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DEGENERATE PERTURBATION THEORY†

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ABSTRACT. The algebraic structure of degenerate Rayleigh-Schroedinger perturbation theory is reviewed. There are a number of different but equivalent algorithms which generate this perturbation series; we argue that the frequent need to carry out infinite-order partial summations selects one of these algorithms as the most efficient. Recent developments include coupled-cluster formulations for open shells, a new diagrammatic representation, and the concept of incomplete model subspaces. These subjects are reviewed, as well as some applications.

1. INTRODUCTION

Degenerate perturbation theory, in the Rayleigh-Schroedinger form which exhibits the linked-cluster feature, is being used in quantum chemistry in several different ways. On the one hand it provides a general *ab initio* theory of effective Hamiltonians. It should, therefore, be able to shed light on the various semi-empirical Hamiltonians employed by quantum chemists, such as π -electron Hamiltonians, the Slater-Condon parametrization for atomic spectra, MINDO etc., and some which have more of a solid-state flavor, such as crystal-field and ligand-field models, and also Heisenberg-like spin Hamiltonians. Of course this formalism also applies when one is only interested in the ground state, for cases where accidental degeneracy leads to several strongly-mixed configurations. Examples are the beryllium atom and molecular potential-surface calculations, particularly at large internuclear separations and for difficult cases such as the N_2 molecule. And even though nondegenerate techniques may often be adequate for the ground states of closed-shell molecules, the excitation spectra of these molecules require some form of open-shell (degenerate or quasi-degenerate) treatment. Another useful feature of the full many-body formalism is that of "core-valence separation." This feature is useful even in cases where degeneracy is of little or no interest, such as for the calculation of ionization potentials and electron affinities. Still another feature, which so far has been largely overlooked by quantum chemists, is that the general formalism

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also provides linked-cluster prescriptions for electronic properties other than energy, i.e., for the calculation of expectation values and transition matrix elements of a general physical operator.

Much of this talk will be tutorial, reviewing material which should be well known to the practitioners in this field. I'm going to focus primarily on algebraic aspects, because I have found that confusion or misunderstanding is frequently rooted in these aspects, and the use of diagrams would tend to obscure these issues. For further details and references, I recommend a recent survey article.¹ I will also review several recent formal developments.

Since I am not a quantum chemist I will not attempt to discuss calculations in any detail; I will simply mention some applications that serve to illustrate various pedagogical points. I hereby apologize to investigators whose work is not mentioned.

2. THE BASIC FORMAL STRUCTURE

The simplest way to introduce the concept of an effective Hamiltonian is by "partitioning the Hamiltonian," as proposed by Löwdin.² One partitions the Hilbert space into two disjoint subspaces, P and Q, and writes the Schroedinger equation in block-matrix form,

$$\begin{pmatrix} H_{PP} & H_{PQ} \\ H_{QP} & H_{QQ} \end{pmatrix} \begin{pmatrix} \psi_P \\ \psi_Q \end{pmatrix} = E \begin{pmatrix} \psi_P \\ \psi_Q \end{pmatrix} \quad (2.1)$$

The (vector) variable ψ_Q is then eliminated to express the Schroedinger equation in terms of ψ_P alone,

$$\left[H_{PP} + H_{PQ} (E - H_{QQ})^{-1} H_{QP} \right] \psi_P = E \psi_P \quad (2.2)$$

This has the form of an effective Hamiltonian (hereafter denoted by $\mathcal{H}$) acting on the model subspace P.

We observe, however, that (2.2) has several defects which must be resolved before one can claim a practical formalism for many-body systems. First, this $\mathcal{H}$ depends explicitly on E. But this E is unknown, and furthermore, it generally takes on different values for different eigenstates. This negates the goal of fully determining $\mathcal{H}$ before any secular diagonalization to obtain the desired eigenstates. Secondly, we note that the ψ_P 's are generally not mutually orthogonal, since they are merely projections of the orthogonal state vectors onto the subspace P. This means that the present $\mathcal{H}$ is, in effect, a non-Hermitean matrix. (It's eigenvalues E remain real, however.) Finally, the form (2.2) is too abstract for most applications, and takes no account of many-body aspects.

The first step towards a practical many-body formalism is to introduce a perturbative analog of (2.2), namely, the degenerate version of

Brillouin-Wigner perturbation theory.³ One selects an H_0 and $V = H - H_0$, and uses the set of H_0 eigenstates

$$H_0 \phi_i = E_i \phi_i \quad (2.3)$$

to define the two subspaces. That is,

$$\begin{aligned} \Psi &= \sum_i a_i \phi_i \\ &= \sum_{i \in P} a_i \phi_i + \sum_{i \in Q} a_i \phi_i \equiv P\Psi + Q\Psi \end{aligned} \quad (2.4)$$

(We use P and Q interchangeably as labels and as projection operators.) One easily obtains the secular equation

$$[H_0 + P\mathcal{Y}(E_\alpha)] A_\alpha = E_\alpha A_\alpha, \quad (2.5)$$

where α labels the total eigenstate, A_α is the column vector of amplitudes a_i within $P\Psi_\alpha$, and the energy-dependent effective interaction matrix P is determined by

$$\begin{aligned} \mathcal{Y} &= VP + V \frac{Q}{E - H_0} \mathcal{Y} \\ &= V \sum_{n=0}^{\infty} \left(\frac{Q}{E - H_0} V \right)^n P. \end{aligned} \quad (2.6)$$

In effect, we have simply cast (2.2) into a perturbative form. This is an important step, because it allows the use of diagrams to help visualize the many-body aspects, and thereby to organize the practical details of calculation. Unfortunately, however, the explicit energy dependence of this $\mathcal{H} = P[H_0 + \mathcal{Y}(E)]P$ is still a serious problem, especially for many-body systems where this leads to unlinked diagrams and lack of size-consistency.

This problem can be resolved^{1,3} just as in the nondegenerate (closed shell) case, by finding a Rayleigh-Schroedinger analog, $\mathcal{H}$, for the effective interaction operator $P\mathcal{Y}$. An easy way to do this is to first assume exact degeneracy of H_0 within the model space, whereby $H_0 A$ can be replaced by $E_0 A$. (This restriction is not essential; it can easily be removed later.) Equation (2.5) then reduces to

$$P\mathcal{Y}(E_\alpha) A_\alpha = \Delta E_\alpha A_\alpha, \quad (2.7)$$

where $E_\alpha = E_0 + \Delta E_\alpha$. A Taylor-series expansion for $\mathcal{H}$ can be developed by repeated use of this result, but it is easier to proceed in an implicit manner. Assuming that $\mathcal{H}$ exists, whereby $\mathcal{H} = (H_0 P + \mathcal{H})$ and

$$\mathcal{H} A_\alpha = \Delta E_\alpha A_\alpha, \quad (2.8)$$

the desired expansion can be expressed formally as

$$\mathcal{W} = \sum_{n=0}^{\infty} \gamma_n [-\mathcal{W}]^n, \quad (2.9)$$

where

$$\gamma_n = \frac{(-1)^n}{n!} \left(\frac{d}{dE_0} \right)^n P \mathcal{Y}(E_0). \quad (2.10)$$

The Rayleigh-Schroedinger expansion for $\mathcal{W}$, i.e. the ordinary power series in V , can now be obtained by first solving (2.9) recursively, in terms of matrix products of the various γ_n 's, and then replacing the latter by their respective perturbation series as deduced from (2.6) and (2.10). Through third order, the result is

$$\begin{aligned} \mathcal{W} &= \gamma_0 + \gamma_1 [-\gamma_0] + \gamma_2 [-\gamma_0]^2 \\ &\quad + \gamma_1 [-\gamma_1] [-\gamma_0] + \mathcal{O}[\gamma_n]^4 \\ &= PVP + PV \frac{Q}{e} VP + PV \frac{Q}{e} V \frac{Q}{e} VP \\ &\quad + PV \left(\frac{Q}{e} \right)^2 V(-PVP) + \mathcal{O}(V^4), \end{aligned} \quad (2.11)$$

where e stands for $E_0 - H_0$. In the resulting many-body diagrams, each matrix-multiplication (and the associated minus sign) between successive γ_n 's is represented by a "fold."^{3,4} Thus, study of (2.8)-(2.11) should dispel the mystery of folded diagrams.

The order of the various γ_n 's in (2.11) is quite important, due to (2.8), which has the consequence that $\mathcal{W}$ is not Hermitean. This is to be expected, of course, because the eigenvectors A_α (of $\mathcal{H} = H_0 P + \mathcal{W}$) are still formally identical to the non-orthogonal Ψ_P^α 's of (2.2).⁵ On the other hand, it is often desirable to have a Hermitean form for $\mathcal{H}$. This is particularly important when one is seeking an ab initio replacement for some semiempirical effective Hamiltonian, since the latter are almost always assumed Hermitean. We simply remark that there is a rigorous "stretching" (non-unitary) transformation which replaces the effective interaction matrix $\mathcal{W}$ by a Hermitean analog $\mathcal{X}$,

$$\mathcal{X} = \frac{1}{2} \left[(1+\theta)^{\frac{1}{2}} (H_0 + \mathcal{W}) (1+\theta)^{-\frac{1}{2}} + \text{h.c.} \right] - H_0, \quad (2.12)$$

where the P-space matrix θ also has a well-defined perturbation expansion of Rayleigh-Schroedinger type. Expansion of $(1+\theta)^{\pm \frac{1}{2}}$ in binomial series thus provides a rigorous Rayleigh-Schroedinger expansion for $\mathcal{X}$. (The indicated treatment of H_0 is necessary only for the quasidegenerate case, where $H_0 A \neq E_0 A$.) On the other hand, the apparently naive approximation

$$\mathcal{K} \approx \frac{1}{2}(\mathcal{W} + \mathcal{W}^\dagger) \quad (2.13)$$

has often been used, and we believe that this should be sufficient for essentially all practical purposes. The lack of Hermiticity in $\mathcal{W}$ has been found to be fairly weak, in all applications to date that we are aware of, provided the calculation is otherwise reasonably converged. [In any event, corrections are straightforward to obtain from (2.12).]

Finally, we want to emphasize that this formalism is "complete" in the sense that expectation values and transition matrix elements of an arbitrary operator $\mathcal{O}$ can also be obtained entirely in terms of model-space quantities. Introducing the effective operator matrix

$$\mathcal{M}(\mathcal{O}) = (I + \Theta)^{-\frac{1}{2}} (\Omega^\dagger \mathcal{O} \Omega) (I + \Theta)^{-\frac{1}{2}}, \quad (2.14)$$

where Ω is the wave operator (for intermediate normalization) defined by $\Psi_\alpha = \Omega |P\Psi_\alpha\rangle$, we obtain the identity

$$\langle \hat{A}_\alpha | \mathcal{M}(\mathcal{O}) | \hat{A}_\beta \rangle = \frac{\langle \Psi_\alpha | \mathcal{O} | \Psi_\beta \rangle}{(\langle \Psi_\alpha | \Psi_\alpha \rangle \langle \Psi_\beta | \Psi_\beta \rangle)^{\frac{1}{2}}} \quad (2.15)$$

The $\hat{A}_\alpha$'s are the orthonormal eigenvectors of the Hermitean operator $\mathcal{H} = (H_0 + \mathcal{K})$. This effective operator technique has been quite useful in nuclear physics.⁵ An obvious use in quantum chemistry would be for the study of electromagnetic transition elements, but I am not aware of any such applications to date.

For many-body systems and "complete" model subspaces (see below), we have shown³ that each $\langle \Phi |$, $|\Phi \rangle$ element of the matrices $\mathcal{W}$, $\mathcal{K}$, and $\mathcal{M}(\mathcal{O})$ has a fully linked Rayleigh-Schroedinger-type expansion. Diagrammatic aspects are reviewed in Refs. 1, 4, and 5.

3. ALTERNATIVE FORMULATIONS AND THE PROBLEM OF CONVERGENCE

A few of the initial exploratory applications of degenerate perturbation theory to chemical systems have shown remarkably good convergence. Unfortunately, however, these results are almost certainly not representative for general chemical systems, since they were obtained for small, few-electron systems where the strong shell structure provides unusually large energy denominators. Indeed, a number of other applications have found convergence to be a serious problem, where acceptable results could be obtained only by some combination of careful choices for H_0 and P and/or some infinite-order partial summation. This is consistent with general experience in nuclear physics, where many of the interesting applications have required some form of infinite-order partial summation.^{5,6} I therefore think it important, for the sake of future progress in this field, to recognize that some form of partial summation will often be necessary.

I also want to emphasize that the variety of possible and potentially useful partial summations is considerably greater than what most quantum chemists have recognized so far. Most chemical applications to date have been restricted to the simplest class of summations, namely those of the denominator-shift type. As an example of a more complex possibility, let me suggest that RPA-type summation may be necessary to deal accurately with σ -polarization effects within effective π -electron Hamiltonians. Good sources for techniques that have been employed in nuclear physics may be found in Refs. 5 and 6.

I now want to mesh these remarks about partial summation with comments about the plethora of alternative and seemingly different versions of degenerate Rayleigh-Schroedinger perturbation theory that can be found in the literature. It is a curious and reassuring fact that almost all of these alternative formulations, for Hermitean quasi-degenerate Rayleigh-Schroedinger n^{th} perturbation theory, lead to identical algebraic expressions for the n^{th} order perturbation terms. That is, they are merely different algorithms for generating a single, uniquely defined, perturbation expansion. This result is not as trivial as it may first appear, because, for a given model space P , the various formulations for $\mathcal{H}$ could conceivably differ by unitary transformations within P . For a summary of these various alternatives and their formal connections, see Refs. 1 and 7.

If one could always be content with, say, a third-order calculation, then any of these equivalent formulations would be quite satisfactory. Performing infinite-order summations is a very different matter, however, since this requires considerable insight about the general structure of the series in high orders. An important corollary is that the "renormalized" expansion (the expansion which remains after performing the partial summation) should also be fairly transparent, so that the remaining perturbative corrections can be studied without ambiguity or danger of double-counting, bearing in mind also that further partial-summation may sometimes be desirable. In short, the formalism should provide an efficient and flexible bookkeeping system.

From this perspective, we believe that the version presented in Section 2 will prove to be most useful in the long run, for the following reason. The exact Hermitean Rayleigh-Schroedinger result was obtained there by means of three successive power-series expansions, as indicated in (2.6), (2.9), and (2.12). The first of these has an obvious geometric-series character, and likewise for the second, since this amounts to expanding ΔE out of all the Brillouin-Wigner energy denominators $(E_0 + \Delta E - H_0)^{-1}$. The practical consequence is that these expansions offer a wide variety of opportunities for partial summation. In contrast, the expansion (2.12) has a far more complex character, but on the other hand we have argued that this difficult step can be avoided by means of the trivial recipe (2.13). The virtue of the above approach is, thus, that it clearly separates these "easy" and "difficult but avoidable" aspects. The other equivalent algorithms are all more opaque because they have these aspects mixed together.

Several of the alternative formalisms deserve some further comment. First, the "unitary transformation" or "canonical transformation" method introduced long ago by Van Vleck⁸ and Kemble.⁹ This is by far the oldest general formulation of effective Hamiltonian theory; it is well-known and has been applied in all branches of quantum mechanics, from quantum chemistry to elementary particle theory. The basic idea is to carry out a unitary transformation of H , such that $\tilde{H} = U^{-1}HU$ becomes block-diagonal in the P and Q subspaces. The desired effective Hamiltonian is then $\mathcal{H} = P\tilde{H}P$. In practice this becomes a perturbative procedure, since one uses $H = H_0 + \lambda V$ and

$$U = e^G = \exp(\lambda G_1 + \lambda^2 G_2 + \dots) \quad (3.1)$$

Also, P and Q are defined by H_0 , just as in (2.4). One expands $U^{-1}HU$, collects terms of each order in λ , and then applies the block-diagonal condition $P\tilde{H}Q = (Q\tilde{H}P)^\dagger = 0$ (together with $G_n^\dagger = -G_n$) successively to each order, to determine the G_n 's. (An indeterminacy in this procedure is removed by imposing the Kemble subsidiary conditions $PG_nP = 0$, $QG_nQ = 0$.)

Quite remarkably, the $\mathcal{H}$ from this procedure turns out to be identical to that from (2.12), in every order of perturbation theory. This result has, in fact, been proven in two independent ways, as discussed in Ref. 1. (The first recognition of this important result was by Klein.¹⁰) This result is important because the conceptual simplicity of the transformation approach is quite appealing, and it has thus been pursued for many-electron systems by a number of quantum chemists.¹¹ In practice, however, this approach turns out to be exceedingly tedious and opaque, and it is therefore one of the worst methods from the standpoint of infinite partial summations. (In every case, the explicit results in Ref. 1! are restricted to low orders in V .) This is partly for the reason given above, but it is also because the algebraic series for U does not turn out to have an exponential character (see below),¹ in contrast to the assumed representation (3.1). The latter (exponential) disadvantage has been avoided in an ingenious iterative algorithm of Kvasnicka and Holubec,¹² but their method is still quite tedious in practice. Nevertheless, their method must also be fully equivalent to (2.12), because they have incorporated the Jørgensen condition¹ $(PUP)^\dagger = PUP$. The latter plays a role equivalent to the Kemble subsidiary conditions mentioned above.

Readers should be warned that when an alternative version of the Van Vleck method is used, based on a succession of unitary transformations,

$$U' = U_1 U_2 U_3 \dots = e^{\lambda G_1} e^{\lambda^2 G_2} e^{\lambda^3 G_3} \dots \quad (3.2)$$

the result is not equivalent to the other methods discussed above. In fact, $U' - U \sim V^3$ and $\mathcal{H}' - \mathcal{H} \sim V^4$. The "generalized Van Vleck" method of Kirtman (see below) is also different.

For completeness, we should also mention the approach of Hirschfelder and Silverstone and their collaborators.¹³ This is notable because its philosophy and formal characteristics are entirely different from all of the methods referred to above. Their basic idea is to develop each of the eigenvalues and eigenfunctions as a strict Taylor series in V , starting from the solution of the first-order effective Hamiltonian, $P(H_0 + V)P$. (This assumes that all degeneracy is lifted in first order; otherwise the procedure becomes more complicated.) In other words, they diagonalize first and then perturb. This approach does not lead to an effective Hamiltonian. Furthermore, in a test calculation¹⁴ this procedure gave lower accuracy than when the corresponding effective Hamiltonian was calculated to the same order and then diagonalized. We shall say no more about this approach. There is still another formulation, due to Kirtman, Certain, and Hirschfelder,¹⁵ which falls somewhere in between Van Vleck-Kemble and Hirschfelder-Silverstone. This has recently been cast into diagrammatic form, but it is not fully linked.¹⁶ Its chief virtue is that it satisfies a " $2n + 1$ rule."

4. RECENT FORMAL DEVELOPMENTS

There are three recent formal developments that are quite interesting and potentially important. These are (a) the coupled-cluster approach for open-shell systems, (b) an alternative diagrammatic representation, and (c) the concept of incomplete model spaces.

The coupled-cluster method originated from the observation of Hubbard¹⁷ and Hugenholtz¹⁸ that the exact (perturbation-theoretic) wavefunction of a closed-shell system can be expressed in the form

$$\Psi = e^{\hat{S}} \Phi_0, \quad (4.1)$$

$$\hat{S} = \sum_{n=1}^N \hat{S}_n, \quad (4.2)$$

where N is the total number of particles. Each $\hat{S}_n$ represents the sum of all linked but open perturbation diagrams which lead to the creation of n particle-hole pairs.⁴ The caret symbol is a reminder that $\hat{S}_n$ is a second-quantized operator, with a creation or annihilation operator attached at the end of each outgoing particle or hole line. Coester and Kümmel¹⁹ noted that by inserting this form of Ψ into the Schrodinger equation, one obtains a set of coupled, nonlinear, and inhomogeneous equations for the various "cluster" component amplitudes.⁴ They suggested that, after some suitable (physically motivated) truncations, one should be able to solve the resulting equations directly, without resorting to a perturbation expansion. In practice, this provides an elegant and convenient way to carry out a number of the partial summation schemes of diagrammatic perturbation theory. (It does not automatically handle all such schemes, however; this method and perturbation theory complement each other by suggesting somewhat different approximations.⁴) There is also some interesting evidence that some approximations which seem "simple"

and "natural" in the context of this approach are well-matched to the quantitative characteristics of correlations in electronic systems.²⁰

It was obviously desirable to extend this approach to open-shell systems, and a number of attempts have been made.²¹ Although some very sophisticated nuclear structure calculations have been done with this approach,²² until a few years ago none of the available formulations were clear, concise, and general. A beautifully clean formulation was finally presented by Lindgren,²³ based on two key ingredients: By elementary manipulation of the Schroedinger equation he obtained the operator identity

$$[\Omega, H_0] = V\Omega - \Omega V\Omega, \quad (4.3)$$

where $\Omega = \Omega P$ and $\Psi_\alpha = \Omega |P\Psi_\alpha\rangle$. He also noted that the form (4.1) is inadequate for open-shell systems, and should be replaced by

$$\Omega = \{e^{\hat{S}}\} = \sum_{r=0}^{\infty} \frac{1}{r!} \{\hat{S}^r\}, \quad (4.4)$$

where $\{ \}$ indicates normal-ordering of the various creation and annihilation operators. Failure to do this would lead to many spurious terms,¹ and thereby greatly complicate the formalism. (This point was also recognized by Kümmel and coworkers,²⁴ but was not clearly stated.)

It is easy to see that systematic use of (4.3) as a recursion formula will generate the Rayleigh-Schroedinger expansion for Ω , and thus for $\mathcal{W} = PV\Omega$, the effective interaction matrix of (2.8)-(2.11). Following this procedure, Lindgren was able to prove by induction that the perturbation-theoretic Ω does indeed have the form (4.4), where each term in $\hat{S}$ is fully connected and is also "open," in the sense of always leading to states in the Q subspace. (It then follows that $\mathcal{W} = PV\Omega$ is fully linked.) In a similar manner, Lindgren then obtained a formal equation for $\hat{S}$ itself, which translates into the desired inhomogeneous and nonlinear set of equations for the cluster amplitudes within $\hat{S}$. This provides an open-shell analog of the coupled-cluster technique. In view of the discussion in Section 2, we argue that the resulting $\mathcal{W}$ may be simply hermitized by means of (2.13). On the other hand, Lindgren states without any detailed justification that the individual matrix elements of $\mathcal{W}$ need not separately conserve the numbers of valence particle and valence hole lines. (See his Figs. 9 and 13.) This feature is very likely wrong, in view of the discussion below about incomplete model spaces.

We now digress for a moment in order to avoid some potential confusion. In commenting on the Van Vleck-Kemle method in Section 3 we remarked that the perturbation expansion of U does not turn out to have an exponential character, whereby the ansatz $U = e^G$ leads to opaque and tedious algebra. This may seem inconsistent with (4.4), but there is really no conflict here. The wave operator Ω is non-unitary [in fact, the connection is $UP = \Omega P(P\Omega^\dagger \Omega P)^{-1/2}$], and furthermore $\hat{S}$ is a second-quant-

tized operator. An elementary (non-many-body) quantum system can always be regarded formally as a "one body" system, for which e^S reduces to $1 + S$. In short, (4.4) is a statement about many-body aspects, and not about the basic algebraic structure.

An alternative to the usual diagrammatic representation³ for $\mathcal{W}$ has been introduced by Hose and Kaldor.²⁵ They express the full correlated wavefunction in the form

$$\Psi_\alpha = \sum_{i \in P} a_{i\alpha} \Omega_i \Phi_i, \quad (4.5)$$

where the diagrams of $\Omega_i \Phi_i$ utilize Φ_i as a "vacuum state," in complete analogy to the usual treatment of the closed-shell case, (4.1). They point out that this leads to fewer diagrams, and also to an automatic cancellation of some terms which appear in both "folded" and "ordinary" diagrams of the usual representation. On the other hand, the detailed rules for deciding which orbitals each internal line is to be summed over are more complicated and tedious to implement. The relation of the diagrams to (2.6)-(2.11) is also less obvious, and we therefore suspect that the range of possibilities for partial summation is reduced. (Their claim of superiority from the partial-summation standpoint is groundless, in view of the many sophisticated nuclear applications.^{5,6}) For low orders of perturbation theory, however, the choice of diagrams is really only a matter of taste.

Quite recently, Jeziorski and Monkhorst²⁶ have developed a coupled-cluster analog of the Hose-Kaldor diagrammatic form, using $\Omega_i = e^{S(i)}$ within (4.5). Since $S(i)$ acts only on Φ_i , its behavior is similar to that of the closed-shell case (4.1), and the explicit normal-ordering of (4.4) is not required. They also employ (4.3), so their analysis has some parallels with that of Lindgren.²³ (Their severe criticism of Ref. 23 is due to a misunderstanding; Lindgren's operational procedure is unambiguous, and does, in fact, determine the desired fully-linked S_n amplitudes. The existence of the latter was established by an independent argument, as outlined above.) If and when this method is applied in practice, the relative merits of this new representation for the correlations should become much clearer.

Another novel feature of Hose and Kaldor²⁵ is their clear specification of the concept of an incomplete model subspace, and their recognition that this leads to a special type of unlinked diagrams. The concept is best explained by example.^{25,26} Consider the calculation of a bound but excited S state of the neutral He atom. Here the natural and obvious model subspace consists of "one-particle, one-hole" states with respect to the $1s^2$ ground configuration, in this case the pair of determinants $1s\alpha ns\beta$ and $1s\beta ns\alpha$. On the other hand, the "complete" model subspace, for which the existence of completely linked expansions is rigorous, would also include the $1s^2$ and ns^2 determinants, since this involves all the ways of distributing two electrons among the $1s$ and ns shells. But here the use of such a complete model subspace is undesirable, for two reasons:

(a) it requires calculation of a larger number of $\mathcal{W}$ (or $\mathcal{X}$) matrix elements, and (b) the wide spread of unperturbed model-state energies₂ may lead to serious convergence problems. (In the present example all ϕ_i states lie in the Auger continuum, for $n > 1$.) Hose and Kaldor emphasize that these motivations for using an incomplete model subspace will arise whenever one considers excited states of a closed-shell system. A further difficulty is that a complete model space for the general case will involve linked many-electron interactions (effective three-electron interactions, etc.).

I thought I had solved this problem back in 1967, by allowing for model spaces P in which each ϕ_i has n' valence holes in addition to n valence particles (see pg. 794¹ of Ref. 3, where the numbers n and n' are required to be the same for every state ϕ_i in P ; the numbers n, n' are "conserved" by $\mathcal{W}$). But I failed to recognize that a special type of unlinked diagram can arise whenever valence particles and valence holes occur simultaneously within P . Examples are shown in Fig. 1, in my diagrammatic representation, for the simplest case where $n' = n = 1$. Hose and Kaldor argue that this special class of unlinked diagrams does no harm, because their effect is still size-consistent. Unfortunately, this is not so, as can be seen by considering a system with many molecules which are well separated from each other. As usual, each linked piece can be summed independently over the entire system. (The necessary corrections for cases where separate linked pieces share common orbital indices, at a common level, are represented by additional diagrams; the latter are all fully linked.)

I have now analyzed these diagrams a bit further, and find that all possible relative "time" orders of the separate linked parts (see Fig. 1) can be combined by means of the factorization theorem,²⁷ giving a net contribution to $\mathcal{W}$ of the form $M_T M_B (E_B^{-1} - E_T^{-1})$, where T and B refer to the top and bottom pairs respectively. For exact degeneracy of the unperturbed particle-hole pair energies, i.e. for $E_T = E_B$, these diagrams cancel identically and may therefore be ignored. Otherwise, in the quasi-degenerate case, their contribution to $\mathcal{W}$ has anti-Hermitean character. But the sum of all such one-particle one-hole linked pieces can be made

Fig. 1. Example of unlinked diagrams resulting from use of an incomplete model subspace.

to vanish, by using orbitals which satisfy the appropriate generalized Brillouin condition. Unfortunately, however, this does not fully resolve the problem, because the foregoing statements apply only to the γ_0 terms in the development (2.11) for $\mathcal{W}$. Unlinked contributions continue to contribute to the higher γ_n 's, and likewise to the θ of (2.12). These residual unlinked terms are undoubtedly small effects, but they are definitely an embarrassment. I regret that at this point I do not see a clean and general formal resolution of this problem. It is important to note, however, that this difficulty arises only for excited states whose overall symmetry is the same as the ground state (e.g., excited $1S$ states of He); in all other cases these unlinked terms must vanish identically, at least after forming the linear combinations required by symmetry. This is reassuring because the present example of "particle-hole" excitations leads to the well-known RPA approximation (as demonstrated in detail on pg. 806 of Ref. 3) and its higher-order generalizations.²⁸ In macroscopic systems, for which the RPA has had many successful applications, the present unlinked terms are all eliminated by momentum conservation.

5. SOME APPLICATIONS

The first quantum-chemical applications of the open-shell linked cluster expansion were by Kaldor.²⁹ These papers are quite pedagogical, and provide a nice introduction for newcomers to this field.

One of my favorite types of applications is to the problem of effective π -electron Hamiltonians.¹ For the relatively simple case of ethylene, with only two π electrons, the present formalism provides rigorous prescriptions for the α , β , and γ parameters, as well as for the "core" energy. This is significant, because some perturbation calculations³⁰ obtained reasonable total correlation energies, for the relevant low-lying eigenstates of ethylene, but failed to properly sort out which correlation contributions should be assigned to which "empirical" parameters. They thereby failed to provide direct ab initio calculations of these parameters (as contrasted to phenomenological fitting of the total eigenenergies). This was due to not using a fully-linked formalism, and/or not using localized instead of molecular π orbitals. Robb and coworkers have recently presented an ethylene calculation which does have these essential features.³¹ Another noteworthy feature is that the so-called "intruder state" problem⁴ was encountered here, and a practical method of dealing with this was developed.³²

Freed and coworkers have done a series of very detailed calculations on the effective valence-shell interactions for light atoms,³³ for a 3d transition metal,³⁴ and for the hydrides CH, NH, and OH.^{35,36} (The latter calculations^{35,36} are directed towards a better understanding of semi-empirical theories such as MNDO.) These papers all emphasize the very important role played by effective many-electron interaction terms (linked contributions involving more than two valence electrons); the latter are absolutely essential for obtaining reasonable agreement with experiment. There is, however, a reward for calculating these additional "nonclassi-

cal" terms--the same set of ab initio interaction parameters provides good ground and low excited energies for a number of different ionization states of the same atom (all the way from F^- to F^{+7} , for example). This is just what the formalism says should happen, but the explicit demonstration is a remarkable tour-de-force. In contrast, semi-empirical schemes generally involve only one and two-body effective interaction terms. This means that the latter parameters must be implicitly including effects of the "true" effective many-electron ("nonclassical") interactions. A number of the above papers^{31,33-36} have examined the "renormalizing" role of these nonclassical terms. This is a murky but very important subject that will surely require much further work.

Potential curves of both ground and excited states have been calculated.^{36,37}

A degenerate application of Lindgren's coupled-cluster approach is described in Ref. 38.

Finally, we wish to comment on applications to ionization potentials and electron affinities, where there is effectively only one valence particle (or valence hole). Here the core-valence-separation aspect is crucial, while degeneracy plays only a very minor role. Several published calculations³⁹ have used the degenerate linked-cluster expansion, arguing that the "energy independent" aspect of this formalism is an advantage as compared to the energy-dependent self-energy operator $\Sigma(E)$ provided by the standard Green's function theory. We disagree. We have shown in detail⁴⁰ that the standard Green's function prescription is equivalent to a partial summation of higher-order terms within our Rayleigh-Schroedinger expansion. Therefore, we consider use of the "Dyson equation" to be a more efficient method for accurate calculation of ionization potentials and electron affinities. (This method can, of course, be implemented either perturbatively or non-perturbatively.) Our type of expansion becomes advantageous only when there is more than one valence particle or hole, where the need for a fully-linked formalism takes precedence.

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