1155	6	2	4	-0.0710
3	3	1	-0.4043	5	7	16	0.0085	6	2	5	-0.0521
3	3	2	0.8904	5	7	17	0.1486	6	3	1	-0.0884
3	3	3	0.1063	5	7	18	-0.1915	6	3	2	-0.0826
3	3	4	0.1302	5	7	19	0.1373	6	3	3	0.6389
3	3	5	0.0218	5	7	20	-0.0548	6	3	4	-0.0000
3	3	6	0.0071	5	7	21	0.1235	6	3	5	-0.0000

TABLE X (continued)

j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$
3	3	7	-0.1418	5	7	22	0.0543	6	4	1	0.0111
3	3	8	-0.3203	5	8	1	0.1347	6	4	2	0.0269
3	3	9	-0.3218	5	8	2	-0.0547	6	4	3	0.0007
3	3	10	-0.0335	5	8	3	-0.0654	6	4	4	0.0662
3	3	11	0.0023	5	8	4	-0.5521	6	4	5	-1.0336
3	4	1	-0.0522	5	8	5	0.0130	6	5	1	-0.4219
3	4	2	-0.0833	5	8	6	-0.0047	6	5	2	-0.2048
3	4	3	0.2297	5	8	7	-0.3297	6	5	3	-0.0831
3	4	4	-0.1223	5	8	8	-0.0669	6	5	4	0.0342
3	4	5	0.0704	5	8	9	0.0856	6	5	5	0.0545
3	4	6	-0.0985	5	8	10	-0.0143	7	1	1	0.4682
3	4	7	0.8704	5	8	11	-0.3649	7	1	2	0.5178
3	4	8	-0.4046	5	8	12	-0.0367	7	2	1	-0.5943
3	4	9	0.7041	5	8	13	0.5713	7	2	2	0.6572
3	4	10	-0.0069	5	8	14	0.0749	8	1	1	0.4592
3	4	11	-0.0231	5	8	15	-0.1136	8	1	2	0.1116
3	5	1	0.0386	5	8	16	0.0606	8	1	3	-0.2222
3	5	2	-0.0081	5	8	17	-0.1438	8	2	1	-0.2550
3	5	3	-0.5711	5	8	18	-0.0578	8	2	2	0.5803
3	5	4	0.0778	5	8	19	0.1144	8	2	3	-0.6438
3	5	5	1.0346	5	8	20	0.1222	8	3	1	-0.0921
3	5	6	0.1073	5	8	21	0.0650	8	3	2	0.5115
3	5	7	-0.0506	5	8	22	0.1388	8	3	3	0.4856
3	5	8	-0.7238	5	9	1	-0.0449	9	1	1	-0.0991
3	5	9	0.1754	5	9	2	-0.0647	9	1	2	0.0105
3	5	10	0.0752	5	9	3	-0.1818	9	1	3	0.5152
3	5	11	-0.0852	5	9	4	0.0485	9	2	1	-0.7377
3	6	1	-0.0711	5	9	5	0.1295	9	2	2	0.0782
3	6	2	-0.1487	5	9	6	-0.2233	9	2	3	0.0692
3	6	3	-0.1672	5	9	7	0.0301	9	3	1	0.1045
3	6	4	0.3702	5	9	8	0.2441	9	3	2	-0.6517
3	6	5	0.2786	5	9	9	-0.5364	9	3	3	-0.0000
3	6	6	0.3712	5	9	10	-0.2369	10	1	1	0.0117
3	6	7	-0.3288	5	9	11	-0.1019	10	1	2	-0.0750
3	6	8	-0.1219	5	9	12	-0.0098	10	1	3	-0.0699
3	6	9	0.5723	5	9	13	0.2290	10	1	4	0.0081
3	6	10	0.1764	5	9	14	-0.0327	10	1	5	0.0074
3	6	11	0.0035	5	9	15	-0.0794	10	1	6	0.7274
3	7	1	-0.1667	5	9	16	0.5745	10	2	1	-0.0857
3	7	2	0.1863	5	9	17	-0.0044	10	2	2	0.5470

TABLE X (continued)

j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$	j	m	n	$B_{nm}^{(j)}$
3	7	3	0.0644	5	9	18	-0.0168	10	2	3	0.5100
3	7	4	0.4206	5	9	19	-0.1854	10	2	4	-0.0589
3	7	5	-0.0407	5	9	20	-0.1104	10	2	5	-0.0542
3	7	6	0.0114	5	9	21	-0.0932	10	2	6	-0.0997
3	7	7	0.0122	5	9	22	-0.1568	10	3	1	0.4582
3	7	8	-0.0761	5	10	1	-0.0048	10	3	2	-0.4005
3	7	9	-0.4540	5	10	2	0.0014	10	3	3	0.3287
3	7	10	-0.4360	5	10	3	-0.0638	10	3	4	0.1714
3	7	11	0.0489	5	10	4	0.1193	10	3	5	-0.1429
3	8	1	-0.5497	5	10	5	-0.0297	10	3	6	0.0000
3	8	2	-0.5117	5	10	6	0.1085	10	4	1	-0.1103
3	8	3	0.2069	5	10	7	-0.1847	10	4	2	-0.1275
3	8	4	0.1562	5	10	8	-0.8677	10	4	3	0.2837
3	8	5	-0.1382	5	10	9	-0.0022	10	4	4	-0.3861
3	8	6	0.0495	5	10	10	-0.1075	10	4	5	-0.4196
3	8	7	-0.1176	5	10	11	0.0747	10	4	6	-0.0000
3	8	8	0.2654	5	10	12	-0.1475	10	5	1	-0.1519
3	8	9	0.1886	5	10	13	-0.3865	10	5	2	-0.3234
3	8	10	-0.1032	5	10	14	0.9736	10	5	3	0.3015
3	8	11	0.0637	5	10	15	0.1353	10	5	4	-0.0069
3	9	1	-0.1403	5	10	16	-0.1827	10	5	5	0.4153
3	9	2	0.0191	5	10	17	-0.1200	10	5	6	-0.0000
3	9	3	0.5934	5	10	18	-0.0926	10	6	1	0.1770
3	9	4	-0.0213	5	10	19	0.1839	10	6	2	0.1453
3	9	5	0.1903	5	10	20	0.0301	10	6	3	-0.1558
3	9	6	-0.0809	5	10	21	0.0777	10	6	4	-0.6191
3	9	7	0.3900	5	10	22	0.0707	10	6	5	0.4399
3	9	8	-0.7830	5	11	1	0.0507	10	6	6	-0.0000

TABLE XI
ONE-ELECTRON ENERGIES

j	n	$E_n^{(j)}$	j	n	$E_n^{(j)}$	j	n	$E_n^{(j)}$
1	1	-0.96884	3	7	-0.31463	5	14	-0.25722
1	2	-0.28640	3	8	-0.50305	5	15	-0.32454
1	3	-0.73757	3	9	-0.72993	5	16	-0.31924
1	4	-0.15827	3	10	-0.32219	5	17	-0.49918
1	5	-0.70036	3	11	-0.41945	5	18	-0.31616
1	6	-0.27396	4	1	-0.23496	5	19	-0.28672
1	7	-0.49404	4	2	-0.71610	5	20	-0.41951
1	8	-0.68277	4	3	-0.27077	5	21	-0.32902
1	9	-0.50971	4	4	-0.50075	5	22	-0.43496
1	10	-0.42291	4	5	-0.93466	6	1	-0.42972
1	11	-0.24020	4	6	-0.70668	6	2	-0.32925
1	12	-0.32205	4	7	-0.32990	6	3	-0.33015
1	13	-0.31065	4	8	-0.28029	6	4	-0.08587
2	1	-0.50983	4	9	-0.31551	6	5	-0.33056
2	2	-0.72639	4	10	-0.42082	7	1	-0.33015
2	3	-0.70333	5	1	-0.51118	7	2	-0.33015
2	4	-0.32580	5	2	-0.50705	8	1	-0.33015
2	5	-0.25538	5	3	-0.24128	8	2	-0.33015
2	6	-0.42290	5	4	+0.06101	8	3	-0.33015
2	7	-0.26870	5	5	-1.00991	9	1	-0.42394
2	8	-0.33015	5	6	-0.25570	9	2	-0.32846
2	9	-0.32000	5	7	-0.72224	9	3	-0.33015
3	1	-0.71076	5	8	-0.73803	10	1	-0.42401
3	2	-0.27563	5	9	-0.27519	10	2	-0.32839
3	3	-0.51159	5	10	-0.70683	10	3	-0.33015
3	4	-0.24944	5	11	-0.68325	10	4	-0.33015
3	5	-0.68243	5	12	-0.30781	10	5	-0.33015
3	6	-0.28816	5	13	-0.71650	10	6	-0.33015

FIGURE 5

ENERGY EIGENVALUES OF MOLECULAR ORBITALS

$$\langle\langle n' (5) || f^{(5)} || n (2) \rangle\rangle = (\varphi_{n'1}^{(5)}, (-y) \varphi_n^{(2)})$$

$$= (\varphi_{n'2}^{(5)}, x \varphi_n^{(2)})$$

$$\langle\langle n' (5) || f^{(5)} || n (3) \rangle\rangle = (\varphi_{n'1}^{(5)}, x \varphi_n^{(3)})$$

$$= (\varphi_{n'2}^{(5)}, (-y) \varphi_n^{(3)})$$

$$\langle\langle n' (5) || f^{(5)} || n (4) \rangle\rangle = (\varphi_{n'1}^{(5)}, y \varphi_n^{(4)})$$

$$= (\varphi_{n'2}^{(5)}, x \varphi_n^{(4)})$$

$$\langle\langle n' (10) || f^{(5)} || n (6) \rangle\rangle = (\varphi_{n'1}^{(10)}, x \varphi_n^{(6)})$$

$$= (\varphi_{n'2}^{(10)}, y \varphi_n^{(6)})$$

$$\langle\langle n' (10) || f^{(5)} || n (7) \rangle\rangle = (\varphi_{n'1}^{(10)}, (-y) \varphi_n^{(7)})$$

$$= (\varphi_{n'2}^{(10)}, x \varphi_n^{(7)})$$

$$\langle\langle n' (10) || f^{(5)} || n (8) \rangle\rangle = (\varphi_{n'1}^{(10)}, x \varphi_n^{(8)})$$

$$= (\varphi_{n'2}^{(10)}, (-y) \varphi_n^{(8)})$$

$$\begin{aligned} \langle\langle n' (10) || f^{(5)} || n (9) \rangle\rangle &= (\varphi_{n'1}^{(10)}, y \varphi_{n1}^{(9)}) \\ &= (\varphi_{n'2}^{(10)}, x \varphi_{n1}^{(9)}) . \end{aligned}$$

$$\langle\langle n' (1) || f^{(6)} || n (6) \rangle\rangle = (\varphi_{n'1}^{(1)}, z \varphi_{n1}^{(6)}) .$$

$$\langle\langle n' (2) || f^{(6)} || n (7) \rangle\rangle = (\varphi_{n'1}^{(2)}, z \varphi_{n1}^{(7)}) .$$

$$\langle\langle n' (3) || f^{(6)} || n (8) \rangle\rangle = (\varphi_{n'1}^{(3)}, z \varphi_{n1}^{(8)}) .$$

$$\langle\langle n' (4) || f^{(6)} || n (9) \rangle\rangle = (\varphi_{n'1}^{(4)}, z \varphi_{n1}^{(9)}) .$$

$$\langle\langle n' (5) || f^{(6)} || n (10) \rangle\rangle = (\varphi_{n'\mu}^{(5)}, z \varphi_{n\mu}^{(10)}) ; \mu = 1, 2 .$$

These are the only nonvanishing matrix elements of x , y , and z .

Using the formulas above and the programs described in Appendices B and C, the reduced matrix elements between the molecular orbitals, given by equations (62), were calculated. The results are presented in Table XII.

After calculating the matrix elements, oscillator strengths for the allowed transitions were calculated using the following formula.

$$f_{n_1(j_1); n_2(j_2)}^{(j)} = 2 \left(E_{n_1}^{(j_1)} - E_{n_2}^{(j_2)} \right) |\langle\langle n_1(j_1) || f^{(j)} || n_2(j_2) \rangle\rangle|^2 . \quad (64)$$

TABLE XII

REDUCED MATRIX ELEMENTS $\langle\langle(j')n' || f^{(J)} || (j)n\rangle\rangle$

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
j' = 1	1	1	0.1842	2	1	0.5425	3	1	0.0926
J = 6		2	-0.1682		2	0.1299		2	0.1196
j = 6		3	-0.0320		3	0.0262		3	0.6816
		4	0.4721		4	-0.4780		4	-0.1193
		5	0.3302		5	-0.2722		5	0.4146
	4	1	2.0641	5	1	0.3303	6	1	0.7999
		2	1.0725		2	-0.0269		2	0.4270
		3	0.1159		3	-0.4504		3	0.2288
		4	-1.6929		4	-0.3467		4	-0.7886
		5	-1.2515		5	0.4575		5	-0.6516
	7	1	-0.2532	8	1	0.1628	9	1	-0.0416
		2	-0.0780		2	-0.6561		2	-0.0395
		3	0.1753		3	0.1553		3	-0.1012
		4	0.2413		4	-0.1478		4	0.0439
		5	-0.0410		5	-0.1720		5	-0.0527
	10	1	-0.3071	11	1	0.3023	12	1	-0.2774
		2	-0.1849		2	0.1244		2	-0.1813
		3	-0.0284		3	-0.1533		3	-0.0032
		4	0.2285		4	-0.3299		4	0.2612
		5	0.2813		5	-0.3965		5	0.1583
	13	1	-0.1231						
		2	-0.0814						
		3	0.0063						
		4	0.1368						
		5	0.0623						
.....									
j' = 2	1	1	0.0850	2	1	0.8280	3	1	-0.1468
J = 6		2	0.0124		2	-0.1693		2	-0.7367
j = 7	4	1	-0.0278	5	1	0.2397	6	1	0.0161
		2	-0.0043		2	-0.0294		2	-0.0025
	7	1	0.0143	8	1	0.0058	9	1	0.0004
		2	0.1877		2	-0.0000		2	-0.0298
.....									
j' = 3	1	1	-0.1780	2	1	0.1924	3	1	-0.0092
J = 6		2	-0.6009		2	0.3030		2	-0.1642
j = 8		3	0.8086		3	0.1362		3	0.1850

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
	4	1	-0.0225	5	1	0.0449	6	1	0.1578
		2	0.2781		2	0.2306		2	0.5562
		3	-0.6663		3	-0.2700		3	-0.2496
	7	1	0.0498	8	1	0.0958	9	1	-0.0300
		2	0.0098		2	0.3963		2	0.0903
		3	0.1952		3	-0.1503		3	-0.2978
	10	1	-0.0488	11	1	0.1168			
		2	0.0687		2	0.2195			
		3	-0.4601		3	-0.1852			
.....									
j' = 4	1	1	0.1695	2	1	0.0145	3	1	0.0661
J = 6		2	-0.2307		2	-0.0942		2	0.1128
j = 9		3	0.0361		3	-0.8329		3	0.2030
	4	1	0.0098	5	1	-0.6723	6	1	0.0101
		2	-0.0921		2	0.0533		2	-0.8207
		3	-0.2200		3	-0.0257		3	0.0317
	7	1	-0.0024	8	1	0.1122	9	1	-0.0023
		2	0.0044		2	0.0345		2	-0.0231
		3	0.0005		3	-0.1377		3	-0.0103
	10	1	-0.0460						
		2	0.0072						
		3	0.0173						
.....									
j' = 5	1	1	-0.0128	2	1	-0.0363	3	1	0.0499
J = 6		2	0.0008		2	-0.0290		2	0.0453
j = 10		3	0.0438		3	0.0389		3	0.1119
		4	0.0190		4	0.0299		4	-0.0652
		5	-0.0007		5	-0.1298		5	-0.1924
		6	0.0604		6	0.0106		6	0.1838
	4	1	-1.7876	5	1	-0.1460	6	1	-0.1560
		2	-1.3428		2	0.2387		2	-0.0227
		3	-0.2733		3	0.0776		3	0.0514
		4	0.6379		4	-0.1648		4	0.1643
		5	0.5250		5	-0.1376		5	0.1782
		6	-0.2974		6	0.0840		6	0.0780
	7	1	0.0841	8	1	0.1906	9	1	-0.0948
		2	-0.3253		2	-0.1079		2	-0.2220
		3	-0.2462		3	-0.3356		3	-0.1193
		4	-0.0646		4	-0.1060		4	0.1742
		5	-0.6869		5	0.4518		5	0.0316

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
	10	6	-0.2356		6	-0.4845		6	0.0425
		1	0.1100	11	1	-0.0727	12	1	-0.1104
		2	-0.3814		2	0.3228		2	-0.0982
		3	-0.1734		3	-0.6054		3	0.0271
		4	-0.3634		4	0.1555		4	-0.0046
		5	0.1303		5	-0.0435		5	0.0385
		6	0.4887		6	0.1803		6	-0.0164
	13	1	-0.2816	14	1	-0.1263	15	1	-0.0782
		2	0.1927		2	-0.0820		2	-0.0387
		3	-0.0150		3	0.0235		3	-0.0196
		4	-0.6631		4	0.2104		4	0.0074
		5	-0.0229		5	-0.0889		5	0.0126
		6	-0.1966		6	-0.0909		6	-0.0024
	16	1	0.0806	17	1	0.1669	18	1	0.1183
		2	0.0857		2	0.0288		2	0.0900
		3	0.0212		3	-0.0423		3	-0.0206
		4	-0.0397		4	0.1551		4	-0.0231
		5	-0.0274		5	-0.0708		5	-0.0502
		6	-0.0041		6	0.0437		6	0.0162
	19	1	0.2280	20	1	0.0092	21	1	0.0877
		2	0.0634		2	0.0425		2	0.0706
		3	0.1078		3	0.0107		3	0.0062
		4	-0.0397		4	-0.0349		4	-0.0289
		5	0.0012		5	-0.0400		5	-0.0178
		6	0.0183		6	0.0072		6	0.0222
	22	1	0.2851						
		2	0.2651						
		3	0.0790						
		4	-0.1507						
		5	-0.1099						
		6	0.0645						
.....									
j' = 5	1	1	-0.0824	2	1	-0.0105	3	1	0.3721
j = 5		2	0.0672		2	-0.4497		2	0.3785
j = 1		3	0.0472		3	-0.1541		3	-0.0945
		4	-0.0191		4	0.0228		4	-0.6932
		5	-0.0734		5	-0.0077		5	-0.0620
		6	-0.1734		6	0.1485		6	0.2223
		7	-0.5166		7	0.7501		7	-0.0196
		8	0.0857		8	0.1203		8	-0.1618

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
		9	4.7226	9	5.2604	9	0.4103		
		10	0.0342	10	-0.0734	10	0.3660		
		11	-0.0659	11	0.1161	11	3.3634		
		12	-0.0292	12	0.3963	12	-0.0565		
		13	-0.9405	13	-0.6017	13	-0.3319		
4	1	-4.4286	5	1	-1.5908	6	1	-0.2515	
	2	0.1613		2	0.5518		2	-1.1565	
	3	1.7920		3	-0.3803		3	-0.2622	
	4	0.0462		4	0.6823		4	0.3850	
	5	4.1522		5	-0.5899		5	0.2450	
	6	1.5362		6	0.3185		6	-1.3584	
	7	-1.7552		7	0.1817		7	-0.5733	
	8	1.8741		8	-0.2545		8	-0.1810	
	9	-0.4633		9	0.0719		9	0.2861	
	10	-2.2897		10	0.8341		10	-0.3713	
	11	0.7126		11	0.1233		11	1.9948	
	12	-0.9218		12	-0.0169		12	-0.2769	
	13	-0.1033		13	-0.0550		13	1.1117	
7	1	0.3865	8	1	0.4135	9	1	-0.6156	
	2	0.5282		2	0.1648		2	1.6238	
	3	-2.3786		3	4.6291		3	-0.3383	
	4	-0.0820		4	0.4355		4	0.8625	
	5	0.6911		5	0.6474		5	0.8609	
	6	0.3598		6	-0.1897		6	-3.1358	
	7	-0.2540		7	0.0638		7	-0.7758	
	8	-0.1576		8	0.0686		8	0.2259	
	9	0.7279		9	0.1086		9	0.2654	
	10	0.0081		10	0.1840		10	-0.4641	
	11	-0.1952		11	0.2547		11	-1.5159	
	12	-0.2249		12	0.2152		12	0.0217	
	13	-1.7030		13	-0.6241		13	-0.6696	
10	1	-0.0536	11	1	0.3161	12	1	-0.3023	
	2	0.6125		2	-0.5962		2	-0.5654	
	3	0.3499		3	0.4766		3	-0.2549	
	4	0.1007		4	-0.2924		4	0.1187	
	5	0.1304		5	1.5433		5	-0.4439	
	6	0.0233		6	0.5228		6	0.7642	
	7	0.0487		7	-0.0065		7	0.4420	
	8	2.8813		8	-3.6408		8	0.3521	
	9	-0.4005		9	-0.2037		9	0.0265	

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
		10	0.0608	10	0.4271	10	-0.3500		
		11	0.5379	11	0.4784	11	-0.0331		
		12	2.0654	12	0.4950	12	1.1134		
		13	-0.2055	13	0.0999	13	4.4359		
13	1	-0.4443	14	1	-0.5736	15	1	-0.1214	
	2	0.4165		2	-0.0049		2	-0.5629	
	3	2.5161		3	0.4386		3	0.4573	
	4	-0.5071		4	0.2696		4	0.3097	
	5	-3.9889		5	1.3151		5	-1.5893	
	6	-0.2931		6	-2.4549		6	-1.2214	
	7	-0.2875		7	-0.4473		7	1.0705	
	8	0.2635		8	0.2018		8	0.5065	
	9	-0.0847		9	-0.0427		9	-0.2848	
	10	-0.1335		10	-0.0974		10	-0.3079	
	11	0.4592		11	2.5632		11	0.4404	
	12	0.0000		12	-1.1629		12	-1.8476	
	13	-0.2457		13	0.0008		13	-0.4320	
16	1	0.6428	17	1	0.5072	18	1	0.0214	
	2	1.4591		2	0.7162		2	0.2131	
	3	-0.7697		3	-0.2601		3	0.2384	
	4	-0.7760		4	-0.1215		4	0.3668	
	5	-1.3319		5	-1.3870		5	0.9530	
	6	0.5055		6	-0.4288		6	-0.4521	
	7	0.6382		7	-6.7113		7	-0.5659	
	8	-1.0178		8	-0.6253		8	-0.0357	
	9	-0.0049		9	1.1933		9	-0.1387	
	10	-0.2851		10	0.3838		10	0.4667	
	11	0.0252		11	0.0325		11	0.5678	
	12	-2.1726		12	-0.2947		12	-1.9845	
	13	-0.6246		13	-0.2573		13	2.9520	
19	1	0.6149	20	1	0.4288	21	1	0.0148	
	2	4.5676		2	0.4319		2	1.5215	
	3	-0.1171		3	-0.2002		3	-0.2974	
	4	-0.9979		4	0.0648		4	0.3557	
	5	-0.7270		5	-0.1272		5	0.0776	
	6	-0.1401		6	-0.3181		6	-0.7460	
	7	0.3366		7	0.1470		7	-0.2574	
	8	-0.1473		8	-0.1413		8	0.5586	
	9	0.0526		9	0.0830		9	0.0938	
	10	0.1508		10	-1.4743		10	0.3888	

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
		11	0.1369	11	-0.1409	11	-0.1736		
		12	0.1955	12	0.1282	12	-3.3314		
		13	0.0623	13	0.1000	13	-0.2827		
	22	1	0.8400						
		2	0.4228						
		3	-0.1364						
		4	0.2410						
		5	-0.0967						
		6	0.6599						
		7	0.5360						
		8	0.0276						
		9	0.0006						
		10	-2.0194						
		11	-0.4146						
		12	-0.2677						
		13	-0.0873						
.....									
j' = 5	1	1	-5.1333	2	1	5.5093	3	1	-0.0043
J = 5		2	0.3615		2	0.1437		2	-0.3932
j = 2		3	0.1487		3	-0.3122		3	0.3380
		4	0.1960		4	-0.2728		4	0.0750
		5	0.4555		5	0.3553		5	-0.6748
		6	-0.0298		6	-0.0248		6	0.0783
		7	0.5372		7	-0.4599		7	-1.4613
		8	0.0189		8	-0.0777		8	-0.9525
		9	0.4468		9	-0.6889		9	-0.0000
	4	1	-0.0075	5	1	0.1042	6	1	-0.4070
		2	-0.1415		2	0.9397		2	-0.6724
		3	-0.0330		3	0.6070		3	0.8213
		4	-0.2289		4	-1.2908		4	0.2092
		5	0.2217		5	0.2344		5	-4.3083
		6	-0.5510		6	-0.3559		6	0.0977
		7	0.0870		7	-0.5469		7	0.3494
		8	0.7749		8	0.6986		8	-0.0089
		9	-0.0249		9	1.1451		9	-0.0366
	7	1	-0.4354	8	1	-0.3668	9	1	-0.1091
		2	3.6746		2	-2.0111		2	-0.5563
		3	-0.8811		3	-0.9739		3	0.4035
		4	0.2082		4	-0.6499		4	0.5977
		5	0.4805		5	0.1769		5	0.5645

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
		6	-0.1123		6	-0.2495		6	-0.2822
		7	0.5481		7	0.5208		7	-3.0187
		8	-1.2088		8	0.8188		8	1.2958
		9	0.1489		9	0.9397		9	-0.7249
10		1	0.1807	11	1	-0.0944	12	1	-0.2195
		2	-0.1160		2	0.4302		2	-0.1768
		3	4.3066		3	1.3639		3	0.1309
		4	0.6067		4	-1.8435		4	1.5896
		5	0.2225		5	-0.2575		5	1.2514
		6	-0.3186		6	0.2492		6	-0.2678
		7	-0.4804		7	0.4274		7	0.5318
		8	1.0065		8	0.5131		8	-1.3141
		9	-0.8860		9	-1.4166		9	-0.7202
13		1	0.0335	14	1	0.7018	15	1	0.3318
		2	0.6845		2	0.5321		2	-0.0452
		3	0.0534		3	-0.6766		3	-0.7669
		4	-0.5620		4	-0.0359		4	-0.7540
		5	-0.0164		5	0.9120		5	-0.5456
		6	-0.0506		6	-0.1223		6	0.0219
		7	0.0139		7	2.7541		7	-0.6947
		8	-1.9974		8	0.8295		8	-2.3584
		9	0.3278		9	-0.2961		9	1.9977
16		1	0.1916	17	1	0.7419	18	1	-0.0940
		2	-0.1607		2	0.1824		2	-1.0114
		3	-0.4718		3	-0.3680		3	-0.4414
		4	-1.4669		4	0.2506		4	-1.8296
		5	-0.2224		5	0.0337		5	0.5162
		6	-0.0278		6	-0.0286		6	0.0829
		7	-1.4282		7	-0.2405		7	-0.6162
		8	-1.8010		8	-0.3315		8	1.3657
		9	-3.8304		9	-0.0044		9	0.5529
19		1	0.0493	20	1	-0.0469	21	1	0.0453
		2	0.2876		2	0.1632		2	0.1472
		3	0.2143		3	0.1197		3	-0.1654
		4	0.3368		4	0.3264		4	2.6820
		5	-0.4830		5	0.0444		5	-0.0920
		6	0.0949		6	2.2371		6	-0.0696
		7	2.2836		7	0.0850		7	-0.7937
		8	1.3433		8	0.1035		8	1.3233
		9	0.4901		9	0.3519		9	0.8192

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
	22	1	0.0354						
		2	0.0320						
		3	0.0359						
		4	0.1898						
		5	0.1810						
		6	-1.2892						
		7	-0.2207						
		8	-0.1051						
		9	-0.1331						
.....									
j' = 5	1	1	-0.1283	2	1	0.6801	3	1	0.5663
J = 5		2	1.1195		2	0.6361		2	-4.4876
j = 3		3	0.2604		3	-0.7667		3	1.4218
		4	0.0288		4	0.1728		4	0.8739
		5	-0.0583		5	0.1198		5	-0.4652
		6	0.2013		6	-0.9177		6	1.9925
		7	0.5398		7	0.9088		7	-4.4336
		8	-0.6145		8	1.2267		8	-0.9769
		9	-0.0701		9	-0.2783		9	0.3849
		10	-0.2559		10	-0.1961		10	0.6670
		11	-0.1352		11	-0.2862		11	1.1850
	4	1	-2.5796	5	1	-1.7551	6	1	-2.0890
		2	-0.4394		2	-0.1797		2	-0.7510
		3	0.0612		3	-0.4154		3	-0.7820
		4	0.7037		4	-0.8387		4	-1.5361
		5	-0.1265		5	-0.6674		5	0.1777
		6	-0.1160		6	0.6948		6	-0.8095
		7	0.7410		7	0.2205		7	0.5187
		8	0.7417		8	0.6081		8	1.2985
		9	-2.0885		9	0.1863		9	-0.1069
		10	0.6803		10	0.6938		10	-0.2705
		11	-0.9794		11	-0.1873		11	-0.1444
	7	1	-0.6981	8	1	1.1542	9	1	-1.9461
		2	2.7603		2	-1.9929		2	-2.3234
		3	-0.6203		3	0.3142		3	0.5984
		4	-0.5710		4	-0.0254		4	-0.6856
		5	-0.6308		5	-0.3516		5	0.7463
		6	0.3929		6	0.4937		6	-0.8656
		7	0.5617		7	-1.7368		7	0.0268
		8	1.7988		8	-0.3425		8	-0.2154

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
		9	-1.1524		9	-0.0009		9	0.8586
		10	-3.4143		10	0.4998		10	1.3501
		11	-0.3585		11	0.6795		11	-0.2028
10		1	1.7156	11	1	0.1239	12	1	-1.3956
		2	0.0943		2	0.3231		2	-0.8923
		3	0.3805		3	-0.1219		3	-1.1278
		4	0.3026		4	0.7859		4	-1.9642
		5	-0.2736		5	-0.5312		5	-0.3322
		6	0.1176		6	0.9817		6	-0.8300
		7	-0.2754		7	-0.4715		7	0.6998
		8	-0.7539		8	0.0217		8	1.1691
		9	-0.1642		9	-0.5161		9	-0.9594
		10	0.2402		10	-0.0661		10	0.4430
		11	0.4847		11	0.0395		11	-0.3943
13		1	-5.1968	14	1	-2.6726	15	1	0.7699
		2	-2.0300		2	-3.7515		2	-0.6392
		3	1.5294		3	0.4641		3	2.2584
		4	-0.4508		4	-0.3120		4	-0.4115
		5	1.4942		5	0.7088		5	-2.3697
		6	0.2511		6	1.4917		6	0.2373
		7	-0.6042		7	-2.4952		7	-0.8422
		8	-0.6147		8	-0.7310		8	-0.5566
		9	2.1680		9	1.5394		9	-3.0819
		10	0.5910		10	1.8303		10	-1.1685
		11	-0.2230		11	0.6334		11	0.1352
16		1	2.2285	17	1	1.8835	18	1	-0.3617
		2	2.0315		2	1.9740		2	-2.7220
		3	2.0261		3	7.9678		3	0.1295
		4	1.2561		4	1.9757		4	0.5228
		5	-1.5290		5	-2.1415		5	0.8807
		6	0.7921		6	1.7671		6	0.7112
		7	-0.1014		7	-0.8354		7	-2.1368
		8	-0.9451		8	-5.2394		8	-0.5509
		9	-1.9639		9	-1.6724		9	1.8281
		10	-1.4236		10	-1.2906		10	0.8265
		11	-0.2354		11	0.4119		11	0.7801
19		1	0.9539	20	1	1.8111	21	1	0.2972
		2	3.1230		2	2.1820		2	0.7945
		3	2.8424		3	0.0157		3	0.4500
		4	3.2505		4	0.6266		4	1.6388

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
		5	-0.8322	5	0.0464	5	0.4639		
		6	3.3108	6	0.4706	6	1.6709		
		7	-1.5814	7	0.8162	7	-1.0432		
		8	-2.2153	8	-0.3931	8	-0.8105		
		9	-0.1512	9	-0.0880	9	0.9983		
		10	-2.2318	10	0.9486	10	-0.2874		
		11	0.2307	11	-0.6691	11	0.0605		
	22	1	-0.5233						
		2	-1.0318						
		3	-0.2210						
		4	0.5474						
		5	-0.2235						
		6	1.1710						
		7	-1.9406						
		8	0.0130						
		9	1.2885						
		10	0.1118						
		11	1.8987						
.....									
j' = 5	1	1	0.2374	2	1	-0.1082	3	1	-2.4070
J = 5		2	0.0768		2	0.4651		2	-0.2072
j = 4		3	-0.4984		3	0.2229		3	2.3409
		4	0.3669		4	-4.2320		4	0.1256
		5	0.0043		5	0.1564		5	-0.6825
		6	0.0731		6	0.3899		6	0.3904
		7	0.0383		7	0.3269		7	0.1162
		8	-0.1538		8	-0.1144		8	-1.2458
		9	-0.1244		9	0.6773		9	-0.5195
		10	0.0147		10	-0.0006		10	-0.5786
	4	1	-3.8866	5	1	-0.3377	6	1	1.9139
		2	-3.4710		2	0.4663		2	-0.5421
		3	-2.2824		3	0.2798		3	-1.1989
		4	-2.2780		4	0.3431		4	-0.0010
		5	8.0939		5	-0.4522		5	1.0378
		6	-5.9646		6	0.8615		6	-0.9089
		7	0.5016		7	-0.2126		7	0.0889
		8	-1.3984		8	-0.0461		8	-2.1479
		9	1.9387		9	-0.0493		9	0.6868
		10	5.0311		10	-1.5201		10	0.4456
	7	1	0.4801	8	1	0.6869	9	1	-0.3524

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
		2	-1.4846		2	1.8140		2	-0.6103
		3	0.3081		3	0.3090		3	2.9094
		4	0.6153		4	-0.1687		4	-0.4039
		5	0.0040		5	-0.4417		5	0.8992
		6	-2.5552		6	-2.0245		6	-1.1813
		7	-0.3338		7	-0.5428		7	0.2915
		8	0.4083		8	1.3715		8	1.4686
		9	-1.3716		9	0.3398		9	1.3764
		10	0.0770		10	-0.4403		10	0.8179
10	1	0.3031	11	1	0.0161	12	1	0.4505	
	2	2.2595		2	-0.8702		2	-1.0491	
	3	0.7039		3	-0.2811		3	-1.1666	
	4	-0.1658		4	-0.4005		4	-0.5623	
	5	-0.2650		5	0.3063		5	0.9135	
	6	-1.6198		6	0.7918		6	-1.3947	
	7	0.2596		7	2.4568		7	-0.3214	
	8	0.1591		8	0.8414		8	1.8796	
	9	1.0111		9	-0.3466		9	-2.4475	
	10	-0.0363		10	0.3226		10	0.7854	
13	1	-0.8046	14	1	1.5657	15	1	0.1214	
	2	4.6816		2	-1.3078		2	-1.1894	
	3	0.5343		3	2.6988		3	-0.7566	
	4	0.2387		4	-1.2636		4	-0.7498	
	5	1.3090		5	0.7920		5	0.3548	
	6	-0.5098		6	-0.7536		6	-0.3731	
	7	-0.1477		7	0.4462		7	1.6556	
	8	-0.5380		8	-2.2859		8	0.3354	
	9	-1.0232		9	-0.0170		9	2.5142	
	10	0.7525		10	0.7210		10	0.3985	
16	1	0.7778	17	1	0.0853	18	1	0.3328	
	2	0.7781		2	0.5383		2	0.3182	
	3	0.4963		3	0.7217		3	-0.5030	
	4	0.2448		4	-5.9159		4	0.0292	
	5	-0.1828		5	-0.9408		5	-0.6845	
	6	-0.2005		6	1.0194		6	0.0658	
	7	-0.1235		7	-0.3458		7	0.7679	
	8	-0.5214		8	-0.0146		8	-2.3465	
	9	3.0205		9	0.2948		9	2.0564	
	10	-0.3709		10	-0.2670		10	-0.8594	
19	1	-1.2370	20	1	-0.0802	21	1	0.5887	

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
		2	0.4908	2	0.1564	2	0.7231		
		3	0.2821	3	-0.6611	3	0.8810		
		4	0.4645	4	0.2697	4	0.5082		
		5	-1.2471	5	-0.1432	5	-0.3789		
		6	1.3586	6	-0.1324	6	0.2291		
		7	-0.6291	7	-0.1078	7	4.5809		
		8	1.5856	8	-0.0503	8	-0.7421		
		9	1.8148	9	0.3070	9	-0.5963		
		10	-0.8687	10	1.3497	10	-0.3185		
22	1	0.2405							
	2	0.8559							
	3	0.6083							
	4	1.0925							
	5	-2.0484							
	6	1.4231							
	7	0.1413							
	8	0.4354							
	9	-0.5129							
	10	1.3346							
.....									
j' = 10	1	1	2.8062	2	1	0.2049	3	1	0.0586
J = 5		2	-0.0355		2	3.7826		2	-2.0804
j = 6		3	-0.0134		3	0.4140		3	-0.1229
		4	0.3385		4	0.2523		4	0.0916
		5	-0.0122		5	-1.3087		5	-2.9431
	4	1	-0.0842	5	1	-0.0567	6	1	0.0269
		2	0.6484		2	-0.4234		2	-0.6030
		3	-4.6262		3	2.9010		3	-2.1575
		4	-0.0698		4	-0.0539		4	0.0404
		5	2.2463		5	1.9458		5	-1.3288
.....									
j' = 10	1	1	-0.3256	2	1	-0.8873	3	1	-0.6067
J = 5		2	0.2882		2	1.1967		2	1.8682
j = 7	4	1	-0.5095	5	1	-4.1355	6	1	-2.1296
		2	1.6786		2	-0.2150		2	-4.1116
.....									
j' = 10	1	1	0.4651	2	1	0.8622	3	1	0.4625
J = 5		2	0.8079		2	2.5466		2	1.3536
j = 8		3	2.2013		3	-2.9500		3	-1.3886
	4	1	-0.8842	5	1	0.1501	6	1	-0.0670

TABLE XII (continued)

Reps.	n'	n	Matrix Element	n'	n	Matrix Element	n'	n	Matrix Element
		2	-2.7425	2	2	-0.0233	2	2	-0.4154
		3	3.0407	3	3	0.7040	3	3	0.7483
.....									
j' = 10	1	1	2.7114	2	1	0.0906	3	1	-0.0718
J = 5		2	-0.3250		2	-3.8327		2	-1.3561
j = 9		3	-0.0623		3	-0.3360		3	0.1907
	4	1	-0.0214	5	1	0.0173	6	1	-0.0217
		2	-0.6833		2	-0.8262		2	-0.3203
		3	5.2444		3	-2.6886		3	0.4665

The results of this calculation are presented in Table XIII. In Table XIII, the molecular orbitals have been ordered according to their one-electron energies. Oscillator strengths for transitions between two orbitals which are filled in the ground state and for transitions between two orbitals which are empty in the ground state are not given in the table. There are sixteen orbitals with energy eigenvalues practically equal to -0.33015 au. It is impossible to determine the order of filling of these orbitals, and transitions connecting them with both empty and filled orbitals have been considered. Transitions involving orbitals with one-electron energies greater than -0.2 au. have been ignored, since molecular orbital theory is known to be poor for highly excited states (Roothaan, 1951).

TABLE XIII

OSCILLATOR STRENGTHS OF ALLOWED TRANSITIONS

$(j_i) \rightarrow (j_f)$	n_i	n_f	f	n_i	n_f	f	n_i	n_f	f
z									
(1) $\rightarrow$ (6)	9	3*	0.0037	7	3*	0.0101	10	3*	0.0001
		2	0.0006		2	0.0020		2	0.0064
(6) $\rightarrow$ (1)	1	12	0.0166	5	12	0.0004	3*	12	
		13	0.0036		13	0.0001		13	
		2	0.0844		2	0.0065		2	
		6	0.1993		6	0.0481		6	0.0059
		11	0.0347		11	0.0284		11	0.0042
z									
(2) $\rightarrow$ (7)	1	1*	0.0026	6	1*		8*	1*	
		2*			2*			2*	
(7) $\rightarrow$ (2)	1*	4		2*	4				
		9			9				
		7			7	0.0043			
		5	0.0086		5	0.0001			
z									
(3) $\rightarrow$ (8)	3	2*	0.0098	8	2*	0.0543	11	2*	0.0086
		3*	0.0124		3*	0.0078		3*	0.0061
		1*			1*	0.0032		1*	0.0024
(8) $\rightarrow$ (3)	2*	10		3*	10	0.0034	1*	10	
		7			7	0.0012		7	
		6	0.0260		6	0.0052		6	0.0021
		2	0.0100		2	0.0020		2	0.0040
		4	0.0125		4	0.0717		4	
z									
(4) $\rightarrow$ (9)	4	3*	0.0165	10	3*				
		3	0.0029		2				
(9) $\rightarrow$ (4)	1	7		3*	7				
		9			9				
		8	0.0036		8	0.0019			
		3	0.0013		3	0.0049			
		1	0.0109		1	0.0002			
z									
(5) $\rightarrow$ (10)	1	5*		2	5*	0.0060	17	5*	0.0017
		4*	0.0001		4*	0.0003		4*	0.0081
		6*	0.0013		6*			6*	0.0006
		3*	0.0007		3*	0.0005		3*	0.0006

TABLE XIII (continued)

$(j_i) \rightarrow (j_f)$	n_i	n_f	f	n_i	n_f	f	n_i	n_f	f
z									
(5) $\rightarrow$ (10)	22	2			2	0.0003		2	0.0003
		5	0.0025	20	5	0.0003			
		4	0.0048		4	0.0002			
		6	0.0009		6				
		3	0.0013		3				
		2	0.0150		2	0.0003			
(10) $\rightarrow$ (5)	1	21	0.0015	5*	21		4*	21	
		15	0.0012		15			15	
		16	0.0014		16			16	
		18	0.0030		18			18	
		12	0.0028		12			12	
		19	0.0143		19			19	0.0001
		9	0.0027		9	0.0001		9	0.0033
		14	0.0050		14	0.0010		14	0.0056
		6	0.0082		6	0.0047		6	0.0040
		3	0.0009		3	0.0066		3	0.0007
	6*	21		3*	21				
		15			15				
		16			16				
		18			18				
		12			12				
		19			19	0.0010			
		9	0.0002		9	0.0016			
		14	0.0010		14				
		6	0.0009		6	0.0004			
		3	0.0060		3	0.0022			
x, y									
(5) $\rightarrow$ (1)	1	12	0.0003	2	12	0.0581	17	12	0.0308
		13	0.3547		13	0.1422		13	0.0250
		2	0.0020		2	0.0892		2	0.2183
		6	0.0143		6	0.0103		6	0.0828
		11	0.0023		11	0.0072		11	0.0005
	22	12	0.0162	20	12	0.0032			
		13	0.0019		13	0.0022			
		2	0.0531		2	0.0497			
		6	0.1402		6	0.0295			
		11	0.0670		11	0.0071			
(1) $\rightarrow$ (5)	9	21	0.0032	7	21	0.0219	10	21	0.0284
		15	0.0300		15	0.3885		15	0.0187
		16			16	0.1424		16	0.0169
		18	0.0074		18	0.1140		18	0.0465
		12	0.0003		12	0.0728		12	0.0282
		19	0.0012		19	0.0470		19	0.0062

TABLE XIII (continued)

$(j_i) \rightarrow (j_f)$	n_i	n_f	f	n_i	n_f	f	n_i	n_f	f				
<hr/>													
x, y													
(1) $\rightarrow$ (5)		9	0.0330		9	0.2634		9	0.0636				
		14	0.0009		14	0.0908		14	0.0029				
		6	0.0416		6	0.1567		6	0.0461				
		3	0.0904		3	0.0002		3	0.0487				
<hr/>													
x, y													
(5) $\rightarrow$ (2)	1	8*	0.0001	2	8*	0.0021	17	8*	0.0371				
		4	0.0142		4	0.0270		4	0.0218				
		9	0.0763		9	0.1775		9					
		7	0.1399		7	0.1008		7	0.0267				
	22	5	0.1062	20	5	0.0635		5	0.0005				
		8*	0.0023		8*	0.0019							
		4	0.0079		4	0.0200							
		9	0.0041		9	0.0246							
	(2) $\rightarrow$ (5)	1	7	0.0162	6	7	0.0022	8*					
			5	0.0118		5	0.0006						
			21	0.0007		21	0.0009		21	0.0039			
			15	0.0408		15			15	0.0623			
(2) $\rightarrow$ (5)	1	16	0.0140	6	16	0.0002	8*	16	0.0708				
		18	0.0034		18	0.0015		18	0.0522				
		12	0.0195		12	0.0165		12	0.0771				
		19	0.0011		19	0.0025		19	0.1569				
		9	0.0056		9	0.0235		9	0.1846				
		14	0.2390		14	0.0047		14	0.0866				
		6	0.0842		6	0.0032		6					
		3			3	0.0022		3	0.1613				
		<hr/>											
		x, y											
		(5) $\rightarrow$ (3)	1		10	0.0247		2	10	0.0142	17	10	0.5896
					7	0.1145			7	0.3178		7	0.2576
6	0.0181			6	0.3687	6	1.318						
2	0.5904			2	0.1873	2	1.742						
22	4		0.0004	20	8	0.0154		4	1.950				
	10		0.0028		10	0.1752							
	7		0.9062		7	0.1398							
	6		0.4026		6	0.0582							
(3) $\rightarrow$ (5)	3	2	0.3392	8	2	1.370	11						
		4	0.1112		4	0.1335							
		21	0.0739		21	0.2286		21	0.0007				
		15	1.908		15	0.1106		15	0.0035				
		16	1.579		16	0.3284		16	0.0111				
		18	0.0065		18	0.1134		18	0.1257				
		12	0.5184		12	0.5337		12	0.0347				
		19	3.634		19	2.123		19	0.0141				

TABLE XIII (continued)

$(j_i) \rightarrow (j_f)$	n_i	n_f	f	n_i	n_f	f	n_i	n_f	f
x, y									
(3)→(5)		9	0.1693		9	0.0211		9	0.0119
		14	0.1053		14	0.2520		14	0.1221
		6	0.3130		6	0.8341		6	0.0068
		3	1.093		3	0.4997		3	0.5004
x, y									
(5)→(4)	1	7	0.0005	2	7	0.0379	17	7	0.0405
		9	0.0061		9	0.1757		9	0.0319
		8	0.0109		8	0.0059		8	
		3	0.1194		3	0.0235		3	0.2380
		1	0.0311		1	0.0064		1	0.0038
	22	7	0.0042	20	7	0.0021			
		9	0.0628		9	0.0196			
		8	0.0586		8	0.0007			
		3	0.1215		3	0.1300			
		1	0.0231		1	0.0024			
(4)→(5)	4	21	0.0887	10	21	0.0186			
		15	0.1981		15	0.0306			
		16	0.0218		16	0.0279			
		18	0.0003		18	0.1546			
		12	0.1220		12	0.1394			
		19	0.0923		19	0.2024			
		9	0.0736		9	0.1948			
		14	0.7458		14	0.1597			
	4	6		10	6	0.0656			
		3	0.0082		3	0.1202			
x, y									
(10)→(6)	1	3*		5*	3*		4*	3*	
		2	0.0002		2	0.0003		2	0.0007
	6*	3*		3*	3*				
		2	0.0007		2	0.0078			
(6)→(10)	1	5*	0.0006	5	5*	0.0031	3*	2	0.0006
		4*	0.0014		4*	0.0042			
		6*	0.0001		6*	0.0014			
		3*	0.0007		3*	0.0071			
		2	0.0085		2	0.0075			

TABLE XIII (continued)

$(j_i) \rightarrow (j_f)$	n_i	n_f	f	n_i	n_f	f	n_i	n_f	f
<hr/>									
x, y									
$(10) \rightarrow (7)$	1	1*	0.0199	5*	1*		4*	1*	
		2*	0.0156		2*			2*	
	6*	1*		3*	1*				
		2*			2*				
$(7) \rightarrow (10)$	1*	2	0.0028	2*	2	0.0051			
<hr/>									
x, y									
$(10) \rightarrow (8)$	1	2*	0.1225	5*	2*		4*	2*	
		3*	0.9097		3*			3*	
		1*	0.0406		1*			1*	
	6*	2*		3*	2*				
		3*			3*				
		1*			1*				
$(8) \rightarrow (10)$	2*	2	0.0229	3*	2	0.0307	1*	2	0.0026
<hr/>									
x, y									
$(10) \rightarrow (9)$	1	3*	0.0007	5*	3*		4*	3*	
		2	0.0202		2	0.0023		2	0.0016
	6*	3*		3*	3*				
		2	0.0003		2	0.0062			
$(9) \rightarrow (10)$	1	5*		3*	2	0.0004			
		4*							
		6*							
		3*	0.0010						
		2	0.0016						

*These states have energies which lie on the Fermi level.

CHAPTER VI

DISCUSSION OF RESULTS

I. FILLING OF STATES

Of magnesium porphin's 172 electrons, 58 have been assigned to low-lying atomic orbitals on the magnesium, nitrogen, and carbon atoms, leaving 114 electrons to be assigned to molecular orbitals. The 49 molecular orbitals with lowest energy eigenvalues can be picked out from Figure 5, page 73. These 49 orbitals can accommodate 98 electrons, leaving 16 to be assigned. However, the next 16 molecular orbitals all have the same energy eigenvalue, -0.33015 a.u., and comparison of orbital energies yields no information about the filling of these states.

The filled orbitals and the 16 degenerate orbitals with eigenvalues lying on the Fermi level are given in Table XIV. The table is constructed so as to indicate roughly the relative positions of the one-electron energy levels and to point out the way in which the one-electron energies fall into bands. Dirac notation is used for the molecular orbitals.

$$|n(j) \lambda \rangle = \varphi_{n \lambda}^o(j).$$

TABLE XIV

MOLECULAR ORBITALS WITH EIGENVALUES BELOW OR AT THE FERMI LEVEL IN ORDER
OF FILLING BY IRREDUCIBLE REPRESENTATIONS

Lowest:	$ 1(1)1\rangle$		$ 5(4)1\rangle$	$ 5(5)\lambda\rangle$				
	$ 3(1)1\rangle$	$ 2(2)1\rangle$	$ 9(3)1\rangle$	$ 2(4)1\rangle$	$ 8(5)\lambda\rangle$			
	$ 5(1)1\rangle$	$ 3(2)1\rangle$	$ 1(3)1\rangle$	$ 6(4)1\rangle$	$ 7(5)\lambda\rangle$			
	$ 8(1)1\rangle$		$ 5(3)1\rangle$		$ 13(5)\lambda\rangle$			
					$ 10(5)\lambda\rangle$			
					$ 11(5)\lambda\rangle$			
	$ 9(1)1\rangle$	$ 1(2)1\rangle$	$ 3(3)1\rangle$	$ 4(4)1\rangle$	$ 1(5)\lambda\rangle$			
	$ 7(1)1\rangle$		$ 8(3)1\rangle$		$ 2(5)\lambda\rangle$			
					$ 17(5)\lambda\rangle$			
	$ 10(1)1\rangle$	$ 6(2)1\rangle$	$ 11(3)1\rangle$	$ 10(4)1\rangle$	$ 22(5)\lambda\rangle$	$ 1(6)1\rangle$	$ 1(9)1\rangle$	$ 1(10)\lambda\rangle$
					$ 20(5)\lambda\rangle$			
<hr/>								
Fermi	$ 8(2)1\rangle$		$ 3(6)1\rangle$	$ 1(7)1\rangle$	$ 1(8)1\rangle$	$ 3(9)1\rangle$	$ 3(10)\lambda\rangle$	
Level				$ 2(7)1\rangle$	$ 2(8)1\rangle$		$ 4(10)\lambda\rangle$	
					$ 3(8)1\rangle$		$ 5(10)\lambda\rangle$	
							$ 6(10)\lambda\rangle$	

II. ABSORPTION SPECTRUM

A transition from a state of energy E to a state of higher energy $E + \Delta E$ is accompanied by the absorption of one photon of wavelength

$$\lambda = \frac{hc}{\Delta E}.$$

If ΔE is expressed in atomic units and λ in angstroms,

$$\lambda = \frac{455.534}{\Delta E}.$$

Table XV lists the principal transitions from the states with energies at the Fermi level and from the states with energies clustered about -0.43 a.u. and from the states with energies near -0.5 a.u. Only transitions with oscillator strengths as great as 0.1 for single transitions or 0.05 for degenerate transitions are listed. Transitions for wavelengths of less than $1,000$ Å. or greater than $10,000$ Å. are not listed.

There are only two listings in Table XV for transitions in the optical region ($3,500$ Å. to $7,000$ Å.) with oscillator strengths which are about one. These are for the transitions from $|22(5)1\rangle$ and $|22(5)2\rangle$ to $|7(3)1\rangle$, which occur at $3,786$ Å. and each of which has oscillator strength 0.9062 and for the transitions $|1(10)1\rangle$ and $|1(10)2\rangle$ to $|3(8)1\rangle$ which occur at $4,853$ Å. and have oscillator strength 0.9097 . Absorption at $4,853$ Å. may be enhanced by the transitions from $|1(10)1\rangle$ and $|1(10)2\rangle$ to $|2(8)1\rangle$ which have oscillator strength 0.1225 .

TABLE XV

PRINCIPAL TRANSITIONS FROM THE BAND AT THE FERMI LEVEL
AND FROM THE TOP TWO FILLED BANDS

Initial State	Final State	f	$\lambda(\text{\AA.})$
$ 8(2)1\rangle$	$ 9(5)_\mu\rangle$	0.1846	8288
	$ 14(5)_\mu\rangle$	0.0866	7239
	$ 3(5)_\mu\rangle$	0.1613	5126
$ 11(3)1\rangle$	$ 18(5)_\mu\rangle$	0.1257	4410
	$ 14(5)_\mu\rangle$	0.1221	2993
	$ 3(5)_\mu\rangle$	0.5004	2557
$ 10(4)1\rangle$	$ 18(5)_\mu\rangle$	0.1546	4353
	$ 12(5)_\mu\rangle$	0.1394	4031
	$ 19(5)_\mu\rangle$	0.2024	3397
	$ 9(5)_\mu\rangle$	0.1948	3128
	$ 14(5)_\mu\rangle$	0.1597	2966
	$ 6(5)_\mu\rangle$	0.0656	2759
	$ 3(5)_\mu\rangle$	0.1202	2537
	$ 2(1)1\rangle$	0.0497	3422
$ 20(5)_\mu\rangle$	$ 10(3)1\rangle$	0.1752	4681
	$ 7(3)1\rangle$	0.1398	4343
	$ 6(3)1\rangle$	0.0582	3468
	$ 2(3)1\rangle$	1.370	3166
	$ 4(3)1\rangle$	0.1335	2679
	$ 3(4)1\rangle$	0.1300	3063
	$ 2(1)1\rangle$	0.0531	3066
	$ 6(1)1\rangle$	0.1402	2829
$ 22(5)_\mu\rangle$	$ 11(1)1\rangle$	0.0670	2339
	$ 7(3)1\rangle$	0.9062	3786
	$ 6(3)1\rangle$	0.4026	3103
	$ 2(3)1\rangle$	0.3392	2859

TABLE XV (continued)

Initial State	Final State	f	$\lambda(A.)$
	$ 4(3)1 >$	0.1112	2456
	$ 9(4)1 >$	0.0628	3813
	$ 8(4)1 >$	0.0586	2945
	$ 3(4)1 >$	0.1215	2775
$ 1(6)1 >$	$ 6(1)1 >$	0.1993	2924
$ 1(10)_\mu >$	$ 2(8)1 >$	0.1225	4853
	$ 3(8)1 >$	0.9097	4853
$ 8(1)1 >$	$ 15(5)_\mu >$	0.3885	2688
	$ 16(5)_\mu >$	0.1424	2606
	$ 18(5)_\mu >$	0.1140	2561
	$ 12(5)_\mu >$	0.0728	2446
	$ 9(5)_\mu >$	0.2634	2081
	$ 14(5)_\mu >$	0.0908	2008
	$ 6(5)_\mu >$	0.1567	1911
$ 9(1)1 >$	$ 3(5)_\mu >$	0.0904	1802
$ 8(3)1 >$	$ 21(5)_\mu >$	0.2286	2618
	$ 15(5)_\mu >$	0.1106	2552
	$ 16(5)_\mu >$	0.3284	2478
	$ 18(5)_\mu >$	0.1134	2437
	$ 12(5)_\mu >$	0.5337	2333
	$ 19(5)_\mu >$	2.123	2106
	$ 14(5)_\mu >$	0.2520	1932
	$ 6(5)_\mu >$	0.8341	1842
	$ 3(5)_\mu >$	0.4997	1740
$ 3(3)1 >$	$ 15(5)_\mu >$	1.908	2435
	$ 21(5)_\mu >$	0.0739	2495
	$ 16(5)_\mu >$	1.579	2368

TABLE XV (continued)

Initial State	Final State	f	$\lambda(A.)$
$ 4(4)1 >$	$ 12(5)_\mu >$	0.5184	2235
	$ 19(5)_\mu >$	3.634	2026
	$ 9(5)_\mu >$	0.1693	1927
	$ 14(5)_\mu >$	0.1053	1864
	$ 6(5)_\mu >$	0.3130	1780
	$ 3(5)_\mu >$	1.093	1685
	$ 21(5)_\mu >$	0.0887	2653
	$ 15(5)_\mu >$	0.1981	2585
	$ 12(5)_\mu >$	0.1220	2361
	$ 19(5)_\mu >$	0.0923	2128
$ 17(5)_\mu >$	$ 9(5)_\mu >$	0.0736	2020
	$ 14(5)_\mu >$	0.7458	1951
	$ 2(1)1 >$	0.2183	2141
	$ 6(1)1 >$	0.0828	2023
	$ 10(3)1 >$	0.5896	2574
	$ 7(3)1 >$	0.2576	2468
	$ 6(3)1 >$	1.318	2159
	$ 2(3)1 >$	1.742	2038
	$ 4(3)1 >$	1.950	1824
	$ 3(4)1 >$	0.2380	1994
$ 2(5)_\mu >$	$ 12(1)1 >$	0.0581	2462
	$ 13(1)1 >$	0.1422	2319
	$ 2(1)1 >$	0.0892	2064
	$ 9(2)1 >$	0.1775	2435
	$ 7(2)1 >$	0.1008	1911
	$ 5(2)1 >$	0.0635	1810
	$ 7(3)1 >$	0.3178	2367

TABLE XV (continued)

Initial State	Final State	f	$\lambda(A.)$
$ 1(5)_\mu >$	$ 6(3)1 >$	0.3687	2081
	$ 2(3)1 >$	0.1873	1968
	$ 9(4)1 >$	0.1757	2378
	$ 13(1)1 >$	0.3547	2272
	$ 9(2)1 >$	0.0763	2383
	$ 7(2)1 >$	0.1399	1879
	$ 5(2)1 >$	0.1062	1781
	$ 7(3)1 >$	0.1145	2318
	$ 2(3)1 >$	0.5904	1934
	$ 3(4)1 >$	0.1194	1895

The target states for the transitions at 4,853 Å. are members of that set of orbitals whose energies lie on the Fermi level. It is not possible to say whether or not these target states are empty. There is, therefore, some doubt as to whether these transitions are allowed. Also the effect of including that part of the Hamiltonian which was neglected is impossible to judge. The degeneracy of the orbitals belonging to irreducible representation eight would, in all probability, be removed, but there is no reliable way to judge in which direction a given eigenvalue would be shifted. The Soret band should probably be attributed to the transitions which occur at 3,786 Å. Since there are no other absorption bands in the optical region comparable with the Soret band, state $|3(8)1\rangle$ is probably filled.

The absorption bands near 6,000 Å. are not accounted for in this calculation. These bands should probably be attributed to transitions involving members of the accidentally degenerate set of orbitals. Inclusion of the neglected part of the Hamiltonian would undoubtedly remove some of the degeneracy of these levels and allow more lower energy transitions.

All the major transitions occur under the influence of light polarized in the plane of the molecule. Magnesium porphin should be practically transparent for light which is linearly polarized perpendicular to the plane of the molecule.

There are calculated transitions from $|20(5)1\rangle$ and $|20(5)2\rangle$ to $|2(3)1\rangle$ with oscillator strength 1.370 which occur at 3,166 Å. Thus, there should be observed a strong absorption band in the near ultraviolet

region. No experimental data has been found on absorption in this region. The neglected part of the Hamiltonian might produce a shift in the energy levels such that this transition contributes to the Soret band. Without further experimental data it is not possible to make a definite conclusion in this regard.

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APPENDICES

APPENDIX A

OVERLAP INTEGRALS OF SLATER ORBITALS

In order to solve for the coefficients of the symmetry orbitals which make up the molecular orbitals, overlap integrals between the symmetry orbitals, as given by equation (54) must be calculated. Since each symmetry orbital is ultimately a linear combination of single-term Slater orbitals of the form shown in equation (41), the calculation of the overlap integrals given by equation (54) requires the calculation of overlap integrals between single-term Slater orbitals. A method for calculating such integrals is described in this appendix.

Referring to equation (41), let

$$\chi_a = \chi_{n_a}^{(\mu_a)} \ell_{a a}^{m_a} (r_a, \theta_a, \varphi_a),$$

and

$$\chi_b = \chi_{n_b}^{(\mu_b)} \ell_{b b}^{m_b} (r_b, \theta_b, \varphi_b)$$

denote Slater orbitals centered respectively on points *a* and *b* which are separated by a distance *R*. Figure 6 shows the chosen orientation. The coordinate systems on the two centers are chosen in such a way that the polar axes are directed along the line of centers and are anti-parallel. The coordinate system with origin on center *b* is a left-handed system. Therefore,

$$\varphi_a = \varphi_b.$$

FIGURE 6

ORIENTATION OF COORDINATES FOR EVALUATION OF TWO-CENTER INTEGRALS

Let

$$S_{ab} = (\chi_a, \chi_b)$$

denote the overlap integral of the two orbitals.

$$S_{ab} = N_a N_b \int \int \int r_a^{n_a-1} e^{-\mu_a r_a} P_{\ell_a}^{m_a}(\cos \theta_a) \Phi_{m_a}(\varphi_a) r_b^{n_b-1} e^{-\mu_b r_b} P_{\ell_b}^{m_b}(\cos \theta_b) \Phi_{m_b}(\varphi_b) dV, \quad (64)$$

where

$$N_a = N(n_a, \ell_a, m_a, \mu_a),$$

and

$$N_b = N(n_b, \ell_b, m_b, \mu_b).$$

The associated Legendre polynomials may be written as follows.

$$P_{\ell}^m(\cos \theta) = \sin^m \theta \sum_{j=0}^{I(\ell, m)} C_{\ell, m, j} (\cos \theta)^{\ell-m-2j}, \quad (65)$$

where

$$I(\ell, m) = \frac{1}{2}(\ell - m) \quad (66)$$

if $(\ell - m)$ is an even number or zero and

$$I(\ell, m) = \frac{1}{2}(\ell - m - 1) \quad (67)$$

if $(\mathcal{L}-m)$ is an odd number, and where

$$C_{\mathcal{L},j} = \frac{(-1)^j (2\mathcal{L}-2j)!}{2^{\mathcal{L}} j! (\mathcal{L}-j)! (\mathcal{L}-2j-m)!} \quad (68)$$

Substituting (65) into (64),

$$S_{ab} = N_a N_b \sum_{j=0}^{I(\mathcal{L}_a, |m_a|)} \sum_{k=0}^{I(\mathcal{L}_b, |m_b|)} C_{\mathcal{L}_a, |m_a|, j} C_{\mathcal{L}_b, |m_b|, k} \int \int \int r_a^{n_a - \mathcal{L}_a + 2j-1} r_b^{n_b - \mathcal{L}_b + 2k-1} e^{-(\mu_a r_a + \mu_b r_b)} (r_a \cos \theta_a)^{\mathcal{L}_a - |m_a| - 2j} (r_a \sin \theta_a)^{|m_a|} (r_b \cos \theta_b)^{\mathcal{L}_b - |m_b| - 2k} (r_b \sin \theta_b)^{|m_b|} \Phi_{m_a}(\varphi_a) \Phi_{m_b}(\varphi_b) dV. \quad (69)$$

Now a transformation is made to confocal elliptic coordinates, which are defined as follows.

$$\xi = \frac{r_a + r_b}{R}$$

$$\eta = \frac{r_a - r_b}{R}$$

$$\varphi = \varphi_a = \varphi_b.$$

The differential element of volume in this coordinate system is

$$dV = \left(\frac{R}{2}\right)^3 (\xi^2 - \eta^2) d\xi d\eta d\varphi.$$

The factors in the integrand of (69) transform as follows.

$$r_a = \frac{R}{2} (\xi + \eta).$$

$$r_b = \frac{R}{2} (\xi - \eta).$$

$$r_a \cos \theta_a = \frac{R}{2} (1 + \xi \eta).$$

$$r_b \cos \theta_b = \frac{R}{2} (1 - \xi \eta).$$

$$r_a \sin \theta_a = r_b \sin \theta_b = \frac{R}{2} \sqrt{\xi^2 - 1} \sqrt{1 - \eta^2}.$$

The exponential factor is

$$\mu_a r_a + \mu_b r_b = \alpha \xi + \beta \eta,$$

where

$$\alpha = \frac{R}{2} (\mu_a + \mu_b),$$

$$\beta = \frac{R}{2} (\mu_a - \mu_b).$$

The integration over φ may be carried out immediately.

$$\int_0^{2\pi} \Phi_{m_a}(\varphi) \Phi_{m_b}(\varphi) d\varphi = \delta_{m_a, m_b} \pi (1 + \delta_{m_a, 0}). \quad (70)$$

Transforming to elliptic coordinates and using (70), equation (69) may be written as follows.

$$S_{ab} = \delta_{m_a, m_b} K_{ab} \sum_{j=0}^{I(\ell_a, m)} \sum_{k=0}^{I(\ell_b, m)} C_{\ell_a, m, j} C_{\ell_b, m, j} J_{jk} (n_a \ell_a n_b \ell_b^{\alpha \beta}),$$

where

$$m = |m_a|,$$

$$K_{ab} = \pi(1 + \delta_{m_a, 0}) N_a N_b, \quad (72)$$

and

$$J_{jk} (n_a \ell_a n_b \ell_b^{\alpha \beta}) = \left(\frac{R}{2}\right)^{n_a + n_b + 1} \int_1^\infty d\xi e^{-\alpha \xi} \int_{-1}^{+1} d\eta e^{-\beta \eta} \\ (\xi + \eta)^{n_a - \ell_a + 2j} (\xi - \eta)^{n_b - \ell_b + 2k} (1 + \xi \eta)^{\ell_a - m - 2j} \\ \ell_b^{-m - 2k} (1 - \xi \eta)^{\ell_b - m - 2k} (\xi^2 - 1)^m (1 - \eta^2)^m. \quad (73)$$

The product of the sum of two quantities to a power times the difference of the same two quantities to a different power may be conveniently written using the binomial product coefficients as follows.

$$(\xi + \eta)^M (\xi - \eta)^{M'} = \sum_{j=0}^{M+M'} f_i(M, M') \xi^{M+M'-i} \eta^i. \quad (74)$$

The binomial product coefficient, $f_i(M, M')$, is defined as follows.

$$f_i(M, M') = (-1)^i \sum_{g=0}^i (-1)^g \binom{M}{g} \binom{M'}{i-g}, \quad (75)$$

where

$$\binom{M}{g} = \frac{M!}{g! (M-g)!}$$

is the ordinary binomial coefficient. Using (74) in (73),

$$J_{jk}(n_a, \ell_a, n_b, \ell_b, m, \alpha, \beta) = \left(\frac{R}{2}\right)^{n_a + n_b + 1} \sum_{i=0}^{2m} \sum_{g=0}^T \sum_{h=0}^{n_a + n_b - i} f_i(m, m)$$

$$f_g(n_a - \ell_a + 2j + 2m - i, n_b - \ell_b + 2k) f_h(\ell_a - m - 2j + i, \ell_b - m - 2k)$$

$$A_{T-g+h}(\alpha) B_{g+h}(\beta), \quad (76)$$

where

$$T = n_a + n_b - \ell_a - \ell_b + 2j + 2k + 2m - i,$$

and

$$A_n(\alpha) = \int_1^\infty e^{-\alpha \xi} \xi^n d\xi,$$

$$B_n(\beta) = \int_{-1}^{+1} e^{-\beta \eta} \eta^n d\eta.$$

The functions $A_n(\alpha)$ and $B_n(\beta)$ are known as the auxiliary functions. They were most conveniently calculated from the following recursion formulas.

$$A_n(\alpha) = [n A_{n-1}(\alpha) + e^{-\alpha}] / \alpha, \quad (77)$$

with

$$A_0(\alpha) = e^{-\alpha} / \alpha. \quad (78)$$

$$B_n(\beta) = [(-1)^n e^{\beta} - e^{-\beta} + n B_{n-1}(\beta)] / \beta, \quad (79)$$

with

$$B_0(\beta) = (e^{\beta} - e^{-\beta}) / \beta. \quad (80)$$

For small values of β , better accuracy in numerical calculations is obtained by expanding the integrand in a power series and then integrating.

$$B_M(\beta) = \sum_{n=0}^{\infty} \frac{(-1)^M + (-1)^n}{(M+n+1) n!} \beta^n. \quad (81)$$

This series converges fairly rapidly. No more than fifteen terms need be taken for eight-place accuracy (Magnusson, 1964).

The program STOLAP, listed in Appendix C, has been written to calculate integrals of the form of (64) using equations (68), (71), (72), (76), (77), (78), (79), (80), (81), and (73).

APPENDIX B

MATRIX ELEMENTS OF x, y, AND z

Using the same notation as in equation (47) for symmetry orbitals the matrix element of a Cartesian coordinate between two symmetry orbitals may be written

$$\left(P_{k'\lambda'}^{(j')} A'_{r'q'}, f_{\Lambda}^{(J)} P_{k\lambda}^{(j)} A_{rq} \right).$$

For D_{4h} ,

$$f_1^{(5)} = x,$$

$$f_2^{(5)} = y,$$

$$f_1^{(6)} = z.$$

Using equation (24),

$$\left(P_{k'\lambda'}^{(j')} A'_{r'q'}, f_{\Lambda}^{(J)} P_{k\lambda}^{(j)} A_{rq} \right) \quad (82)$$

$$= \sqrt{\frac{l_{j'}}{h}} \sum_R D^{(j')}(R^{-1})^*_{k'\lambda'} \left(P_R A'_{r'q'}, f_{\Lambda}^{(J)} P_{k\lambda}^{(j)} A_{rq} \right).$$

The post-factor of the inner product may be written as follows.

$$f_{\Lambda}^{(J)} P_{k\lambda}^{(j)} A_{rq} = \sum_{j''=1}^c \sum_{\mu=1}^{j''} S_{\Lambda\lambda; j''\mu}^{(J, j)*} \psi_{\mu}^{(j'')}, \quad (83)$$

where c is the number of irreducible representations of the group, the $S_{\Lambda\lambda;j''\mu}^{(J,j)}$ are elements of the matrix which reduced the representation formed by the direct product of irreducible representation J and j (Wigner coupling coefficients), and

$$\psi_{\mu}^{(j'')} = \sum_{\Lambda'=1}^j \sum_{\mu'=1}^j S_{\Lambda'\mu';j''\mu}^{(J,j)} f_{\Lambda'}^{(J)} p_{k\mu'}^{(j)} A_{rq} \quad (84)$$

is a function which belongs to row μ of irreducible representation j'' and which depends upon J , j , k , and A_{rq} . Substituting (83) in (82), using the unitary character of the functional substitution operator P_R and equation (20) gives the following.

$$\begin{aligned} & (p_{k'\lambda'}^{(j')} A'_{r'q'}, f_{\Lambda}^{(J)} p_{k\lambda}^{(j)}) \\ &= \sqrt{\frac{\ell_{j'}}{h}} \sum_{j''=1}^c \sum_{\mu=1}^{j''} \sum_{\nu=1}^{j''} S_{\Lambda\lambda;j''\mu}^{(J,j)*} \sum_R D^{(j)}(R^{-1})^*_{k'\lambda'} D^{(j'')}(R^{-1})_{\nu\mu} \\ & (A'_{r'q'}, \psi_{\nu}^{(j'')}). \end{aligned}$$

Using equation (22) and (84),

$$\begin{aligned} & (p_{k'\lambda'}^{(j')} A'_{r'q'}, f_{\Lambda}^{(J)} p_{k\lambda}^{(j)} A_{rq}) \\ &= \sqrt{\frac{h}{\ell_{j'}}} S_{\Lambda\lambda;j'\lambda'}^{(J,j)*} \sum_{\Lambda'=1}^j \sum_{\lambda''=1}^j S_{\Lambda'\lambda'';j'k'}^{(J,j)} (A'_{r'q'}, f_{\Lambda'}^{(J)} p_{k\lambda''}^{(j)} A_{rq}) . \end{aligned} \quad (85)$$

For the magnesium porphin molecule, the use of this formula reduces the number of integrals which must be calculated between Slater orbitals by a factor of eight.

Matrix elements of the Cartesian coordinates between single-term Slater orbitals on two different centers may be expressed in terms of overlap integrals involving other Slater orbitals on the same center. These expressions are derived below.

A Slater orbital, as given in equation (41) may be written as follows.

$$\chi_{n\ell m}^{(\mu)}(r, \theta, \varphi) = N(n \ell |m| \mu) f_{n \ell |m|}(\mu; r, \theta) \Phi_m(\varphi),$$

where

$$f_{n \ell |m|}(\mu; r, \theta) = r^{n-1} e^{-\mu r} P_{\ell}^{|m|}(\cos \theta). \quad (86)$$

Using the standard recursion relations

$$(\ell + 1) P_{\ell+1}(z) - (2\ell + 1) z P_{\ell}(z) + P_{\ell-1}(z) = 0$$

and

$$P_{\ell}'(z) - 2z P_{\ell-1}'(z) + P_{\ell-2}'(z) = P_{\ell-1}(z)$$

and the definition

$$P_{\ell}^m(z) = (1-z^2)^{m/2} \frac{d^m}{dz^m} P_{\ell}(z),$$

the following relations are easily obtained.

$$\cos \theta P_{\ell}^m(\cos \theta) = \frac{1}{2\ell+1} \left[(\ell+m) P_{\ell-1}^m(\cos \theta) + (\ell-m+1) P_{\ell+1}^m(\cos \theta) \right]. \quad (87)$$

$$\sin \theta P_{\ell}^m(\cos \theta) = \frac{1}{2\ell+1} \left[P_{\ell+1}^{m+1}(\cos \theta) - P_{\ell-1}^{m+1}(\cos \theta) \right]. \quad (88)$$

Using (86), (87), and (88),

$$r \cos \theta f_{n\ell}^{(\mu;r,\theta)} = \frac{\ell+|m|}{2\ell+1} f_{n+\ell,\ell-1,|m|}^{(\mu;r,\theta)} + \frac{\ell-|m|+1}{2\ell+1} f_{n+\ell,\ell+1,|m|}^{(\mu;r,\theta)}, \quad (89)$$

$$r \sin \theta f_{n\ell}^{(\mu;r,\theta)} = \frac{1}{2\ell+1} f_{n+1,\ell+1,|m|+1}^{(\mu;r,\theta)} - \frac{1}{2\ell+1} f_{n+1,\ell-1,|m|+1}^{(\mu;r,\theta)} \quad (90)$$

The following relations may be obtained by straightforward integration.

$$\int_0^{2\pi} \tilde{\Phi}_{m'}(\varphi) \cos \varphi \tilde{\Phi}_m(\varphi) d\varphi$$

$$= 0 \text{ if } m' \geq 0 \text{ and } m < 0 \text{ or if } m' < 0 \text{ and } m \geq 0,$$

$$= \frac{\pi}{2} \left\{ \delta_{|m'|, |m|+1} + \delta_{m', 1} \delta_{m, 0} + \delta_{|m|, |m'|+1} + \delta_{m, 1} \delta_{m', 0} \right\} \quad (91)$$

otherwise.

$$\int_0^{2\pi} \Phi_{m'}(\varphi) \Phi_m(\varphi) d\varphi$$

= 0 if $|m'|$ and $|m|$ are either both even or both odd,

$$= (-1)^{\frac{1}{2}(|m|+|m'|-1)} \frac{(-m)}{|m|} \int_0^{2\pi} \Phi_{m'}(\varphi) \cos \varphi \Phi_{(-m)}(\varphi) d\varphi$$

$$= (-1)^{\frac{1}{2}(|m|+|m'|-1)} \frac{(-m')}{|m|} \int_0^{2\pi} \Phi_{(-m')}(\varphi) \cos \varphi \Phi_m(\varphi) d\varphi \quad (92)$$

if $|m|$ is even.

With the coordinate system chosen in the standard orientation shown in Figure 6, page ,

$$x = r_a \sin \theta_a \cos \varphi = r_b \sin \theta_b \cos \varphi,$$

$$y = r_a \sin \theta_a \sin \varphi = r_b \sin \theta_b \sin \varphi,$$

$$z = r_a \cos \theta_a - \frac{R}{2} = \frac{R}{2} - r_b \cos \theta_b.$$

Using these expressions and equations (89), (90), (91), and (92), the relations between matrix elements and overlap integrals involving Slater orbitals which are given below can be obtained in a straightforward manner.

Let

$$\langle \chi_{n_a} \ell_{a a} m_a \mu_a | x | \chi_{n_b} \ell_{b b} m_b \mu_b \rangle = \left(\chi_{n_a} \ell_{a a}^{(\mu_a)} \right) \times \left(\chi_{n_b} \ell_{b b}^{(\mu_b)} \right),$$

and let the matrix elements of y and z be denoted similarly. Let

$$\begin{aligned}
 \langle n_a \ell_a m_a \mu_a | n_b \ell_b m_b \mu_b \rangle &= \begin{pmatrix} \mu_a \\ \ell_a m_a \end{pmatrix} \begin{pmatrix} \mu_b \\ \ell_b m_b \end{pmatrix} \\
 \langle n_a \ell_a m_a \mu_a | z | n_b \ell_b m_b \mu_b \rangle &= \delta_{m_a, m_b} \left\{ \frac{R}{2} \langle n_a \ell_a m_a \mu_a | n_b \ell_b m_b \mu_b \rangle \right. \\
 &\quad - \frac{\sqrt{(2n_b+2)(2n_b+1)}}{2\mu_b \sqrt{2\ell_b+1}} \left[\sqrt{\frac{(\ell_b+|m_b|)(\ell_b-|m_b|)}}{(2\ell_b-1)} \langle n_a \ell_a m_a \mu_a | n_b+1, \ell_b+1, m_b, \mu_b \rangle \right. \\
 &\quad \left. \left. + \sqrt{\frac{(\ell_b-|m_b|+1)(\ell_b+|m_b|+1)}}{2\ell_b+3} \langle n_a \ell_a m_a \mu_a | n_b+1, \ell_b+1, m_b, \mu_b \rangle \right] \right\}.
 \end{aligned}$$

Because of the choice of coordinate system and because the Slater orbitals are real, it is possible to exchange the prefactor and post-factor in matrix elements of x or y . To use the formulas given below, the functions should be chosen such that

$$|m_a| \leq |m_b|.$$

$$\langle n_a \ell_a m_a \mu_a | x | n_b \ell_b m_b \mu_b \rangle$$

$$= \delta_{|m_a|, |m_b|+1} \frac{\sqrt{(1+\delta_{m_b,0})(2n_b+1)(2n_b+2)}}{4\mu_b \sqrt{2\ell_b+1}}$$

$$\left\{ \sqrt{\frac{(\ell_b+|m_b|+2)(\ell_b+|m_b|+1)}{2\ell_b+3}} \langle n_a \ell_a m_a \mu_a | n_b+1, \ell_b+1, |m_b|+1, \mu_b \rangle \right. \\ \left. - \sqrt{\frac{(\ell_b-|m_b|)(\ell_b-|m_b|-1)}{2\ell_b-1}} \langle n_a \ell_a m_a \mu_a | n_b+1, \ell_b-1, |m_b|+1, \mu_b \rangle \right\}.$$

$$\langle n_a \ell_a m_a \mu_a | y | n_b \ell_b m_b \mu_b \rangle$$

= 0 if m_a and m_b are both even or both odd,

$$= (-1)^{\frac{1}{2}(|m_b|+|m_a|-1)} \frac{(-m_b)}{|m_b|} \langle n_a \ell_a m_a \mu_a | x | n_b \ell_b (-m_b) \mu_b \rangle$$

if $|m_b|$ is odd and $|m_a|$ even,

$$= (-1)^{\frac{1}{2}(|m_b|+|m_a|-1)} \frac{(-m_a)}{|m_a|} \langle n_a \ell_a (-m_a) \mu_a | x | n_b \ell_b m_b \mu_b \rangle$$

if $|m_b|$ is even and $|m_a|$ odd.

APPENDIX C

LISTINGS OF COMPUTER PROGRAMS

\$IBFTC STOLAP

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      SUBROUTINE STOLAP(NA,LA,MA,ZA,NB,LB,MB,ZB,R,S)
C   THIS SUBROUTINE CALCULATES THE OVERLAP INTEGRAL BETWEEN
C   TWO SLATER ORBITALS. NA,LA,MA AND NB,LB,MB ARE THE
C   QUANTUM NUMBERS OF THE TWO ORBITALS. ZA AND ZB ARE THE
C   ORBITAL EXPONENTS, AND R IS THE DISTANCE BETWEEN THE TWO
C   CENTERS. THE VALUE OF THE OVERLAP INTEGRAL IS RETURNED
C   IN S.
      IF (R.EQ.0.) S=SING(NA,LA,MA,ZA,NB,LB,MB,ZB)
      IF(R.EQ.0.) GO TO 99
      ALPHA=R*(ZA+ZB)/2.
      BETA=R*(ZA-ZB)/2.
      IF(MA.EQ.MB) GO TO 10
      S=0
      GO TO 99
10  M=MA
      CNORM=(2*LA+1)*(2*LB+1)
      CNORM=SQRT(CNORM)
      CNORM=CNORM*SQRT(FACT(LA-M)*FACT(LB-M))
      CNORM=CNORM/SQRT(FACT(LA+M)*FACT(LB+M))
      CNORM=CNORM/SQRT(FACT(2*NA)*FACT(2*NB))
      OCNORM=0.5*(2.*ZA)**NA*(2.*ZB)**NB*SQRT(4.*ZA*ZB)
      I*CNORM*(R/2.)**(NA+NB+1)
      JMAX=IBIG(LA,M)+1
      KMAX=IBIG(LB,M)+1
      S=0.
      MN=M+1
      DO 11 J=1,JMAX
      DO 11 K=1,KMAX
      DO 11 I=1,MN
      W=0.
      IGX=NA+NB-LA-LB+2*J+2*K+2*M-2*I-2
      IHX=NA+NB-IGX
      IGX=IGX+1
      IHX=IHX+1
      DO 12 IG=1,IGX
      DO 12 IH=1,IHX
      W1=FBPC(IG-1,NA-LA+2*J+2*M-2*I,NB-LB+2*K-2)
      W2=FBPC(IH-1,LA-M-2*J+2*I,LB-M-2*K+2)
12  W=W1*W2*AUX(IGX-IG+IHX-1,ALPHA)*BAUX(IG+IHX-2,BETA)+W
      SNOM=(-1)**(I-1)*NOM(M,I-1)
11  S=SNOM*CLEG(LA,M,J-1)*CLEG(LB,M,K-1)*W+S

```

```

      S=S*CNORM
99  RETURN
    END

```

```

$IBFTC AUX      NODECK
      FUNCTION AUX(K,ALPHA)
C   THIS FUNCTION CALCULATES THE FIRST AUXILIARY FUNCTION.
      D=EXP(-ALPHA)
      AK=D/ALPHA
      IF(K.EQ.0) GO TO 10
      DO 11 I=1,K
      AI=I
11  AK=(AI*AK+D)/ALPHA
10  AUX=AK
      RETURN
    END

```

```

$IBFTC BAUX      NODECK
C   THIS FUNCTION CALCULATES THE SECOND AUXILIARY FUNCTION.
      FUNCTION BAUX(K,BETA)
      DIMENSION T(30)
      IF(ABS(BETA).GT.1.E-12) GO TO 10
      DENOM=K+1
      B=1+(-1)**K
      B=B/DENOM
      GO TO 99
10  IF(K.NE.0) GO TO 11
      D=EXP(BETA)
      B=(D-1./D)/BETA
      GO TO 99
11  IF(BETA.GT.0.) GO TO 12
      SN=(-1)**K
      SUB=-BETA
      GO TO 13
12  SUB=BETA
      SN=1
13  IF(SUB.LE.4.) GO TO 14
      D=EXP(SUB)
      B=(D-1./D)/SUB
      DO 20 I=1,K
      AI=I
20  B=((-1.)**I*D-1./D+AI*B)/SUB
      B=SN*B
      GO TO 99
14  B=(-1)**K+1
      DENOM=K+1
      B=B/DENOM
      DO 30 N=1,30

```



```

22 FAC=1
   DO 23 I=1,N
     AI=I
23  FAC=FAC*AI
     T(N)=((-1.)**K+(-1.)**N)*SUB**N
     DENOM=K+N+1
     DENOM=DENOM*FAC
     IF(DENOM.GT.1.E+15) T(N)=0.
30  T(N)=T(N)/DENOM
     DO 31 N=1,30
31  B=B+T(N)
     B=SN*B
99  BAUX=B
     RETURN
     END

```

```

$IBFTC NOM      NODECK
      FUNCTION NOM(N,M)
C  NOM IS THE BINOMIAL COEFFICIENT.
      DIMENSION NPAS(15,15)
      IF(N-M) 13,14,15
13  NOM=0
      GO TO 10
14  NOM=1
      GO TO 10
15  N1=N+1
      M1=M+1
      DO 17 I=1,N1
        DO 17 J=1,M1
17  NPAS(I,J)=0.
      DO 11 I=1,N1
        NPAS(I,1)=1
11  NPAS(I,I)=1
      IF(M.EQ.0.OR.M.EQ.N) GO TO 16
      DO 12 J=2,M1
        DO 12 I=J,N1
12  NPAS(I,J)=NPAS(I-1,J)+NPAS(I-1,J-1)
16  NOM=NPAS(N1,M1)
10  RETURN
     END

```

```

$IBFTC FBPC      NODECK
      FUNCTION FBPC(I,J,K)
C  THIS FUNCTION FINDS THE BINOMIAL PRODUCT COEFFICIENT FOR
C  THE ITH TERM OF THE EXPANSION OF (X-Y)**J*(X+Y)**K.
      IF(I.NE.0) GO TO 11
      FBPC=1
      GO TO 12

```

```

11 NF=NOM(K,I)
   DO 10 L=1,I
10 NF=(-1)**L*NOM(J,L)*NOM(K,I-L)+NF
   FBPC=(-1)**I*NF
12 RETURN
   END

```

```

$IBFTC IBIG      NODECK
      FUNCTION IBIG(L,M)
C   THIS FUNCTION FINDS THE LARGEST INTEGER WHICH IS EQUAL TO
C   OR LESS THAN (1/2)(L-M).
      LM=L-M
      IF(LM.LT.0) LM=-LM
      W=LM
      N=LM
      C=W/2.
      D=N/2
      IF(C-D) 10,11,10
11 IBIG=N/2
      GO TO 12
10 IBIG=(N-1)/2
12 RETURN
   END

```

```

$IBFTC CLEG      NODECK
      FUNCTION CLEG(L,M,J)
C   THIS FUNCTION RETURNS THE VALUE OF THE COEFFICIENT OF THE
C   JTH TERM OF THE ASSOCIATED LEGENDRE POLYNOMIAL WITH
C   INDICES L AND M.
      MFAC=1
      IF(M.EQ.0) GO TO 10
      DO 11 I=1,M
11 MFAC=I*MFAC
10 CLEG=NOM(2*L-2*J,L+M)*NOM(L,J)*NOM(L+M,M)*MFAC
      CLEG=(-1.)**J*CLEG/2.**L
      RETURN
   END

```

```

$IBFTC FACT      NODECK
      REAL FUNCTION FACT(N)
C   THIS FUNCTION CALCULATES N FACTORIAL.
      FACT=1
      IF(N.EQ.0) GO TO 12
      DO 11 I=1,N
      AN=I
11 FACT=FACT*AN
12 RETURN

```

END

\$IBFTC SING NODECK

FUNCTION SING(N,L,M,Z,NN,LL,MM,ZZ)

C THIS FUNCTION CALCULATES THE OVERLAP INTEGRAL FOR TWO

C SLATER ORBITALS ON A SINGLE CENTER.

IF(L.EQ.LL.AND.M.EQ.MM) GO TO 10

SING=0.0

GO TO 99

10 SING=Z**N*ZZ**NN*SQRT(Z*ZZ)*FACT(N+NN)*2.0**(N+NN+1)

SING=SING/((Z+ZZ)**(N+NN+1)*SQRT(FACT(2*N)*FACT(2*NN)))

99 RETURN

END

\$IBFTC SYMAS

SUBROUTINE SYMAS (A,VALU,N,D)

C SYMAS DIAGONALIZES THE N BY N MATRIX A. THE EIGENVALUES

C ARE RETURNED IN THE VECTOR VALU, AND THE EIGENVECTORS

C IN A. A SMALL NUMBER SUCH AS 1.0E-15 SHOULD BE ENTERED

C IN D TO CHECK CONVERGENCE.

DIMENSION A(22,22),V(22,22),VALU(22)

E=0.

DO 101 I=1,N

101 E=E+ABS(A(I,I))

R=N

E=E/(5.*R)

DO 102 I=1,N

DO 102 J=1,N

IF (I-J) 103,104,103

104 V(I,J)=1.

GO TO 102

103 V(I,J)=0.

102 CONTINUE

105 DO 106 J=2,N

L=J-1

DO 106 I=1,L

IF (ABS(A(I,J))-E) 106,126,126

126 IF (A(I,I)-A(J,J)) 107,125,107

125 Q=A(I,J)

GO TO 109

107 Q=A(I,J)/(2.*(A(I,I)-A(J,J)))

IF(ABS(Q)-.41421)108,109,109

108 S=2.*Q/(1.+Q*Q)

C=(1.-Q*Q)/(1.+Q*Q)

GO TO 110

109 S=.707106781187

C=.707106781187

IF (Q) 111,110,110

```

111 S=-S
110 Q=A(I,J)*(C*C-S*S)+S*C*(A(J,J)-A(I,I))
    R=A(I,I)*C*C+A(J,J)*S*S+2.*S*C*A(I,J)
    A(J,J)=A(I,I)*S*S+A(J,J)*C*C-2.*S*C*A(I,J)
    A(I,J)=Q
    A(I,I)=R
    A(J,I)=A(I,J)
    DO 112 K=1,N
    IF (K-I) 113,114,113
113 IF (K-J) 115,114,115
115 R=A(I,K)*C+A(J,K)*S
    A(J,K)=A(J,K)*C-A(I,K)*S
    A(K,J)=A(J,K)
    A(I,K)=R
    A(K,I)=A(I,K)
114 R=V(K,I)*C+V(K,J)*S
    V(K,J)=V(K,J)*C-V(K,I)*S
112 V(K,I)=R
106 CONTINUE
    DO 116 J=2,N
    L=J-1
    DO 116 I=1,L
    IF (ABS(A(I,J))-E) 116,105,105
116 CONTINUE
    IF (E-D) 117,117,118
118 E=E/10.
    GO TO 105
117 DO 119 I=1,N
    VALU(I)=A(I,I)
    DO 119 J=1,N
119 A(I,J)=V(I,J)
    RETURN
    END

```

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