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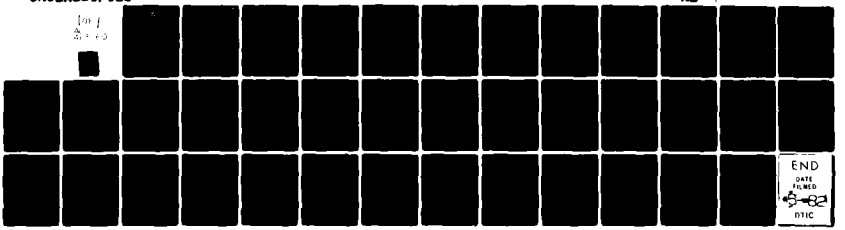

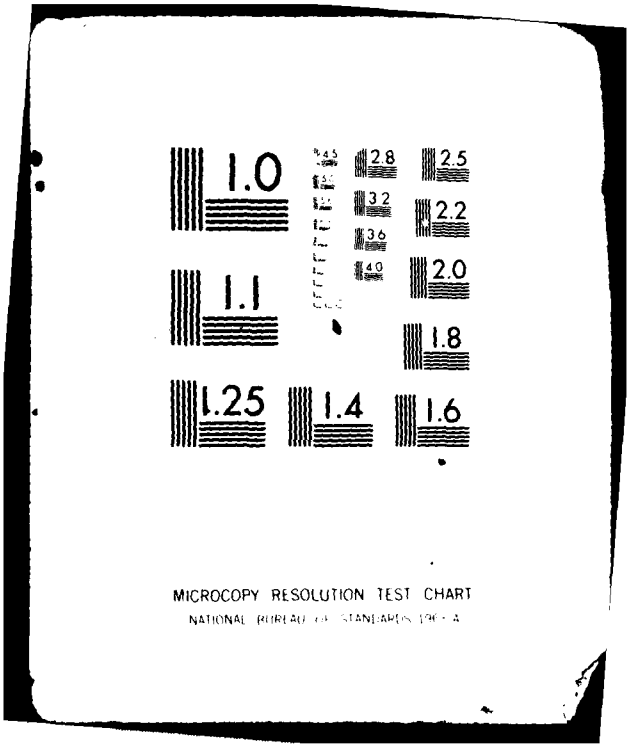
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MULTIDIMENSIONAL MANY-BODY THEORY

to

U. S. OFFICE OF NAVAL RESEARCH

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report, which includes three published papers as Appendices, summarizes the development of a theoretical foundation for the ab-initio calculation of potential energy surfaces for ground and excited states of molecular systems and the nonadiabatic coupling matrix elements between these states. The energies are obtained from an effective Hamiltonian, based on a canonical van Vleck formalism, for which a diagrammatic perturbative expansion is developed. A novel analogous diagrammatic expansion for the nonadiabatic couplings required for dynamical calculations is also presented.

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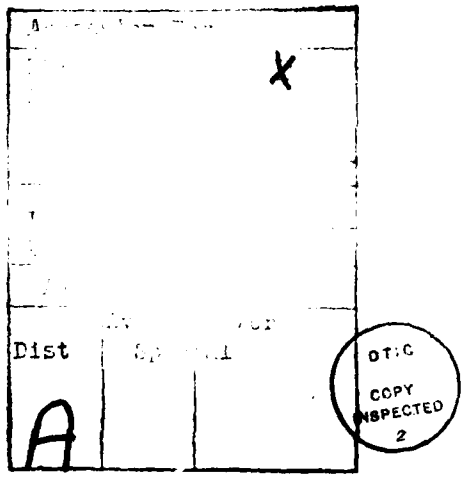

Summary of Technical Effort

This report summarizes the theoretical development of a new approach to calculating molecular ground and excited adiabatic potential energy surfaces and their nonadiabatic coupling matrix elements. The fundamentals of the method will be briefly described herein; the details can be found in the published papers resulting from our investigations, which are included as Appendices to this report.

Methods based on single-reference many-body perturbation theory (MBPT) have been shown to give highly accurate results for a large number of molecules. These methods have become widely used, and the diagrammatic theory has provided an understanding of correlation effects that has led to the now almost universal practice of adding approximately correcting terms to energies calculated by configuration interaction methods. However, the single model-function methods are not appropriate for many systems of chemical interest or for excited states in general. These methods cannot describe the breaking of multiple bonds, and they can obtain only a single state of a given symmetry. Since most geometrical arrangements of a polyatomic system do not have any symmetry, this means that no excited states may be calculated. Furthermore, the proper description of ground states of open shell species often requires more than a single model function. A method with the capability of treating open shell systems and excited states is a necessary tool for the theoretical investigation of many chemical phenomena. In turn, the basic and detailed understanding of these processes is critical to many areas of defense technology.

The development of multidimensional many-body perturbation theory retains the beneficial characteristics of MBPT and extends the potential applicability to all of the cases described above. This generalization ultimately requires a prescription for the energy denominators in the diagrammatic expansion. In place of the single zeroth-order model-state

energy required in MBPT, a set of differing energies, each appropriate for an excited state of interest, must be incorporated. There are several alternatives for this. We have chosen to base our method on a canonical van Vleck formalism. This leads to equal treatment of the states of interest, which are obtained from a single diagonalization of an inherently symmetric effective Hamiltonian matrix. This formalism is presented in detail and compared with other approaches in Appendix A. Our efforts in this phase of development included the adoption of a concise notation which simplified the description of our formalism, as well as that of others. This was important because so many different notations and diagrams have been employed by various authors that the similarities and relationships among their approaches have often been obscured.

We chose to implement the van Vleck formalism analogously to the MBPT method; i.e., in terms of diagrams drawn with respect to an SCF (self-consistent field) determinant. These diagrams provide a compact visual representation and classification of the terms in the arithmetic expressions for each order of the effective Hamiltonian matrix elements. Diagrammatic rule can be set forth which make them entirely sufficient for construction of these matrix elements to any order for an arbitrary set of model space determinants. Appendix B demonstrates the diagrammatic implementation of the method through second order for a model space of non-, singly-, and doubly-excited model states.

Traditionally, quantum chemists and chemical physicists could be divided into two mutually exclusive groups: electronic structure specialists and dynamicists. So far, the interaction between these two factions has been limited to the former providing potential energy surfaces (PES), usually for ground states, to the latter. However, many chemical phenomena involve more than one electronic state. Some of the most interesting processes involve the avoided crossing of states of the same symmetry. The accurate simulation

of such phenomena requires not only the PES but also the nonadiabatic coupling matrix elements. These quantities are not ordinarily calculated; even when they are, a problem arises from their coordinate system dependence because the structure calculations use a different system from the dynamical one. The last phase of our method development was devoted to narrowing this information gap.

Appendix C gives the details of a novel scheme: the diagrammatic perturbative determination of nonadiabatic coupling matrix elements. This approach prescribes the couplings directly in terms of expressions (or diagrams) whose components consist of (1) components of the effective Hamiltonian matrix elements (i.e., two-electron integrals and orbital energy differences) and (2) a set of one-electron-type integrals. With this method, the wavefunction is never explicitly calculated or differentiated. The perturbative approach prescribes the direct construction of increasingly accurate values of the couplings. Furthermore, the same set of diagrams can be used to obtain all of the information required to transform between coordinate systems by simply substituting different one-electron integrals. Thus, the theoretical foundation necessary for the accurate study of dynamical systems using ab initio electronic states and couplings has been laid.

In addition to the subjects of the published works in the Appendices, considerable effort has been devoted to detailed examination of the cancellation of unlinked diagrams and the form of the renormalization terms in third and higher orders. We have also begun implementation of the method into a computer code. Although we do not have final results yet, the results of similar effective Hamiltonian methods indicate their potential successful application to systems of technological interest. To our knowledge, the diagrammatic perturbative calculation of nonadiabatic couplings is unprecedented.

4

Quasidegenerate perturbation theories. A canonical van Vleck formalism and its relationship to other approaches

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Three forms of quasidegenerate perturbation theory are discussed and compared in terms of a common general formulation based on a similarity transformation which decouples the model space and complementary space components of the Hamiltonian. The discussion is limited to formal, rather than many-body (diagrammatic), aspects. Particular attention is focused on a "canonical" form of van Vleck perturbation theory, for which new and highly compact formulas are obtained. Detailed comparisons are made with the Kirtman–Certain–Hirschfelder form of the van Vleck approach and with the approach based on intermediate normalization which has been used as the basis for most of the diagrammatic formulations of quasidegenerate perturbation theory.

I. INTRODUCTION

Quasidegenerate perturbation theory (QDPT) has been receiving increasing attention in recent years (for several excellent discussions and reviews see Refs. 1–10). It provides the perturbation theory analog of "multireference" configuration interaction (CI) techniques,[11,12] which have proved effective in the treatment of potential surfaces and excited states of molecular systems. "One-dimensional" perturbation theory (based on a single-configuration zero-order function) has been quite successful in applications to many near-equilibrium ground state systems and in some other cases in which a single configuration provides a reasonably adequate starting point (for some examples see Refs. 13–21). Practically all such applications have used the many-body form of Rayleigh–Schrödinger perturbation theory (RSPT) (for reviews see, for example, Refs. 22 and 23). This approach has significant advantages over CI techniques because of its use of the linked cluster expansion[24,25] and its "extensivity" property,[2,16,18,26,27] i.e., its correct scaling with the size of the system. While coupled cluster techniques[28] appear capable of extending the range of usefulness of single-configuration based treatments considerably,[27,29] including some nearly degenerate or even fully degenerate cases,[30,31] it still appears desirable to have practical computational techniques based on a multidimensional "model space" as the zero-order approximation. (An alternative strategy is to use unrestricted Hartree–Fock zero-order functions,[18,19] but this appears to have some serious disadvantages.[27]) In fact, QDPT may be expected to provide faster convergence and more general applicability than one-dimensional perturbation expansions, and should become an increasingly important tool for the calculation of highly correlated electronic wave functions and energies of atoms and molecules. (A coupled cluster analog of QDPT has also been formulated.[7,32])

In the present contribution we are concerned primarily with a particular form of van Vleck perturbation theory[4,5,33–42] (VVPT) which, in the spirit of Klein's treatment[5] (see also Jørgensen[42] and Brandow[4]), we shall call "canonical" VVPT. (Klein, as well as Primas,[38,39] treated the case of exactly degenerate, rather than quasidegenerate, zero-order subspaces.) Combining some elements from the treatments of Primas[38,39] and of Jørgensen,[40,41] we shall present a simple derivation of the canonical VVPT formalism, and obtain highly compact expressions for the decoupling operator and the resulting effective Hamiltonian. We shall compare this formalism with another version of VVPT discussed by Kirtman[43,44] and Certain and Hirschfelder,[45,46] and shall present simple derivations of explicit equations connecting canonical VVPT with the more common QDPT formulation based on intermediate normalization and a non-Hermitian model Hamiltonian.[2–10] The different quasidegenerate approaches will be discussed in terms of a common general formulation (see also Klein[5] and Brandow[4]) which clearly shows their relationships. Only the formal aspects of the QDPT expansions will be discussed here. We expect to discuss their many-body realization in terms of diagrammatic expansions in future contributions.

The notation to be used and the common framework for the treatments of the different formalisms are presented in Sec. II. Canonical VVPT is derived in Sec. III. The Kirtman–Certain–Hirschfelder (KCH) form of VVPT and the intermediate normalization form of QDPT are discussed in Secs. IV and V, respectively. The results are discussed in Sec. VI.

II. COMMON FRAMEWORK FOR QUASIDEGENERATE PERTURBATION FORMALISMS

A. Notation

The Hamiltonian H is partitioned into a zero-order part and a perturbation

$$H = H_0 + V \ . \tag{1}$$

The eigenfunctions of H_0 will be written in the form $|t\rangle$, with eigenvalues ϵ_t, as

$$H_0|t\rangle = \epsilon_t|t\rangle \ , \tag{2}$$

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and the set of these eigensolutions will be partitioned into two subsets

$$\{t,u,\ldots\}=\{\alpha,\beta,\ldots\}\cup\{i,j,\ldots\} \tag{3}$$

defining the "model space" $\{\alpha,\beta,\ldots\}$ and its orthogonal complement. The projection operator into the model space is

$$P=\sum_{\alpha}|\alpha\rangle\langle\alpha| \ , \tag{4}$$

and its orthogonal complement is

$$Q=1-P=\sum_{i}|i\rangle\langle i| \ . \tag{5}$$

Any operator A can be partitioned[47] into a block diagonal part A_D and a block off-diagonal part A_X

$$A=A_D+A_X \ , \tag{6}$$

$$A_D=PAP+QAQ \ , \quad A_X=PAQ+QAP \ . \tag{7}$$

For a product of two operators we have

$$(AB)_D=A_D B_D+A_X B_X \ , \quad (AB)_X=A_D B_X+A_X B_D \ . \tag{8}$$

For the Hamiltonian we note that, since H_0 is diagonal,

$$H_D=H_0+V_D \ , \tag{9}$$

$$H_X=V_X \ . \tag{10}$$

B. Quasidegenerate perturbation theory

The essential feature of the various QDPT formalisms is a similarity transformation which block diagonalizes the Hamiltonian

$$\mathcal{H}=U^{-1}HU \ , \tag{11}$$

with

$$\mathcal{H}=\mathcal{H}_D=H_0+W \ , \quad \mathcal{H}_X=0 \ . \tag{12}$$

This is not always the form in which the formalisms are presented (particularly for the intermediately normalized form[1-10]), but it provides a common and simple starting point for straightforward derivation of the equations for all of them. The decoupling operator U is unitary in the van Vleck formalisms and produces a Hermitian effective (or "model") Hamiltonian $P\mathcal{H}P$. It is nonunitary in the intermediate normalization approach (where it is referred to as the "wave operator") and leads to a non-Hermitian $\mathcal{H}$ (which can easily be transformed to a Hermitian form, if desired[4]). The operator W defined in Eq. (12) is referred to as the "level shift" operator, particularly in the exactly degenerate case.

Obviously, $\mathcal{H}$ has the same eigenvalues as H, so that diagonalization of the model Hamiltonian $P\mathcal{H}P$ provides a subset of the eigenvalues of H. The perturbed model functions are

$$U|\alpha\rangle=\sum_{t}|t\rangle\langle t|U|\alpha\rangle \ , \tag{13}$$

and the overlap matrix between them is $PU^{\dagger}UP$ (which is a unit matrix in the van Vleck case). The corresponding eigenfunctions ψ_a of H are obtained by transforming the perturbed model functions (13) with the matrix C of eigenvectors (right eigenvectors in the non-Hermitian case) of $P\mathcal{H}P$:

$$\psi_\alpha=\sum_{\beta}U|\beta\rangle C_{\beta\alpha}=U|\tilde{\alpha}\rangle \ , \tag{14}$$

where

$$|\tilde{\alpha}\rangle=\sum_{\beta}|\beta\rangle C_{\beta\alpha} \tag{15}$$

are the "bonne functions" referred to by Bloch[48] and by Jørgensen and Pedersen.[40,41]

Rewriting Eq. (11) in the form

$$U\mathcal{H}=HU \ , \tag{16}$$

and splitting it into diagonal and off-diagonal blocks using Eqs. (8)–(10), we find that the condition (12) leads to the following implicit equations:

$$H_D U_X=-V_X U_D+U_X\mathcal{H} \ , \tag{17}$$

or, using the definition of W in Eq. (12),

$$[H_0, U_X]=-V_X U_D-V_D U_X-U_X W \ , \tag{18}$$

and

$$W=[H_0, U_D]+V_X U_X+V_D U_D-(U_D-1)W \ . \tag{19}$$

Expanding the operators in orders of the perturbation

$$U=\sum_{n=0}^{\infty}U^{(n)}, \quad \mathcal{H}=\sum_{n=0}^{\infty}\mathcal{H}^{(n)}=H_0+\sum_{n=1}^{\infty}W^{(n)} \ , \tag{20}$$

with

$$U^{(0)}=1 \ , \quad \mathcal{H}^{(0)}=H_0 \ , \quad \mathcal{H}^{(n)}=W^{(n)} \quad (n>0) \ , \tag{21}$$

explicit recursive equations are obtained for $n>0$:

$$[H_0, U_X^{(n)}]=-V_X U_D^{(n-1)}-V_D U_X^{(n-1)}+\sum_{m=1}^{n-1}U_X^{(m)}W^{(n-m)} \ , \tag{22}$$

and

$$W^{(n)}=[H_0, U_D^{(n)}]+V_X U_X^{(n-1)}+V_D U_D^{(n-1)}-\sum_{m=1}^{n-1}U_D^{(m)}W^{(n-m)} \ . \tag{23}$$

However, the decoupling operator U is not fully determined by the condition (12) or, equivalently, by Eqs. (22) and (23) (note that no equation for $U_D^{(n)}$ has been obtained). In fact, multiplication of U by any block diagonal operator does not destroy the decoupling of $\mathcal{H}$. Different supplementary conditions on U (i.e., specification of U_D) then lead to the different QDPT formalisms discussed in the next three sections.

Different choices of U produce different model Hamiltonians, and, while they give the same infinite order eigenvalues and eigenfunctions [ψ_a, Eq. (14)], their truncated (finite-order) results are not generally equivalent. Thus, the choice of subsidiary conditions to complete the specification of U may affect the rate of convergence.

It is well known, of course, that once U_D has been specified, Eq. (22) does provide an explicit equation for $U_X^{(n)}$ through the resolvent operator

$$R_a^{(0)}=\frac{Q}{\epsilon_a-H_0}=\sum_{i}\frac{|i\rangle\langle i|}{\epsilon_a-\epsilon_i} \ , \tag{24}$$

since

$$U_X|\alpha\rangle=-R_a^{(0)}[H_0, U_X]|\alpha\rangle \ . \tag{25}$$

III. CANONICAL VAN VLECK PERTURBATION THEORY

The unitarity of the decoupling operator U in VVPT can be ensured by expressing it in exponential form[35,49]

$$U = e^G \ , \tag{26}$$

with G an anti-Hermitian operator

$$G = -G^\dagger \ . \tag{27}$$

The canonical form of VVPT (compare Klein,[5] Jørgensen,[42] and Brandow[4]) is obtained by completing the specification of U through

$$G = G_X, \quad G_D = 0 \ . \tag{28}$$

The decoupling operator and the transformed Hamiltonian obtained from this condition will be denoted by U_C and $\mathcal{H}_C = H_0 + W_C$, respectively.

In order to obtain a compact formalism we shall use a superoperator notation,[38,39] in which with any operator A we associate a superoperator $\hat{A}$ defined by[50]

$$\hat{A}X = [X, A] = XA - AX \tag{29}$$

(where X is any operator). Positive powers of $\hat{A}$ produce repeated commutators

$$\hat{A}^2 X = [[X, A], A] \ , \tag{30}$$

etc., and the zero power is the identity superoperator

$$\hat{A}^0 X = X \ . \tag{31}$$

As noted by Primas,[38,39] this allows a compact representation of the Baker–Campbell–Hausdorff expansion

$$e^{-G} H e^G = H + [H, G] + \frac{1}{2!}[[H, G], G] + \cdots$$
$$= \sum_{n=0}^{\infty} \frac{1}{n!} \hat{G}^n H = e^{\hat{G}} H \ . \tag{32}$$

It is convenient to partition this expansion into even and odd functions of $\hat{G}$:

$$e^{\hat{G}} = \cosh\hat{G} + \sinh\hat{G} \ . \tag{33}$$

Then, if G satisfies Eq. (28), we find that

$$(\mathcal{H}_C)_D = (e^{\hat{G}} H)_D = \cosh\hat{G}\, H_D + \sinh\hat{G}\, H_X \ , \tag{34}$$

$$(\mathcal{H}_C)_X = (e^{\hat{G}} H)_X = \cosh\hat{G}\, H_X + \sinh\hat{G}\, H_D \ . \tag{35}$$

The decoupling condition (12) can now be written in the form

$$0 = (\mathcal{H}_C)_X = \cosh\hat{G}\, H_X + \frac{\sinh\hat{G}}{\hat{G}} [H_D, G] \ , \tag{36}$$

(note that the superoperator function $\hat{G}^{-1}\sinh\hat{G}$ involves no inverse powers of $\hat{G}$ in its power series expansion). We thus obtain a commutation relation for G:

$$[H_D, G] = -\hat{G}\coth\hat{G}\, H_X \ , \tag{37}$$

or, noting Eqs. (9) and (10),

$$[H_0, G] = -[V_D, G] - \hat{G}\coth\hat{G}\, V_X$$
$$= -[V_D, G] - \sum_{n=0}^{\infty} c_n \hat{G}^{2n} V_X \ , \tag{38}$$

where the power series coefficients c_n are related to the Bernoulli numbers B_{2n} (see, for example, Abramowitz and Stegun[51]):

$$c_n = \frac{2^{2n}}{(2n)!} B_{2n} \ . \tag{39}$$

(Other notations for the Bernoulli numbers are also in use; see, for example, Jolley.[52]) The first few coefficients in the series are

$$c_0 = 1, \quad c_1 = \tfrac{1}{3}, \quad c_2 = -\tfrac{1}{45}, \quad c_3 = \tfrac{2}{945}, \quad c_4 = -\tfrac{1}{4725}, \ \ldots \ . \tag{40}$$

Equation (38) can be expanded order by order:

$$[H_0, G^{(1)}] = -V_X \ ,$$
$$[H_0, G^{(2)}] = -[V_D, G^{(1)}] \ ,$$
$$[H_0, G^{(3)}] = -[V_D, G^{(2)}] - \tfrac{1}{3}[[V_X, G^{(1)}], G^{(1)}] \ ,$$
$$[H_0, G^{(4)}] = -[V_D, G^{(3)}] - \tfrac{1}{3}\{[[V_X, G^{(1)}], G^{(2)}] + [[V_X, G^{(2)}], G^{(1)}]\} \ ,$$
$$[H_0, G^{(5)}] = -[V_D, G^{(4)}] - \tfrac{1}{3}\{[[V_X, G^{(1)}], G^{(3)}] + [[V_X, G^{(2)}], G^{(2)}] + [[V_X, G^{(3)}], G^{(1)}]\} + \tfrac{1}{45}[[[[V_X, G^{(1)}], G^{(1)}], G^{(1)}], G^{(1)}] \ , \tag{41}$$

etc., and converted into explicit equations for the $G^{(n)}$ using the resolvent formalism [Eqs. (24) and (25)]. (Note that $G^{(0)} = 0$.)

The transformed Hamiltonian $\mathcal{H}_C = (\mathcal{H}_C)_D$ can also be obtained compactly in terms of the hyperbolic functions of the superoperator

$$\mathcal{H}_C = \cosh\hat{G}\, H_D + \sinh\hat{G}\, H_X$$
$$= H_D + \frac{\cosh\hat{G} - 1}{\hat{G}} [H_D, G] + \sinh\hat{G}\, H_X$$
$$= H_D - (\cosh\hat{G} - 1)\coth\hat{G}\, H_X + \sinh\hat{G}\, H_X$$
$$= H_D - \mathrm{csch}\hat{G}(\cosh^2\hat{G} - \cosh\hat{G} - \sinh^2\hat{G})\, H_X$$
$$= H_D - \mathrm{csch}\hat{G}(1 - \cosh\hat{G})\, H_X$$
$$= H_D + \tanh(\tfrac{1}{2}\hat{G})\, H_X \ , \tag{42}$$

or

$$W_C = V_D + \tanh(\tfrac{1}{2}\hat{G})\, V_X$$
$$= V_D + \sum_{n=0}^{\infty} t_n (\tfrac{1}{2}\hat{G})^{2n+1} V_X \ , \tag{43}$$

where the power series coefficients t_n are also related to the Bernoulli numbers

$$t_n = \frac{2^{2n+2}(2^{2n+2} - 1)}{(2n+2)!} B_{2n+2} \ . \tag{44}$$

The first few coefficients in this series are

$$t_0 = 1, \quad t_1 = -\tfrac{1}{3}, \quad t_2 = \tfrac{2}{15}, \quad t_3 = -\tfrac{17}{315}, \quad t_4 = \tfrac{62}{2835}, \ \ldots \ . \tag{45}$$

The order-by-order computation of W_C (and of $\mathcal{H}_C$) easily follows:

$$W_C^{(1)} = V_D \ ,$$
$$W_C^{(2)} = \tfrac{1}{2}[V_X, G^{(1)}] \ ,$$
$$W_C^{(3)} = \tfrac{1}{2}[V_X, G^{(2)}] \ ,$$
$$W_C^{(4)} = \tfrac{1}{2}[V_X, G^{(3)}] - \tfrac{1}{24}[[[V_X, G^{(1)}], G^{(1)}], G^{(1)}] \ .$$

$$W_C^{(5)} = \tfrac{1}{2}[V_X, G^{(4)}] - \tfrac{1}{24}\{[[[V_X, G^{(1)}], G^{(1)}], G^{(2)}] + [[[V_X, G^{(1)}], G^{(2)}], G^{(1)}] + [[[V_X, G^{(2)}], G^{(1)}], G^{(1)}]\}, \quad (46)$$

etc. We observe that $W_C^{(n)}$ depends on $G^{(m)}$, $m = 1, 2, \ldots, n-1$. The operator U_C, and thus the perturbed model functions (13), can be obtained from Eq. (26) to the same order as G.

It is clear that the canonical VVPT formalism is entirely expressible within the domain of a Lie algebra, and should thus lead to fully linked diagrammatic expansions which satisfy the extensivity requirement order by order.[26,38,39]

IV. THE KIRTMAN–CERTAIN–HIRSCHFELDER FORM OF VVPT

The canonical form of VVPT was derived from the choice $G_D = 0$. In some earlier work on the van Vleck approach,[53] and more recently in the work of Kirtman[43,44] and of Certain and Hirschfelder[45,46] (KCH), a different choice was made to complete the specification of the decoupling operator. It does not appear possible to specify this choice in terms of a single order-independent equation, so it is stated as a condition connecting different orders of U.

The unitarity condition of U through any order $n > 0$ can be stated in the form

$$\sum_{m=0}^{n} U^{(m)\dagger} U^{(n-m)} = 0 \quad (n > 0) . \quad (47)$$

The sum in Eq. (47) can be split into two parts

$$\sum_{m=0}^{n} U^{(m)\dagger} U^{(n-m)} = \sum_{m=0}^{[n/2]} (1 - \tfrac{1}{2}\delta_{2m,n}) U^{(m)\dagger} U^{(n-m)} + \sum_{m=0}^{[n/2]} (1 - \tfrac{1}{2}\delta_{2m,n}) U^{(n-m)\dagger} U^{(m)} , \quad (48)$$

where $[x]$ denotes the integral part of x. The KCH orthonormalization condition for the perturbed model functions (13) can be obtained by requiring that the diagonal blocks vanish for each of the two sums on the rhs of Eq. (48) separately. Denoting the resulting decoupling operator and transformed Hamiltonian by U_K and $\mathcal{H}_K = H_0 + W_K$, respectively, we get[46]

$$(U_K^{(n)})_D = -\sum_{m=1}^{[n/2]} (1 - \tfrac{1}{2}\delta_{2m,n}) (U_K^{(m)\dagger} U_K^{(n-m)})_D \quad (n > 0) . \quad (49)$$

Together with the decoupling condition (12), or with Eqs. (22) and (23), this completely specifies U_K. It is possible to write U_K in exponential form

$$U_K = e^K , \quad (50)$$

with $K = -K^\dagger$, but there appears to be no advantage for this form in the KCH treatment.[43–46]

Using Eqs. (16) and (20), we can derive the recursion relation[54]

$$U^{(m)\dagger} V U^{(n)} = U^{(m+1)\dagger} V U^{(n-1)} + \sum_{k=0}^{m+1} \mathcal{H}^{(k)} U^{(m-k+1)\dagger} U^{(n)} - \sum_{k=0}^{n} U^{(m+1)\dagger} U^{(n-k)} \mathcal{H}^{(k)} . \quad (51)$$

By repeated use of this relation, together with Eq. (49), it is possible to convert Eq. (23) into a form in which $W_K^{(2n)}$ and $W_K^{(2n+1)}$ are expressed in terms of $U_K^{(m)}$, $m = 1, 2, \ldots, n$. The resulting equations can be written in the form[55]

$$W_K^{(2n)} = \tfrac{1}{2}(U_K^{(n-1)\dagger} V U_K^{(n)} + U_K^{(n)\dagger} V U_K^{(n-1)})_D - \sum_{m=1}^{n} \sum_{k=0}^{[m/2]} (1 - \tfrac{1}{2}\delta_{0,k} - \tfrac{1}{2}\delta_{2k,m}) \{W_K^{(m)} (U_K^{(n-m+k)\dagger} U_K^{(n-k)})_D + (U_K^{(n-k)\dagger} U_K^{(n-m+k)})_D W_K^{(m)}\} , \quad (52)$$

$$W_K^{(2n+1)} = (U_K^{(n)\dagger} V U_K^{(n)})_D - \sum_{m=1}^{n} \sum_{k=0}^{[(m-1)/2]} (1 - \tfrac{1}{2}\delta_{2k,m-1}) \{W_K^{(m)} (U_K^{(n-m+k+1)\dagger} U^{(n-k)})_D + (U_K^{(n-k)\dagger} U_K^{(n-m+k+1)})_D W_K^{(m)}\} , \quad (53)$$

and represent an extension of Wigner's $(2n+1)$ rule to quasidegenerate perturbation theory. This should result in computational economies, and is the principal advantage of the KCH formalism.[43–46] It does not appear possible to obtain a similar result for the other QDPT formalisms.

The unitary transformation which connects U_K and U_C can best be expressed in terms of an operator M, defined by

$$U_K = e^K = e^G e^M = U_C e^M . \quad (54)$$

This operator is block diagonal ($M_X = 0$) and anti-Hermitian, and tedious order-by-order comparison of the equations for U_K and U_C shows that

$$\begin{aligned} M^{(0)} &= M^{(1)} = M^{(2)} = 0 , \\ M^{(3)} &= \tfrac{1}{2}[G^{(1)}, G^{(2)}] , \\ M^{(4)} &= \tfrac{1}{2}[G^{(1)}, G^{(3)}] , \\ M^{(5)} &= \tfrac{1}{2}[G^{(1)}, G^{(4)}] + \tfrac{1}{2}[G^{(2)}, G^{(3)}] \\ &\quad + \tfrac{1}{8}[G^{(2)}, (G^{(1)})^3] - \tfrac{1}{8} G^{(1)}[G^{(1)}, G^{(2)}] G^{(1)} , \end{aligned} \quad (55)$$

etc. No simple, order-independent equation for M could be found.

A recent diagrammatic treatment[44] of the KCH formalism finds that the expressions for $W_K^{(n)}$ can be written in fully linked form through fourth order, but that some unlinked diagrams remain in fifth order. It appears likely that this is related to the lack of an order-independent equation for U_K (or, equivalently, for K or M), since it can be shown that any formalism in which $\mathcal{H}$ can be expressed in the exponential form (32) satisfies the separability theorem[28,8] and is thus fully linked, order by order, provided general order-independent equations for the exponential operator exist.

V. INTERMEDIATELY NORMALIZED QDPT

The most widely used form of QDPT is based on intermediate normalization and leads to a non-Hermitian model Hamiltonian.[2–10] We shall denote the decoupling operator (wave operator) and the transformed Hamiltonian obtained from the intermediate normalization condition by U_I and $\mathcal{H}_I = H_0 + W_I$, respectively. This condition takes the simple form

$$(U_I)_D = 1 \ . \tag{56}$$

It is convenient to define an operator[58]

$$X = (U_I)_X = U_I - 1 \ . \tag{57}$$

Substituting Eqs. (56) and (57) into Eq. (19) and then Eq. (18) provides a very simple direct derivation of the equations determining X and W_I:

$$W_I = V_D + V_X X \ , \tag{58}$$

$$[H_D, X] = -V_X + XV_X X \ . \tag{59}$$

We also find from Eq. (59) that X is anti-Hermitian:

$$X = -X^\dagger \ . \tag{60}$$

Order-by-order equations for X and W_I follow directly from Eqs. (58) and (59):

$$[H_0, X^{(1)}] = -V_X \ ,$$

$$[H_0, X^{(2)}] = -[V_D, X^{(1)}] \ ,$$

$$[H_0, X^{(n)}] = -[V_D, X^{(n-1)}] + \sum_{m=1}^{n-2} X^{(m)} V_X X^{(n-m-1)}$$

$$= -[V_D, X^{(n-1)}] + \sum_{m=1}^{n-2} X^{(m)} W_I^{(n-m)} \quad (n>2) \ , \tag{61}$$

$$W_I^{(1)} = V_D \ ,$$

$$W_I^{(n)} = V_X X^{(n-1)} \quad (n>1) \ . \tag{62}$$

Comparing the recursion relations (61) for X with those for G [Eq. (41)], we find that

$$G^{(1)} = X^{(1)}, \quad G^{(2)} = X^{(2)} \ . \tag{63}$$

A more tedious comparison shows that

$$G^{(3)} = X^{(3)} + \tfrac{1}{3}(X^{(1)})^3 \ ,$$

$$G^{(4)} = X^{(4)} + \tfrac{1}{3}\{(X^{(1)})^2 X^{(2)} + X^{(1)} X^{(2)} X^{(1)} + X^{(2)} (X^{(1)})^2\} \ . \tag{64}$$

In fact, these are special cases of the general relationship between G and X, proved in the Appendix,

$$G = \operatorname{arctanh} X = \sum_{n=0}^{\infty} \frac{1}{2n+1} X^{2n+1} \ , \tag{65}$$

or

$$X = \tanh G = \sum_{n=0}^{\infty} t_n G^{2n+1} \tag{66}$$

[see Eqs. (44) and (45)]. Since $\operatorname{arctanh} x = \frac{1}{2}\ln[(1+x)/(1-x)]$, we have[57]

$$U_C = e^G = \left(\frac{1-X}{1-X}\right)^{1/2}$$

$$= (1-X)(1-X^2)^{-1/2}$$

$$= U_I (U_I^\dagger U_I)^{-1/2} \ . \tag{67}$$

As seen in Sec. II, $U_I^\dagger U_I$ is the overlap matrix for the perturbed functions $U_I(t)$. Thus, as noted by Brandow[4] (see also des Cloizeaux,[37] Klein,[5] Kvasnička,[8] and Levy[10]), the canonical van Vleck functions $U_C(\alpha)$ may be viewed as the result of the symmetric orthonormalization[58] of the $U_I(\alpha)$ functions. The connection between the corresponding model Hamiltonians is then

$$\mathcal{H}_C = e^{G^\dagger} H e^G$$

$$= (U_I^\dagger U_I)^{-1/2} U_I^\dagger H U_I (U_I^\dagger U_I)^{-1/2}$$

$$= (U_I^\dagger U_I)^{-1/2} U_I^\dagger U_I \mathcal{H}_I (U_I^\dagger U_I)^{-1/2}$$

$$= (U_I^\dagger U_I)^{1/2} \mathcal{H}_I (U_I^\dagger U_I)^{-1/2}$$

$$= (1-X^2)^{1/2} \mathcal{H}_I (1-X^2)^{-1/2} \ , \tag{68}$$

or[57]

$$\mathcal{H}_I = \cosh G \, \mathcal{H}_C \, \operatorname{sech} G \ . \tag{69}$$

An equation for the direct determination of the Hermitian model Hamiltonian $\mathcal{H}_C$ in terms of X instead of G is given in the Appendix.

VI. DISCUSSION

Three forms of quasidegenerate perturbation theory have been examined here in terms of a common general formulation based on a similarity transformation of the Hamiltonian. This approach, together with the symmetric treatment of the P and Q subspaces represented by the $D-X$ (block-diagonal/off-diagonal) partitioning of operators, has enabled simple and direct derivations of the relevant equations and has clearly brought out the relationships between the different QDPT forms. This derivation bypasses the complications of the usual development of the intermediate normalization formalism which often involves iterative removal of energy dependence from the denominators and treatment of zero-order energy differences as perturbations (see, for example, Kvasnička,[8] but see also his more direct "algebraic theory" in Sec. III C). The use of the $D-X$ partitioning also allows us to avoid the extensive use of projection operators, which tends to obscure the formalism (see, for example, Klein[5]).

Except in the Kirtman–Certain–Hirschfelder formalism,[43–46] in which order-independent formulation is not possible, the equations for the wave (or decoupling) operator and for the transformed Hamiltonian have been obtained initially in order-independent (implicit) form, from which recursive order-by-order equations for all orders easily follow. The use of a superoperator notation and hyperbolic functions of the superoperator has allowed a very compact and simple derivation of the general equations for the canonical VVPT formalism.

The infinite-order model Hamiltonians of the different formalisms are related by similarity transformations, but when these model Hamiltonians are truncated at a finite order, the similarity transformation relationships are no longer exact. Thus, they would generally produce different results order by order, with possibly different convergence characteristics. The selection of the method to be used would thus be governed by convergence behavior as well as by computational considerations.[4] In this regard the KCH formalism has the advantage of the $(2n+1)$ rule,[59] while the other forms benefit from having fully linked diagrammatic expansions in all orders. The intermediate normalization form (with or without Hermitization) appears to be the most convenient for applications involving infinite order partial summations.[4]

Equation (A5) of the Appendix provides a hybrid ap-

proach for QDPT calculations, using the intermediate normalization formalism for the determination of the wave operator $U_I = 1 + X$, but obtaining the Hermitian model Hamiltonian $\mathcal{H}_C = H_0 + W_C$. This type of approach has been advocated by Brandow.[4]

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APPENDIX

In this appendix we derive Eq. (66), connecting the canonical van Vleck and the intermediately normalized forms of the wave operator. We also present an equation expressing $\mathcal{H}_C - H_D$ (or, equivalently, $W_C - V_D$) in terms of V_X and X directly.

From Eqs. (11) and (26) we have

$$H = e^G \mathcal{H}_C e^{-G}$$
$$= (\cosh G + \sinh G)\mathcal{H}_C(\cosh G - \sinh G) \ . \tag{A1}$$

Taking the block-diagonal and block off-diagonal parts of this equation separately, we find

$$H_D = \cosh G \mathcal{H}_C \cosh G - \sinh G \mathcal{H}_C \sinh G \ , \tag{A2}$$

$$V_X = -\cosh G \mathcal{H}_C \sinh G + \sinh G \mathcal{H}_C \cosh G \ . \tag{A3}$$

Therefore,

$$\begin{aligned}[H_D, \tanh G] &= (\cosh G \mathcal{H}_C \cosh G - \sinh G \mathcal{H}_C \sinh G)\tanh G \\ &\quad - \tanh G(\cosh G \mathcal{H}_C \cosh G - \sinh G \mathcal{H}_C \sinh G) \\ &= \cosh G \mathcal{H}_C \sinh G - \sinh G \mathcal{H}_C \cosh G \\ &\quad - \tanh G(\cosh G \mathcal{H}_C \sinh G - \sinh G \mathcal{H}_C \cosh G)\tanh G \\ &= -V_X - \tanh G \, V_X \tanh G \ . \end{aligned} \tag{A4}$$

Thus, $\tanh G$ satisfies the same commutation equation as X [Eq. (59)]. Since also $(\tanh G)_D = 0$ [this follows from Eq. (28) and the fact that $\tanh G$ is an odd function of G], $\tanh G$ must be identical to the X operator.

The equation referred to above for $W_C - V_D$ is obtained by a lengthy and tedious sequence of algebraic manipulations, beginning with Eq. (68) and using Eqs. (58) and (59) and the properties of the binomial expansions of $(1-x)^{\pm 1/2}$. The result can be expressed in any of the forms

$$\begin{aligned} W_C &= V_D + \tfrac{1}{2}[V_X, X] + \frac{1}{2}\sum_{m=0}^{\infty}\sum_{n=1}^{\infty} \frac{n}{(n+2m)(n+2m+1)} q_m q_{n+m} \\ &\quad \times \{X^{2m}[V_X, X^{2n+1}]X^{2m} + X^{2m+1}[V_X, X^{2n-1}]X^{2m+1}\} \\ &= V_D + \tfrac{1}{2}[V_X, X] \\ &\quad + \frac{1}{2}\sum_{m=0}^{\infty}\sum_{n=1}^{\infty} \frac{n}{(n+2m)(n+2m+1)} q_m q_{n+m} X^{2m} \\ &\quad \times [V_X X - X V_X, X^{2n}] X^{2m} \\ &= V_D + \tfrac{1}{2}[V_X, X] \\ &\quad + \frac{1}{2}\sum_{\substack{n=0 \\ (n+m>0)}}^{\infty}\sum_{m=0}^{\infty} \frac{n-m}{(n-m)(n+m+1)} q_m X^{2m}(V_X X + X V_X) q_n X^{2n} \ , \end{aligned} \tag{A5}$$

where

$$q_n = 2^{-2n}\binom{2n}{n} \tag{A6}$$

is the coefficient of x^n in the binomial power series for $(1-x)^{-1/2}$. The first two terms in these expressions represent the Hermitian average

$$(W_I)_H = \tfrac{1}{2}(W_I + W_I^\dagger) = V_D + \tfrac{1}{2}[V_X, X] \ . \tag{A7}$$

The additional terms contribute to W_C beginning in fourth order. The third order form of this model Hamiltonian has been used by Freed and co-workers[60] in their work on the effective valence shell Hamiltonian.

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Multidimensional many-body theory: Diagrammatic implementation of a canonical van Vleck formalism

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A size-extensive multidimensional many-body theory is developed from an order-expanded van Vleck transformation. This provides an effective Hamiltonian in a model space consisting of a set of determinants whose zeroth-order energies may be nondegenerate. Expressions for the effective Hamiltonian in terms of the perturbation and a set of resolvents generalized from the Rayleigh–Schrödinger form are given. Perturbative evaluation of the resultant formulas via diagrammatic expansion is illustrated and discussed. The diagrams required through second order for a model space consisting of a Hartree–Fock solution plus selected singly and doubly excited determinants are presented, and their relation to those employed in the method of Hose and Kaldor is discussed.

I. INTRODUCTION

Two problems of current theoretical interest are (1) the calculation of highly correlated excited state energies and potential surfaces for molecules and (2) the description of ground states of multiply-bonded or open-shell species. The first *ab initio* method used for these purposes was that of configuration interaction (CI).[1] Original applications involved only a few selected configurations, but today they routinely include all single and double excitations relative to a given configuration or set of reference configurations.

In recent years, the CI approach has been joined by many-body perturbation theories (MBPT)[2–5] [based on Rayleigh–Schrödinger perturbation theory (RSPT), diagrammatic expansions, and the linked cluster theorem of Goldstone[3]], including infinite-order coupled-cluster techniques.[6–10] MBPT calculations based on a single determinant have become routine for ground states of many systems,[5,11] and their usefulness for a wide variety of molecular problems has been demonstrated.[12–15]

In MBPT, it has proved convenient to adopt a diagrammatic formulation since, just as it is not feasible to solve the full CI problem in a basis of sufficient size to quantitatively study interesting molecular systems, the RSPT energy expansion must be truncated. The linked diagram expansion provides a useful subdivision of the terms to be evaluated or neglected. Even so, complete evaluation of fourth order involves terms from triple and quadruple excitations (relative to the Hartree–Fock ground state). Various fourth-order approximations (or particularly the analogous CI treatments) are still formidable problems. On the other hand, stopping with third-order RSPT does not include any effects of single excitations or higher-than-double excitations. Furthermore, any less-than-full CI treatment or nondiagrammatic RSPT approximation, which is not complete to a given order, will suffer from size inextensivity (also called size inconsistency or unlinked cluster) errors; i.e., the energy is not proportional to the number of noninteracting subsystems.[10,14,15]

The connection of RSPT to diagrammatic perturbation theory and the linked cluster theorem of Goldstone provides a solution to these problems. Each diagram possesses the important property of size extensivity. This means that approximations consisting of evaluation of subsets of the full set of diagrams for a given order will also have this property as long as complete diagrams are included. Furthermore, diagrammatic studies have enabled the observation that often the major function (in fourth order) of including the CI quadruple excitations is merely to cancel the spurious (unlinked) parts of the effect of double excitations in CI, which are not included in the linked cluster expansion.[10,17] Most importantly, diagrammatic perturbation theory has led to formulations for the further effects of quadruple excitations which are feasible to calculate.[10,11]

Although one-dimensional MBPT has been shown to provide highly accurate binding and activation energies,[18–20] potential surfaces,[21–25] and spectroscopic parameters, such as the quartic force field of the water molecule,[13] it is not universally applicable, particularly when exact or near degeneracies are encountered in a molecular problem. For example, even with unrestricted Hartree–Fock reference functions, it is usually insufficient for potential surfaces involving the dissociation of multiple bonds,[11] and it is not ordinarily applicable to excited states other than the lowest state of each symmetry. The study of these problems necessitates a multidimensional treatment.

Several multidimensional perturbative methods have been proposed. The completely degenerate case was considered by Bloch and Horowitz,[26] and later by Morita.[27] The first thorough quasidegenerate linked-diagram approach was formulated by Brandow.[28] Lindgren presented a direct and particularly transparent development of the theory, which he then extended to a multidimensional generalization of the infinite-order coupled-cluster approach.[29] More recently, Hose and Kaldor (HK),[30] Mukherjee *et al.*,[31] and others[32–35] have contributed to this field of study. The results of Freed and co-workers,[35] Kaldor,[36] Hegarty and Robb,[37] and HK[38] indicate the promise of these theories.

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TABLE I. Characterization of methods.

Method	a	b	c	d
Brandow[e]	I	N	C	S(C)
Freed[f]	I	S	C	N
Hose and Kaldor[g,h]	I	N	G	T
Lindgren[i]	D	N	C	S(C)
Present	D	H	G	S(HF)

[a]Direct (D) or indirect (I) formalism for denominators.
[b]Hermitean (H), non-Hermitean (N), or symmetrized (S) effective Hamiltonian formalism.
[c]General (G) or complete (C) model space implementation.
[d]Single reference state (S), such as core state (C) or Hartree–Fock determinant (HF); or transition (I) diagrammatic notation; or nondiagrammatic implementation (N).
[e]Reference 28.
[f]Reference 35.
[g]Reference 30.
[h]Reference 38.
[i]Reference 29.

The relationships among these methods can be examined on both formalistic and implementational levels. One formal difference involves whether the energy denominators are obtained directly (D) or indirectly (I, employing a degeneracy-breaking perturbation and resumming). Also, formalisms can lead to Hermitean (H) or non-Hermitean (N) effective Hamiltonians. Some of the former are explicitly Hermitean, while others are symmetrized by brute force (S). This aspect is analogous to the choice of fully or intermediately normalized perturbed model functions. It has been shown[39,40] that the canonical van Vleck functions can be viewed as the symmetrically orthogonalized version of the intermediately normalized functions.

On the implementational level, the basic difference is whether a complete valence model space is required (C) or the model space is allowed to be general (G, or incomplete). A related matter for the specification of diagrams is the choice of reference state(s) from which particles and holes are defined. The options here are the use of a single state (S), which could be a core state with less than N orbitals or a given state (e.g., the Hartree–Fock determinant, as in the present method), or the use of several different states [as in the HK transition (T) method]. Each of the various methods offers a combination of these features. Table I summarizes the characteristics of several approaches, including the present one, using the notations introduced above.

Brandow's[23] non-Hermitean wave operator approach uses a core reference and a complete model space. It expands the Brillouin–Wigner (BW) denominators, relative to a reference energy, and incorporates a degeneracy-breaking perturbation, from which a Rayleigh–Schrödinger size-extensive expansion is regained via resummation techniques. Although it is equivalent to Brandow's approach, Lindgren's formalism[29] uses a generalization of the degenerate Block–Horowitz[26] method to dispense with the energy dependence of the effective Hamiltonian initially, and yield a non-Hermitean order-by-order perturbation expansion for the wave operator, without considering BW denominators. In addition, when the cluster operator e^S is put into normal-product form, a convenient development of multidimensional coupled-cluster theory emerges.

The approach of Hose and Kaldor[30] differs in two significant ways from the earlier methods. First, it permits a general model space rather than a complete space. This flexibility is important for reducing computation time and for handling the problem of intruder states. Also, it specifies each matrix element in perturbation theory with respect to its ket vector (e.g., the ket vector of $H_{\alpha\beta}$ is $|\beta\rangle$), rather than to a single core state. This approach introduces some cancellations that are not present in the Brandow development. These authors handle their energy denominators as Brandow does, in a quasidegenerate fashion.

The approach proposed in this paper appears to have advantages over these earlier techniques. We believe it is necessary that multidimensional methods be size-extensive, permit arbitrary choices of model functions, and still retain clearly defined hole and particle labels so that categories of higher excitations may be easily identified. A method that offers these elements and is manifestly Hermitean is the canonical van Vleck transformation.[10–42] Brandow has discussed the similarity of this method to his apprach,[39] but he has not considered the generality of the method for arbitrary model spaces.

Another diagrammatic (noncanonical) van Vleck approach has been proposed by Kirtman.[33] This formalism (referred to as KCH in Ref. 40) has the advantage of a $2n+1$ rule; i.e., The $(2n-1)$th-order effective Hamiltonian can be expressed in terms of the nth-order perturbed functions. His results are size-extensive through fourth order, but not in higher orders, in which only a "quasicancellation" of unlinked diagrams occurs unless the model states are exactly degenerate.

In the following, we implement the canonical van Vleck transformation formalism for nondegenerate MBPT in an arbitrary multidimensional model space. We present an example of the diagrammatic expansion through second order. The advantages of this method are: (1) The method yields a Hermitean effective Hamiltonian and, thus, a set orthogonal eigenvectors; (2) the resultant energies will be specified by an expansion of size-extensive[1] diagrams; (3) in our diagrammatic expansion, we observe cancellations that do not occur in the other methods; (4) because we construct all diagrams with reference to a Hartree–Fock determinant (UHF for an open-shell problem), higher-excitation contributions are easily identified, and useful approximations for actual computations may be more readily apparent; (5) a single evaluation and diagonalization of the effective Hamiltonian will yield a set of nearly equivalently treated states (bias resulting from the choice of orbitals, a common problem shared by all multistate methods, is not considered here); and (6) implementation within a general model space of selected determinants increases the practicality of applications.

II. THE CANONICAL VAN VLECK (CVV) TRANSFORMATION

Multidimensional perturbation theories begin from the specification of a model space spanned by functions $\{\Phi_\gamma, \gamma = 1, d\}$. If the Φ's are orthonormal, the projectors P for the model space and Q for its orthogonal complement are given by

$$P = \sum_{\gamma=1}^{d} |\Phi_\gamma\rangle\langle\Phi_\gamma|\Phi_\gamma\rangle^{-1}\langle\Phi_\gamma| = \sum_{\gamma} |\gamma\rangle\langle\gamma| , \tag{1}$$

$$Q = \sum_{i>d} |\Phi_i\rangle\langle\Phi_i|\Phi_i\rangle^{-1}\langle\Phi_i| = \sum_{i} |i\rangle\langle i| . \tag{2}$$

P and Q are idempotent and self-adjoint, and form a resolution of the identity. The objective is to solve for a subset of eigenvalues (and eigenvectors) of the Schrödinger equation

$$H\Psi = \Psi\mathbf{E} \tag{3}$$

by means of an effective Hamiltonian equation in a space of reduced dimension, that of the model space

$$\mathcal{H}_{eff}\mathbf{D} = \mathbf{D}\mathbf{E} . \tag{4}$$

$\mathcal{H}_{eff}$ is composed of matrix elements within the model space of a transformed operator

$$\mathcal{H} = U^{-1}HU , \tag{5}$$

$\mathbf{D}$ is a matrix of eigenvectors, and $\mathbf{E}$ is a diagonal matrix of eigenvalues. The transformation U is required to be unitary and to decouple the P and Q spaces[13]

$$U^{-1} = U^\dagger , \tag{6}$$

$$\mathcal{H}_X \equiv P\mathcal{H}Q + Q\mathcal{H}P = 0 . \tag{7}$$

The exact eigenfunctions, if needed, are given by

$$\Psi = UP\Phi\mathbf{D} . \tag{8}$$

The unitarity of U results in full normalization since

$$\langle\Psi|\Psi\rangle = \mathbf{D}^\dagger\langle\Phi|PU^\dagger UP\Phi\rangle\mathbf{D} = 1 . \tag{9}$$

We identify $P\Phi\mathbf{D}$ as the perturbed model functions Ψ^0:

$$\Psi^0 = P\Phi\mathbf{D} = U^\dagger\Psi . \tag{10}$$

Using Eqs. (10) and (5) in the form

$$HU = U\mathcal{H} , \tag{11}$$

Eq. (4) is easily derived by the following sequence of manipulations of Eq. (3):

$$\begin{aligned}
&H\Psi = \Psi\mathbf{E} ,\\
&HUU^\dagger\Psi = UU^\dagger\Psi\mathbf{E} ,\\
&HU\Psi^0 = U\Psi^0\mathbf{E} ,\\
&U\mathcal{H}\Psi^0 = U\Psi^0\mathbf{E} ,\\
&\mathcal{H}\Psi^0 = \Psi^0\mathbf{E} ,\\
&P\mathcal{H}P\Phi\mathbf{D} = P\Phi\mathbf{D}\mathbf{E} ,\\
&\Phi^\dagger P\mathcal{H}P\Phi\mathbf{D} = \mathbf{D}\mathbf{E} .
\end{aligned} \tag{12}$$

Perturbative expressions for U and $\mathcal{H}$ may be obtained from Eq. (11). Using the notations of Ref. 10

$$\mathcal{H}_D = P\mathcal{H}P + Q\mathcal{H}Q , \tag{13}$$

and the usual separation of the Hamiltonian $H = H^{(0)} + V$, along with Eq. (7), and analogous terms for the blocks of H, V and U, we have

$$H_X = V_X , \tag{14}$$

$$H_D = H^{(0)} + V_D , \tag{15}$$

and we define W by

$$\mathcal{H}_D = H^{(0)} + W . \tag{16}$$

Partitioning Eq. (11) into diagonal and off-diagonal blocks leads to

$$[H^{(0)}, U_X] = -V_X U_D - V_D U_X + U_X W , \tag{17}$$

and

$$U_D W = [H^{(0)}, U_D] + V_X U_X + V_D U_D . \tag{18}$$

When U and $\mathcal{H}$ (or W) are expanded in orders of the perturbation with

$$U^{(0)} = 1 , \tag{19}$$

$$\mathcal{H}^{(0)} = H^{(0)} , \tag{20}$$

$$\mathcal{H}^{(n)} = W^{(n)} \quad (n>0) , \tag{21}$$

these equations lead to explicit recursive equations for $U^{(n)}$ and $W^{(n)}$ (for $n>0$):

$$[H^{(0)}, U_X^{(n)}] = -V_X U_D^{(n-1)} - V_D U_X^{(n-1)} + \sum_{m=1}^{n-1} U_X^{(m)} W^{(n-m)} , \tag{22}$$

$$W^{(n)} = [H^{(0)}, U_D^{(n)}] + V_X U_X^{(n-1)} + V_D U_D^{(n-1)} - \sum_{m=1}^{n-1} U_D^{(m)} W^{(n-m)} . \tag{23}$$

Unitarity is ensured by defining

$$U = e^G , \tag{24}$$

with G being anti-Hermitean

$$G = -G^\dagger . \tag{25}$$

It is then convenient to obtain ordered equations in terms of G rather than U. We note that U has not yet been completely specified. This is accomplished by the Kemble condition,[11] requiring that

$$G_D = 0 . \tag{26}$$

This ensures that G has the least possible effect upon the model functions[39] and that the perturbed model eigenvectors optimally resemble the exact ones.[39,11]

From Eqs. (24) and (5), it follows[16,39] that

$$\mathcal{H} = e^{-G}He^G = (He^G)_L . \tag{27}$$

The subscript L means that all effective Hamiltonian matrix elements are represented entirely in terms of "linked" diagrams. In general, linked diagrams must not contain separate closed parts. However, diagrams consisting solely of noninteracting open lines and a single closed part (which appear on the diagonal) are considered linked. Disconnected open diagrams are also permitted. The meaning of "open" is given in Sec. III.

As is shown elsewhere[10] the expansions of $G = G_n$ and $\mathcal{H}$ are given in commutator form by

$$
\begin{aligned}
&[H^{(0)}, G^{(1)}] = -V_X ,\\
&[H^{(0)}, G^{(2)}] = -[V_D, G^{(1)}] ,\\
&[H^{(0)}, G^{(3)}] = -[V_D, G^{(2)}] - \tfrac{1}{3}\{[[V_X, G^{(1)}], G^{(1)}] ,\\
&[H^{(0)}, G^{(4)}] = -[V_D, G^{(3)}] - \tfrac{1}{3}\{[[V_X, G^{(1)}], G^{(2)}]\\
&\qquad\qquad + [[V_X, G^{(2)}], G^{(1)}]\} ,\\
&[H^{(0)}, G^{(5)}] = -[V_D, G^{(4)}] - \tfrac{1}{3}\{[[V_X, G^{(1)}], G^{(3)}]\\
&\qquad\qquad + [[V_X, G^{(2)}], G^{(2)}] + [[V_X, G^{(3)}], G^{(1)}]\}\\
&\qquad\qquad + (1/45)[[[[V_X, G^{(1)}], G^{(1)}], G^{(1)}], G^{(1)}]
\end{aligned}
\tag{28}
$$

and

$$
\begin{aligned}
&\mathcal{H}^{(0)} = H^{(0)} ,\\
&\mathcal{H}^{(1)} = W^{(1)} = V_D ,\\
&\mathcal{H}^{(2)} = W^{(2)} = \tfrac{1}{2}[V_X, G^{(1)}] ,\\
&\mathcal{H}^{(3)} = W^{(3)} = \tfrac{1}{2}[V_X, G^{(2)}] ,\\
&\mathcal{H}^{(4)} = W^{(4)} = \tfrac{1}{2}[V_X, G^{(3)}]\\
&\qquad - (1/24)[[[V_X, G^{(1)}], G^{(1)}], G^{(1)}] ,\\
&\mathcal{H}^{(5)} = W^{(5)} = \tfrac{1}{2}[V_X, G^{(4)}]\\
&\qquad - (1/24)\{[[[V_X, G^{(1)}], G^{(1)}], G^{(2)}]\\
&\qquad + [[[V_X, G^{(1)}], G^{(2)}], G^{(1)}]\\
&\qquad + [[[V_X, G^{(2)}], G^{(1)}], G^{(1)}]\} .
\end{aligned}
\tag{29}
$$

The Hermiticity of the expansion for $\mathcal{H}_{\text{eff}}$ is apparent, and no explicit symmetrizing procedure need be applied. Unlike Kirtman's generalized van Vleck approach,[33] no powers of $G^{(n)}$ appear within the commutators of Eq. (29).[45] Thus, the results of the canonical van Vleck model will be size-extensive since $\mathcal{H}$ is represented in the domain of a Lie algebra.[16] Furthermore, this property is not dependent on using a complete reference space. Thus, this treatment incorporates a flexibility crucial to solving the multidimensional many-body problem.

The explicit diagrammatic construction of the effective Hamiltonian matrix elements follows conveniently, as in the one-dimensional MBPT case, from expressions given in terms of the perturbation V and, in this case, a set of generalized Rayleigh–Schrödinger resolvents. These resolvents arise in $\mathcal{H}$ from the commutator with $H^{(0)}$ in the equation for G. The expressions for $G^{(n)}$ are realized by substituting Eq. (28) into

$$
G_X = -\sum_\gamma \{R_\gamma^{(0)}[H^{(0)}, G_X]P_\gamma - P_\gamma[H^{(0)}, G_X]R_\gamma^{(0)}\} ,
\tag{30}
$$

where

$$
P_\gamma = |\gamma\rangle\langle\gamma| ,
\tag{31}
$$

and $R_\gamma^{(0)}$ is a generalized Rayleigh–Schrödinger type resolvent involving the zeroth-order energies of the complementary states and a particular model state:

$$
R_\gamma^{(0)} = \sum_i \frac{|i\rangle\langle i|}{[E_\gamma^{(0)} - E_i^{(0)}]} .
\tag{32}
$$

These energies will be specified in the following section. Thus,

$$
\begin{aligned}
&G^{(1)} = \sum_\gamma [R_\gamma^{(0)} V_X P_\gamma - P_\gamma V_X R_\gamma^{(0)}] ,\\
&G^{(2)} = \sum_\gamma \{R_\gamma^{(0)}[V_D, G^{(1)}]P_\gamma - P_\gamma[V_D, G^{(1)}]R_\gamma^{(0)}\} ,\\
&G^{(3)} = \sum_\gamma \{R_\gamma^{(0)}([V_D, G^{(2)}] + \tfrac{1}{3}[[V_X, G^{(1)}], G^{(1)}])P_\gamma\\
&\qquad - P_\gamma([V_D, G^{(2)}] + \tfrac{1}{3}[[[V_X, G^{(1)}], G^{(1)}])R_\gamma^{(0)}\} ,\\
&G^{(4)} = \sum_\gamma \{R_\gamma^{(0)}([V_D, G^{(3)}] + \tfrac{1}{3}([[V_X, G^{(1)}], G^{(2)}]\\
&\qquad + [[V_X, G^{(2)}], G^{(1)}]))P_\gamma - P_\gamma\\
&\qquad \times (\cdots \text{same terms} \cdots)R_\gamma^{(0)}\} .
\end{aligned}
\tag{33}
$$

These expressions are sufficient to obtain the energy through fifth order. The equations are quite lengthy in their Rayleigh–Schrödinger form, so we shall give the results only through third order:

$$
\begin{aligned}
&\mathcal{H}_{\alpha\beta}^{(0)} = \delta_{\alpha\beta} E_\alpha^0 ,\\
&\mathcal{H}_{\alpha\beta}^{(1)} = \langle\Phi_\alpha| V|\Phi_\beta\rangle ,\\
&\mathcal{H}_{\alpha\beta}^{(2)} = \tfrac{1}{2}\langle\Phi_\alpha| V[R_\alpha^{(0)} + R_\beta^{(0)}]V|\Phi_\beta\rangle ,\\
&\mathcal{H}_{\alpha\beta}^{(3)} = \tfrac{1}{2}\Big\{\langle\Phi_\alpha| VR_\alpha^{(0)}VR_\alpha^{(0)}V|\Phi_\beta\rangle\\
&\qquad - \sum_\gamma \langle\Phi_\alpha| V|\Phi_\gamma\rangle\langle\Phi_\gamma| VR_\gamma^{(0)}R_\alpha^{(0)}V|\Phi_\beta\rangle\\
&\qquad + \langle\Phi_\alpha| VR_\beta^{(0)}VR_\beta^{(0)}V|\Phi_\beta\rangle\\
&\qquad - \sum_\gamma \langle\Phi_\alpha| VR_\beta^{(0)}R_\gamma^{(0)}V|\Phi_\gamma\rangle\langle\Phi_\gamma| V|\Phi_\beta\rangle\Big\} .
\end{aligned}
\tag{34}
$$

Each order (≥ 3) includes renormalization terms similar to those resulting from the bracketing theorem of ordinary RSPT, except for the specific combinations of the various model state resolvents. Through third order, the CVV effective Hamiltonian of Eq. (34) is exactly equivalent to a Hermitized combination of the Hamiltonian of Lindgren[29] or HK.[30] It already differs from Kirtman's Hamiltonian in third order.

III. DIAGRAMMATIC EXPANSION

In the previous section, we obtained Rayleigh–Schrödinger type formulas for the order-by-order determination of an effective Hamiltonian matrix, which when diagonalized will yield a set of ground and excited states. At that point, the type of model functions and the diagrammatic expansion were left unspecified. The main objectives of a multidimensional treatment are (1) to obtain sets of uniformly described excited states and (2) to properly correlate ground state potential surfaces, which require more than a single reference function because of spin symmetry requirements, breaking of multiple bonds, or open-shell products, etc. We will consider, as an example, a model space consisting of a Hartree–Fock (SCF) determinant plus selected singly and doubly excited determinants.

We begin by specifying the separation of the Hamiltonian. In second quantization, the electronic Hamiltonian is given by

$$
H = \sum_{pq} h_{pq} p^\dagger q + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle p^\dagger q^\dagger s r ,
\tag{35}
$$

where

$$h_{pq} = \int \chi_p^*(1)\left[-\tfrac{1}{2}\nabla^2 - \sum_A \frac{Z_A}{r_A}\right]\chi_q(1)\,d\tau_1 , \tag{36}$$

$$\langle pq \mid rs\rangle = \int \chi_p^*(1)\chi_q^*(2)\,r_{12}^{-1}(1-P_{12})\chi_r(1)\chi_s(2)\,d\tau_1\,d\tau_2 , \tag{37}$$

and we have designated the creation and annihilation operators by their subscripts alone. In terms of quantities in normal product form,[16] H is given by

$$H = H^N + \langle\Phi_0|H|\Phi_0\rangle , \tag{38}$$

where

$$H^N = H_0^N + V^N , \tag{39}$$

$$H_0^N = \sum_{pq}\left[h_{pq} + \sum_t \langle pt \mid qt\rangle\right]N[p^\dagger q] , \tag{40}$$

$$V^N = \frac{1}{4}\sum_{pqrs}\langle pq \mid rs\rangle N[p^\dagger q^\dagger sr] . \tag{41}$$

The use of the V^N potential significantly reduces the number of diagrams when a SCF orbital basis is employed.[17] Alphabetically, $(a, b, \ldots)$ will be reserved for virtual orbitals of the Hartree–Fock solution, $(i, j, \ldots)$ will be for those orbitals originally occupied, and $(p, q, \ldots)$ will be undesignated. Particle or hole designation is always defined with respect to Φ_0.

The SCF orbitals satisfy

$$h_{pq} + \sum_t \langle pt \| qt\rangle = \delta_{pq}\,\epsilon_p , \tag{42}$$

so that

$$\langle\Phi_0|H|\Phi_0\rangle = E_0^{HF} . \tag{43}$$

Thus, we have the separation

$$H = H^0 + V^N , \tag{44}$$

with

$$H^0 = H_0^N + E_0^{HF} . \tag{45}$$

The model states are defined in terms of creation and annihilation operators working on the Hartree–Fock determinant. A singly excited state will be denoted

$$|\Phi_i^a\rangle = N[a^\dagger i]\,|\Phi_0\rangle . \tag{46}$$

Similarly, a doubly excited model determinant is given by

$$|\Phi_{ij}^{ab}\rangle = N[a^\dagger b^\dagger ji]\,|\Phi_0\rangle . \tag{47}$$

Note the equivalences

$$N[a^\dagger i] = a^\dagger i , \tag{48}$$

$$N[a^\dagger b^\dagger ji] = a^\dagger b^\dagger ji = a^\dagger i b^\dagger j , \tag{49}$$

resulting from the designation of occupied and virtual labels.

Diagrammatically, each model function is represented by a diamond vertex with appropriately labeled particle and hole lines entering and leaving. Thus, any vector originating or terminating at a diamond vertex will represent a specific orbital rather than an index of summation. These lines are the so-called "open" lines. A diagram containing open lines may also be described as open. The convention of not redefining hole and particle labels results in allowing open lines on either side of the diagrams.

TABLE II. Zeroth-order effective Hamiltonian matrix elements.

HF | HF:
$\langle\Phi_0\|H^0\|\Phi_0\rangle = E_0^{HF}$
HF | SE = 0
HF | DE = 0
SE | SE:
$\langle\Phi_i^a\|H^0\|\Phi_k^c\rangle = \delta_{ik}\,\delta_{ac}\,[E_0^{HF} + \epsilon_a - \epsilon_i]$
SE | DE = 0
DE | DE:
$\langle\Phi_{ij}^{ab}\|H^0\|\Phi_{kl}^{cd}\rangle = \delta_{jlkl}^2\,\delta_{bacd}^2\,[E_0^{HF} + \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j]$

A. Zeroth and first orders

The zeroth-order effective Hamiltonian

$$\mathcal{H}_{\alpha\beta}^{(0)} = \langle\Phi_\alpha|H_0^N\Phi_\beta\rangle + \delta_{\alpha\beta}\,E_0^{HF} \tag{50}$$

is diagonal. Matrix elements between the non-, singly-, and doubly-excited determinants (HF, SE, and DE, respectively) are evaluated using the generalized Wick's theorem.[16] The results relative to E_0^{HF} for the chosen model space are given in Table II. We see that H_0^N acts as an excitation operator.

The first-order contributions

$$\mathcal{H}_{\alpha\beta}^{(1)} = \langle\Phi_\alpha|V^N\Phi_\beta\rangle \tag{51}$$

are evaluated similarly. For the Hartree–Fock determinant

$$\langle\Phi_0|V^N\Phi_0\rangle = 0 , \tag{52}$$

because of the normal product form of V^N. In accordance with Brillouin's Theorem, we obtain

$$\langle\Phi_0|V^N\Phi_i^a\rangle = \langle\Phi_0|\frac{1}{4}\sum_{pqrs}\langle pq \| rs\rangle \times N[p^\dagger q^\dagger sr]N[a^\dagger i]\,\Phi_0\rangle = 0 , \tag{53}$$

because the two normal products cannot be fully contracted. The diagrammatic analog is that there is no way to properly connect the Hartree–Fock bra (no lines), the perturbation interaction (four lines), and a single excitation ket (two lines).

The first-order interaction between the Hartree–Fock determinant and a double excitation from it is given by

$$\begin{aligned}\langle\Phi_0|V^N\Phi_{ij}^{ab}\rangle &= \langle\Phi_0|\frac{1}{4}\sum_{pqrs}\langle pq \| rs\rangle N[p^\dagger q^\dagger sr] \times N[a^\dagger b^\dagger ji]\,\Phi_0\rangle \\ &= \frac{1}{4}\sum_{pqrs}\langle pq \| rs\rangle\,\delta_{pqji}^2\,\delta_{srab}^2 \\ &= \langle ij \| ab\rangle ,\end{aligned} \tag{54}$$

TABLE III. First-order effective Hamiltonian matrix elements.

HF | HF = 0
HF | SE = 0
HF | DE:
$\langle \Phi_0 \mid V^N \Phi_{ij}^{ab} \rangle = \langle ij \Vert ab \rangle$
SE | SE:
$\langle \Phi_i^a \mid V^N \Phi_k^c \rangle = \langle ic \Vert ak \rangle$
SE | DE:
$\langle \Phi_i^a \mid V^N \Phi_{kl}^{cd} \rangle = \{\delta_{i(kl)} \langle a(lk) \Vert cd \rangle\} - \{\text{phr}\}$
DE | DE:
$\langle \Phi_{ij}^{ab} \mid V^N \Phi_{kl}^{cd} \rangle = \delta_{(ba)(cd)} \delta_{(ji)(kl)} \langle (ij)(dc) \Vert (ab)(lk) \rangle + \{\delta_{ijlk}^2 \langle ab \Vert cd \rangle\} + \{\text{phr}\}$

where the δ^2 notation is defined by

$$\delta_{pqjk}^2 \equiv \delta_{pi}\,\delta_{qj} - \delta_{pj}\,\delta_{qi} \,. \tag{55}$$

Proceeding as in these examples, we find the results listed in Table III, where the notation

$$\delta_{i(kl)} \langle X(lk) \Vert XX \rangle = \delta_{ik} \langle Xl \Vert XX \rangle - \delta_{il} \langle Xk \Vert XX \rangle \tag{56}$$

has been used. Similarly,

$$\delta_{(ba)(cd)} \langle X(dc) \Vert (ab)X \rangle = \delta_{bc} \langle Xd \Vert aX \rangle - \delta_{bd} \langle Xc \Vert aX \rangle - \delta_{ac} \langle Xd \Vert bX \rangle + \delta_{ad} \langle Xc \Vert bX \rangle \,. \tag{57}$$

Thus, the first term of the last matrix element in Table III represents 16 possible terms, all of which have the same Hugenholtz diagrammatic skeleton.

The first-order effective Hamiltonian energy diagram forms are summarized in Fig. 1. Note that terms involved in the parenthetic notations always share a common form. Forms related by particle–hole reversal, which will be omitted for brevity in subsequent figures, have been shown explicitly.

The algebraic expressions can, of course, be derived from the diagrams. As usual, it is necessary to expand the (antisymmetrized) Hugenholtz diagrams to (antisymmetrized) Goldstone form in order to determine the sign of the contribution. Through second order (in which no folded diagrams or equivalent complications arise) the sign is $(-1)^{l+h}$, where h is the number of hole lines and l is the number of loops. For the purpose of loop counting, double- and higher-excitation diamond vertices must be split into two and more (respectively) single particle–single hole vertices, with the pairing of open lines corresponding to the second-quantized definitions; for example, a with i and b with j in Eq. (49). A factor of $\frac{1}{2}$ must be included for each pair of equivalent lines. Note that the open lines of the model states are never equivalent. The factors of $\frac{1}{2}$ in Eq. (34) are in addition to those above.

B. Second-order theory

The second-order effective Hamiltonian is given as

$$\kappa_{\alpha\beta}^{(2)} = \tfrac{1}{2} \langle \Phi_\alpha \mid V^N (R_\alpha^0 + R_\beta^0) V^N \Phi_\beta \rangle \,. \tag{58}$$

The numerators, which comprise most of the information explicitly illustrated in a diagram, are identical for these two terms. However, in second order, we encounter the first summations and denominators of the resolvent. We may rewrite Eq. (58)

$$\kappa_{\alpha\beta}^{(2)} = \frac{1}{2} \sum_{(i \neq \gamma)} \langle \Phi_\alpha \mid V^N \Phi_i \rangle \langle \Phi_i \mid V^N \Phi_\beta \rangle \left(\frac{1}{E_\alpha^0 - E_i^0} + \frac{1}{E_\beta^0 - E_i^0} \right), \tag{59}$$

where E_i^0 is defined by

$$H^0 \Phi_i = E_i^0 \Phi_i \,, \tag{60}$$

and Φ_i is an external (i.e., nonmodel or complementary) state determinant. We find that if Φ_α is a single excitation, the interactions may contribute if Φ_i is a single, double, or triple excitation. If Φ_α is doubly excited, Φ_i may even be a quadruple excitation. Since E_α^0 and E_i^0 both contain E_0^{HF}, the denominators are functions of only those orbital energies ϵ which correspond to labeled particle and hole lines in the diagram. For example, the numerator of the matrix element between two singly

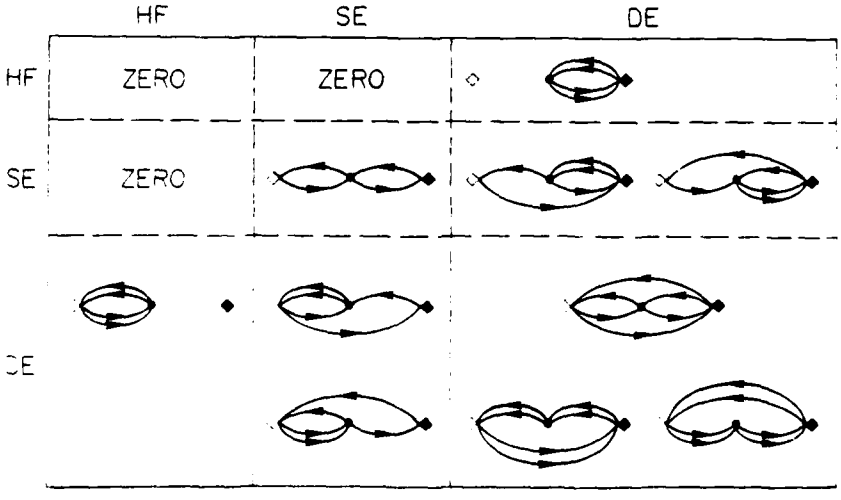

FIG. 1. First-order effective Hamiltonian matrix element diagrams. Lines above (below) the horizontal midline of the diagrams represent particles (holes). The arrows, provided for clarity, are redundant with this notation.

excited determinants involving a singly excited intermediate state is

$$\sum_{c,k}{}' \langle \Phi_i^a | V^N \Phi_k^c \rangle \langle \Phi_k^c | V^N \Phi_j^b \rangle = \sum_{c,k}{}' \langle ak||ci\rangle\langle cj||bk\rangle . \tag{61}$$

The prime is a reminder that model states are not to be included in the sum. The "denominator" factor [which multiplies Eq. (61)] is given by

$$\frac{1}{2}\left\{\left[(\epsilon_a-\epsilon_i)-\left(\sum_h \epsilon_h-\sum_p \epsilon_p\right)\right]^{-1} + \left[(\epsilon_b-\epsilon_j)-\left(\sum_h \epsilon_h-\sum_p \epsilon_p\right)\right]^{-1}\right\}, \tag{62}$$

where the sums over h and p designate all hole and particle lines which would be intersected by a vertical line drawn between the two interaction vertices. In the case of a singly excited intermediate state, these sums consist of a single orbital index each.

The algebraic expressions for the second-order effective Hamiltonian matrix elements are given in Table IV and their diagrammatic forms are shown in Fig. 2. To save space, we have indicated roughly half of the required diagrams as particle–hole reversals (phr) of the illustrated diagrams. From top to bottom, the subdivisions correspond to the HF|HF, HF|SE, SE|SE,

TABLE IV. Second-order effective Hamiltonian matrix elements.

HF|HF:

$$\langle \Phi_0 | V^N R_0^0 V^N \Phi_0\rangle = \tfrac{1}{2}\sum_{abmn}{}' \frac{\langle ef\|mn\rangle^2}{D_{mn}^{ef}}$$

HF|SE:

$$\tfrac{1}{2}\langle \Phi_0 | V^N (R_0^0+R_\beta^0) V^N \Phi_k^c\rangle = \tfrac{1}{4}\tfrac{1}{4}\sum_{\substack{emn\\(cmn)}}{}' \langle ce\|mn\rangle\langle nm|ke\rangle[(m+n-e-c)^{-1}+(m+n-e-k)^{-1}] - \{\text{phr}\}$$

SE|SE:

$$\begin{aligned}\tfrac{1}{2}\langle \Phi_i^a | V^N (R_\alpha^0+R_\beta^0) V^N \Phi_k^c\rangle &= \tfrac{1}{2}\sum_{\substack{em\\(am)}}{}' \langle am\|ie\rangle\langle mc\|ek\rangle[(a+m-i-e)^{-1}+(c+m-k-e)^{-1}]\\ &+\tfrac{1}{4}\tfrac{1}{4}\delta_{ik}\sum_{\substack{efm\\(efim)}}{}'\langle am\|fe\rangle\langle ef\|mc\rangle[(m+a-e-f)^{-1}+(m+c-e-f)^{-1}] - \tfrac{1}{4}\delta_{ik}\sum_{mne}\langle ce\|nm\rangle\langle nm\|ae\rangle[D_{mn}^{ae-1}+D_{mn}^{ae-1}]\\ &-\tfrac{1}{4}\sum_{\substack{ef\\(efik)}}{}'\langle ka\|ef\rangle\langle fe\|ic\rangle[(k+a-e-f)^{-1}+(i+c-e-f)^{-1}] + \tfrac{1}{2}\sum_{\substack{em\\(ceim)}}{}'\langle ce\|am\rangle\langle ke\|mi\rangle[(a+m-e-c)^{-1}\\ &+(i+m-k-e)^{-1}]\tfrac{1}{4}+\{\text{phrs}\}+\tfrac{1}{2}\sum_{em}\langle km\|ce\rangle\langle ae\|im\rangle[D_{km}^{ae-1}+D_{im}^{ae-1}]+\tfrac{1}{2}\sum_{efmn}\frac{\langle ef\|mn\rangle^2}{D_{mn}^{ef}}\end{aligned}$$

HF|DE:

$$\begin{aligned}\tfrac{1}{2}\langle \Phi_0 | V^N (R_0^0+R_\beta^0) V^N \Phi_{kl}^{cd}\rangle &= \tfrac{1}{2}\sum_{\substack{em\\((dc)e|(lk)m)}}{}'\langle (dc)e\|(lk)m\rangle\langle m(cd)\|e(kl)\rangle[(l+m-d-e)^{-1}+(c+m-k-e)^{-1}]\\ &+\tfrac{1}{4}\tfrac{1}{4}\sum_{\substack{ef\\(efkl)}}{}'\langle kl\|ef\rangle\langle ef\|cd\rangle[(k+l-e-f)^{-1}+(c+d-e-f)^{-1}]\}+\{\text{phr}\}\end{aligned}$$

SE|DE:

$$\begin{aligned}\tfrac{1}{2}\langle \Phi_i^a | V^N (R_\alpha^0+R_\beta^0) V^N \Phi_{kl}^{cd}\rangle &= \tfrac{1}{4}\tfrac{1}{2}\sum_{\substack{e\\(e|(lk))}}{}'\langle a(lk)\|ie\rangle\langle e(kl)\|dc\rangle[(a+l-i-e)^{-1}+(c+d-k-e)^{-1}]\tfrac{1}{4}+\{\text{phr}\}\\ &+\tfrac{1}{4}\tfrac{1}{4}\delta_{i(lk)}\sum_{\substack{ef\\(efkl)}}{}'\langle (kl)a\|ef\rangle\langle ef\|cd\rangle[(a+(kl)-e-f)^{-1}+(c+d-e-f)^{-1}] - \tfrac{1}{2}\sum_{\substack{e\\(aekl)}}{}'\langle kl\|ie\rangle\langle ae\|cd\rangle\\ &\times[(k+l-i-e)^{-1}+(c+d-a-e)^{-1}]+\tfrac{1}{2}\sum_{\substack{e\\((dc)e|(lk))}}{}'\langle a(lk)\|e(dc)\rangle\langle (kl)e\|(cd)i\rangle\\ &\times[(a+l-(dc)-e)^{-1}+((cd)+i-(kl)-e)^{-1}]+\tfrac{1}{2}\delta_{i(lk)}\sum_{\substack{em\\((dc)e|(lk))}}{}'am\|(dc)e\rangle\langle (kl)e\|(cd)m\\ &\times[(a+m-(dc)-e)^{-1}+((cd)+m-e-(kl))^{-1}]\tfrac{1}{4}-\{\text{phrs}\}+\tfrac{1}{4}-\tfrac{1}{2}\delta_{a(dc)}\sum_{ef}\langle kl\|ef\rangle\langle ef\|(cd)i\\ &\times[D_{kl}^{ef-1}+(i+(cd)-e-f)^{-1}]\tfrac{1}{4}-\tfrac{1}{4}\delta_{i(lk)}\delta_{a(dc)}\sum_{efm}\langle (kl)m\|ef\rangle\langle ef\|(cd)m\\ &\times[D_{(kl)m}^{ef-1}+(m+(cd)-e-f)^{-1}]+\tfrac{1}{2}\delta_{a(dc)}\sum_{em}\langle (cd)e\|(kl)m\rangle\langle m\|i(lk)e\rangle[D_{(lk)m}^{ad-1}+(i+m-(lk)-e)^{-1}]\\ &-\tfrac{1}{2}\sum_{m}\langle cd\|m(lk)\rangle\langle (kl)m\|ai\rangle[D_{(lk)m}^{ad-1}+(i+m-(kl)-a)^{-1}]\tfrac{1}{4}-\{\text{phrs}\}\end{aligned}$$

TABLE IV (*Continued*)

DE | DE:

$$\tfrac{1}{2}\langle \Phi_{ij}^{ab} | V^N (R_\alpha^0 + R_\beta^0) V^N \Phi_{kl}^{cd}\rangle = \{ \tfrac{1}{2}\, \delta_{(ji)(lk)} \sum_{e}{}' \langle ab \| (ij)e\rangle \langle (kl)e \| cd\rangle [(a+b-(ij)-e)^{-1} + (c+d-(kl)-e)^{-1}] \}_{ij}^{kl} + \{\text{phr}\}$$

$$+\tfrac{1}{2}\, \delta_{(ji)(lk)}\, \delta_{(ba)(dc)} \sum_{\substack{em \\ [(ba)e(ji)m]}}{}' \langle (ab)m \| (ij)e\rangle \langle (kl)e \| (cd)m\rangle [((ab)+m-(ij)-e)^{-1} + ((cd)+m-(kl)-e)^{-1}]$$

$$+ \{ \tfrac{1}{4}\, \delta_{jikl}^2 \sum_{\substack{ef \\ [efij]}}{}' \langle ab \| ef\rangle \langle ef \| cd\rangle [(a+b-e-f)^{-1} + (c+d-e-f)^{-1}]$$

$$-\tfrac{1}{2}\, \delta_{(ji)(lk)} \sum_{\substack{m \\ [(ba)(dc)(ji)m]}}{}' \langle (ij)(dc) \| (ab)m\rangle \langle (cd)m \| (kl)(ba)\rangle [(m+(ab)-(ij)-(dc))^{-1} + (m+c(d)-(kl)-(ba))^{-1}]$$

$$+\tfrac{1}{2}\, \delta_{(ji)(lk)} \sum_{\substack{e \\ [(dc)eij]}}{}' \langle ab \| e(dc)\rangle \langle e(kl) \| (ij)(cd)\rangle [(a+b-e-(dc))^{-1} + ((cd)+(ij)-(kl)-e)^{-1}]$$

$$+\tfrac{1}{2}\, \delta_{(ji)(lk)} \sum_{\substack{e \\ [(ba)ekl]}}{}' \langle (kl)(ab) \| e(ij)\rangle \langle e(ba) \| cd\rangle [((ab)+(kl)-(ij)-e)^{-1} + (c+d-e-(ba))^{-1}] \}_{ij}^{kl} + \{\text{phrs}\}$$

$$+ \{ \tfrac{1}{4}\, \delta_{jikl}^2\, \delta_{(ba)(dc)} \sum_{efm} \langle ef \| (ab)m\rangle \langle (cd)m \| ef\rangle [((ab)+m-e-f)^{-1} + ((cd)+m-e-f)^{-1}]$$

$$-\tfrac{1}{2}\, \delta_{jikl}^2 \sum_{em} \langle e(dc) \| (ab)m\rangle \langle (cd)m \| e(ba)\rangle [((ab)+m-e-(dc))^{-1} + ((cd)+m-e-(ba))^{-1}]$$

$$+\tfrac{1}{4}\, \delta_{(ij)(lk)}\, \delta_{(ab)(dc)} \sum_{ef} \langle ef \| (kl)(ba)\rangle \langle (cd)(ji) \| ef\rangle [((ba)+(kl)-e-f)^{-1} + ((cd)+(ji)-e-f)^{-1}]$$

$$+\tfrac{1}{2}\, \delta_{(ij)(kl)} \sum_{e} \langle e(dc) \| (ab)(lk)\rangle \langle (cd)(ji) \| e(ba)\rangle [((ab)+(lk)-e-(dc))^{-1} + ((cd)+(ji)-e-(ba))^{-1}]$$

$$+\tfrac{1}{2}\, \delta_{(ij)(kl)} \sum_{m} \langle (cd)(ji) \| (lk)m\rangle \langle (dc)m \| ab\rangle [(m+(lk)-(ji)-(cd))^{-1} + (m+(dc)-b-a)^{-1}]$$

$$-\tfrac{1}{2}\, \delta_{(ji)(kl)} \sum_{m} \langle (ba)m \| cd\rangle \langle (ij)m \| (ab)(lk)\rangle [(m+(ba)-c-d)^{-1} + (m+(ij)-(lk)-(ab))^{-1}]$$

$$-\tfrac{1}{2}\, \delta_{(ba)(cd)}\, \delta_{(ji)(kl)} \sum_{em} \langle (ij)e \| m(lk)\rangle \langle m(dc) \| (ab)e\rangle [(m+(lk)-(ij)-e)^{-1} + (m+(dc)-e-(ab))^{-1}] \}_{ij}^{kl} + \{\text{phrs}\}$$

$$+\tfrac{1}{4}\, \delta_{jikl}^2\, \delta_{bacd}^2 \sum_{efmn} \frac{\langle ef \| mn\rangle^2}{D_{mn}^{ef}} + \tfrac{1}{2}\, \delta_{(ij)(kl)}\, \delta_{(ab)(cd)} \sum_{em} \langle (ji)m \| (ba)e\rangle \langle e(dc) \| m(lk)\rangle [D_{(ji)m}^{(ba)e^{-1}} + D_{(lk)m}^{(dc)e^{-1}}]$$

$$+ \{ \tfrac{1}{4} - \tfrac{1}{4}\, \delta_{jikl}^2\, \delta_{(ab)(cd)} \sum_{emn} \langle (ba)e \| mn\rangle \langle nm \| e(dc)\rangle [D_{mn}^{(ba)e^{-1}} + D_{mn}^{(dc)e^{-1}}] + \tfrac{1}{4}\, \delta_{jikl}^2 \sum_{mn} \langle ab \| mn\rangle \langle nm \| dc\rangle [D_{mn}^{ab^{-1}} + D_{mn}^{cd^{-1}}]$$

$$-\tfrac{1}{2}\, \delta_{(ab)(cd)} \sum_{e} \langle ij \| (ab)e\rangle \langle e(dc) \| lk\rangle [D_{ij}^{(ba)e^{-1}} + D_{kl}^{(dc)e^{-1}}] \}_{ij}^{kl} + \{\text{phrs}\}$$

$$+\{\text{If } \Phi_{(lk)}^{(ba)} \text{ is a model SE, include}$$

$$-\tfrac{1}{2}\langle (kl)(ba) \| cd\rangle \langle (ab)(lk) \| ij\rangle [((ba)+(kl)-c-d)^{-1} + (i+j-(lk)-(ab))^{-1}]\} + \{\text{phr}\}$$

$$+\{\text{If } \Phi_{ij}^{cd} \text{ is a model DE and } \Phi_{kl}^{ab} \text{ is not, include } \tfrac{1}{2}\langle ij \| kl\rangle \langle cd \| ab\rangle [(k+l-i-j)^{-1} + (c+d-a-b)^{-1}]\} + \{\text{phr}\}$$

$$+\text{If } \Phi_{(ji)(lk)}^{(ba)(dc)} \text{ is not a model DE and } \Phi_{(ij)(kl)}^{(ab)(cd)} \text{ is, include } \tfrac{1}{2}\langle ab \| cd\rangle \langle kl \| ij\rangle [(a+b-c-d)^{-1} + (i+j-k-l)^{-1}]$$

$$+\tfrac{1}{2}\langle ij \| ab\rangle \langle cd \| kl\rangle [D_{ij}^{ab^{-1}} + D_{kl}^{cd^{-1}}]$$

HF | DE, SE | DE, and DE | DE blocks. The SE | HF, DE | HF, and DE | SE diagrams could be obtained by time reversal of the HF | SE, HF | DE, and SE | DE diagrams, respectively, but they are not required because of the Hermiticity of $\mathcal{H}_{eff}$. Except for the denominator factors (which are not shown in the figure) and the ground state term on the diagonal, the SE | SE diagrams are equivalent to those of Paldus and Čížek.[18] Each intermediate state (in Fig. 2) has been labeled as singly (S), doubly (D), triply (T), or quadruply (Q) excited, relative to Φ_0.

In the table, {phrs} represents the phr contributions analogous to the terms in the immediately preceding brackets. Except that the phr terms are grouped together, the order in the table corresponds to that in Fig. 2. The algebraic expressions for the phr terms are obtained by exchanging (relabeling) a and i, b and j, etc. in the illustrated terms. Sign changes, when required (due diagrammatically to a change in the parity factor with particle hole reversal when the numbers of particles and holes are not both even or both odd), have been explicitly indicated. Since the type of inter-

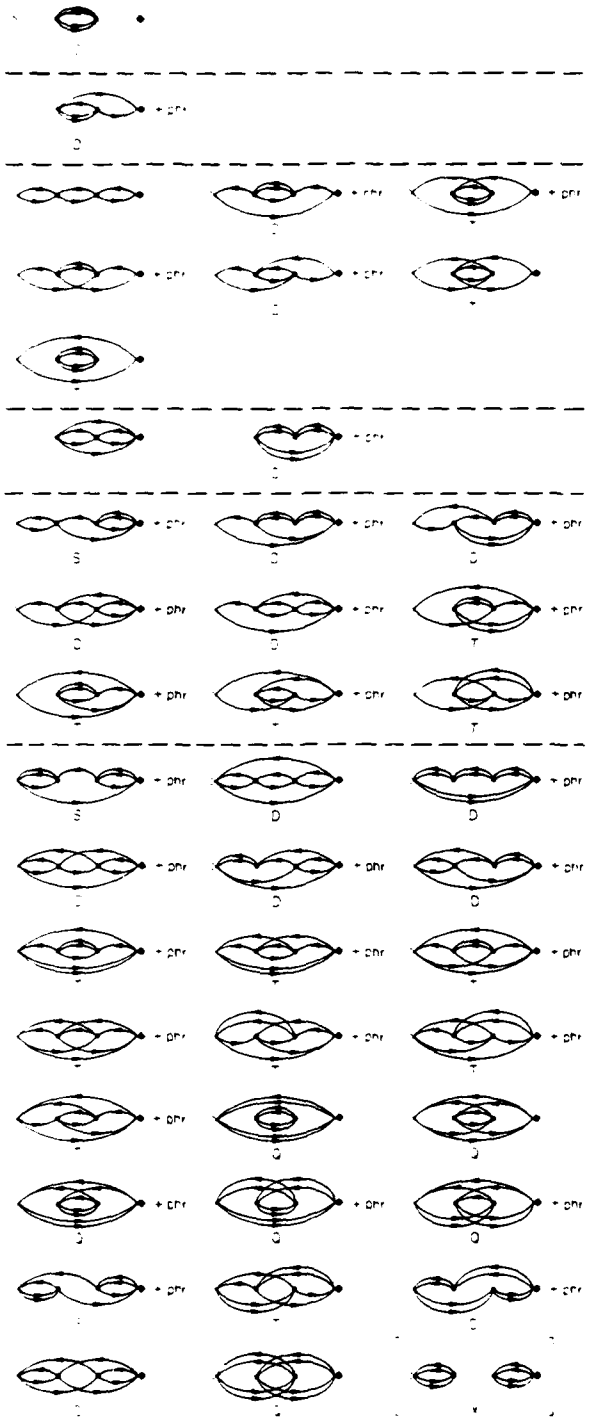

FIG. 2. Second-order effective Hamiltonian matrix element diagrams.

mediate state is not always obvious in the algebraic form, the superscripts and subscripts of the terms to be omitted from the primed sums when they correspond to model states have been enclosed in curly brackets below the summation sign. The level of excitation is determined by the number of labels provided.

Note that the parenthetic notations sometimes appear without delta functions. In these cases, they indicate multiple terms which must all be included. Terms containing parenthetic notations are indicated in the figures by single diagrams, since with unlabeled lines their skeletons are identical. The negative double excitation energy notation

$$D_{ij}^{ab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b \tag{63}$$

has been employed within the table, and orbital energies have been indicated by their subscripts alone.

We see that the second-order (closed) ground state correlation contribution appears along the diagonal. These terms are considered linked, since noninteracting open lines merely represent delta functions which, in this case, indicate that the diagram contributes only to diagonal elements. They arise from triply excited intermediates for singly excited determinants, and from quadruply excited states for doubly excited model states. Since each intermediate (including the open line parts) is doubly excited relative to the model state, the denominator dependence on the model state is removed and the denominators are identical to those of the ground state terms. Assuming that the model space does not contain any triply or quadruply excited states, the value of this term is exactly equal to that obtained from ordinary MBPT, except that, in the HF|HF matrix element, the contributions from any doubly excited determinants included in the model space must be omitted. These omitted terms correspond to the couplings (i.e., off-diagonal effective Hamiltonian matrix element) between Φ_0 and the doubly excited model states, which are explicitly included. The identical terms contributing to the excited state diagonal elements are not omitted. Subtraction of the full ground state diagrams from the diagonal gives the effective excitation energy matrix relative to the one-dimensional MBPT ground state energy.

In the second order, the diagrammatic differences between general and complete model space implementations appear. We find that because the general methods allow the Q space to include states that are related to (i.e., consist of particle and hole labels in common with) the selected P space states, certain disconnected "irreducible"[30] diagrams must be included. These diagrams consist entirely of open lines, and thus they are trivial to calculate because no summations are required. In addition, many of them cancel each other. These disconnected diagrams are those in the last two rows of Fig. 2 for DE|DE matrix elements. The last diagram, with Φ_0 as the intermediate state labeled X, is not used when the model space includes Φ_0. However, if Φ_0 is included in Q rather than P, this diagram is considered and is found to cancel the immediately preceding quadruple intermediate diagram exactly, so that neither diagram need be calculated. In fact, close examination reveals that none of these disconnected diagrams would remain if the complication of excluding the model states as intermediates did not arise. We find for the case that the model space has no singly excited states that the single and triple intermediate diagrams of the penultimate row cancel each other. However, if

the model space does include singly excited determinants, the corresponding terms must be omitted from the S diagram. Assuming that the model space does not include triply excited states, the related terms from the T diagram do appear and must therefore be calculated, since they are not cancelled. Thus, in Table IV the sixth term from the end (counting phrs, i.e., the first "conditional" term) gives the net contribution of S and T in the presence of model singles.

Similarly, the last two D diagrams need only be considered for special cases involving model intermediates. The first is usually cancelled by its phr diagram. However, there may be instances in which the cancellation is not permitted. For example, (assuming that Φ_{ij}^{ab} and Φ_{kl}^{cd} are model states) if Φ_{ij}^{cd} is a model determinant but Φ_{kl}^{ab} is not, the term with Φ_{kl}^{ab} as intermediate must be calculated while the term with Φ_{ij}^{cd} is omitted. The remaining D form represents sixteen individual terms, which cancel with each other unless, for example, Φ_{ik}^{ac} is a model state and Φ_{jl}^{bd} is not.

The last six diagrams are not required if a "complete" model space is specified, i.e., if P contains all possible excitations among a group of "active" orbitals $\{i, j \cdots - a, b \cdots\}$. In this event, the diagrammatic expansion has been described as "fully linked." Unfortunately, an undue stigma has been associated with the disconnected open diagrams which must be included for the general ("incomplete") model space. These terms are necessary and are size extensive. Hose and Kaldor have discussed the size extensivity of similar terms which arise in their method.[30,38]

Although the present diagrams appear to be quite different because we have chosen to show the explicit diagrams for the chosen model space and to include all of the open lines in them, the diagrams we require are analogous to the pure two-electron interaction forms given by HK,[30,38] except for our denominator combinations. The complete equivalence through third order, achieved by constructing Hermitean combinations of their terms, may be easily verified. If one does not make Hermitean combinations, the non-Hermitean formulation requires that the entire effective Hamiltonian matrix be calculated, rather than its upper (or lower) triangular part. Additionally, we find that the cancellations described above for our disconnected diagrams do not occur for the non-Hermitean form.

It appears that we have more diagrams than HK, but this is because we explicitly show the various labelings of the open diagrams that must all be included in either method. Also, since our particle and hole states are not redefined, unlike the HK transition method, it is easier to recognize the model states, which in either method must be omitted as intermediates. For example, the similar appearance of Φ_0 and of a quadruple excitation from Φ_0, when represented relative to a double excitation from Φ_0, can be confusing. Furthermore, with our convention, a given model state has one definition rather than a set of definitions of the dimension of the model space. This should simplify programming.

The provision for deleting the possibly large numbers of more highly excited model states from P is an attractive practical feature of general model space methods. This greatly reduces the number of effective Hamiltonian matrix elements to be evaluated, and also the number of potential intruder states. The method is not restricted to the single and double excitation model space illustrated in this paper, and could be applied to other problems.

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Perturbative determination of nonadiabatic coupling matrix elements

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Equations for the first- and second-derivative coupling matrix elements between the adiabatic electronic wave functions of a canonical Van Vleck approach are derived for the case of a single nuclear coordinate. Expressions for their order-by-order evaluation, analogous to the multidimensional perturbative expansion of the effective Hamiltonian (given elsewhere) are presented. Diagrammatic notations useful for enumerating certain components of the derivatives are introduced, and the diagrams required through first order are shown.

I. INTRODUCTION

The Born-Oppenheimer adiabatic approximation[1] is one of the most fundamental and widely used approximations in the theory of molecular structure. When the electronic wave function is slowly varying with respect to nuclear displacements, solution of the electronic Schrödinger equation leads to accurate calculations of the properties of molecules. Adiabatic potential energy curves and surfaces are used in the interpretation of spectroscopic data, the prediction of thermochemical quantities (heats of reaction and formation and activation energies), and in the approximate description of the dynamics of molecular collisions (at energies of chemical interest) usually involving a single electronic state. Nonadiabatic treatments (direct solution of the unseparated Schrödinger equation) have also been pursued.[2] The Born-Oppenheimer adiabatic representation can still be used to accurately describe dynamical phenomena, such as radiationless transitions between electronic states of bound molecules or electronic transitions in molecular collisions, by consistently including the nonadiabatic coupling terms in the process of solving the nuclear Schrödinger equation.[3] The most important coupling terms for many systems (and those generally most difficult to obtain) are the matrix elements of the nuclear derivative operator.[4]

Recently there has been increasing interest in the calculation of nondiabatic couplings for *ab initio* electronic states.[5-11] Analytical methods of evaluation must, of course, be derived specifically for each electronic-structure method. Those addressed thus far are the Hartree-Fock self-consistent-field (SCF) and configuration-interaction (CI) methods. Investigations of the utility of the Hellmann-Feynman theorem[5] or the Sidis formula[6] (both valid for exact states) in the case of practical (inexact) wave functions have been made. Numerical methods based on finite-difference formulas,[7,8] although applicable to any type of wave functions, need repetitive solutions of the electronic problem, a nontrivial requirement when highly correlating methods are employed. The approach of fitting a polynomial followed by analytical evaluation of the derivatives[8,9] becomes cumbersome for large CI wave functions and/or for systems with high coordinate dimensionality.

The present paper derives analytical expressions for the nuclear derivatives between electronic wave functions employed in multidimensional diagrammatic perturbation theory. As in that theory, explicit calculation of the wave functions is unnecessary. The approach uses a formulation for the first derivatives that avoids numerical differentiation procedures and provides an order-by-order prescription for obtaining increasingly accurate values. The theory incorporates the effects of configurations omitted from the model space and is, in principle, exact.

For comparison, the expressions for the matrix elements of the first- and second-derivative operators using CI wave functions are given in Sec. II. In Secs. III and IV the nonadiabatic coupling matrix elements corresponding to the perturbative expansion of the electronic wave function are derived. In Sec. V the evaluation of these matrix elements at the orbital level for a specific illustrative model space is presented in the conventional and second-quantized notations, and diagrammatic notations for the required elementary components are introduced. The derivation of an exact Hellmann-Feynman-like relation is included as an Appendix.

II. DERIVATIVE MATRIX ELEMENTS IN THE CI FORMALISM

Solution of the full Schrödinger equation can be accomplished by separating the Hamiltonian into nuclear and electronic parts

$$H = H^{\mathrm{nu}} + H^{\mathrm{el}} \tag{1}$$

and assuming a sum-of-products form of the total wave function

$$\Psi_\alpha^{\mathrm{tot}} = \sum_\gamma \Psi_\gamma^{\mathrm{el}}(\underline{r};\underline{R})\chi_{\gamma\alpha}^{\mathrm{nu}}(\underline{R}) . \tag{2}$$

We use the subscripts $\{ \alpha,\beta,\gamma \dots \}$ to indicate the members of the set of states of interest. The Born-Oppenheimer functions $\{ \Psi_\gamma^{\mathrm{el}} \}$ are solutions of the electronic Schrödinger equation

$$(H^{\mathrm{el}} - E_\gamma^{\mathrm{el}})\Psi_\gamma^{\mathrm{el}} = 0 . \tag{3}$$

In principle, a complete set of Ψ^{el}'s is required, but for practicality it is assumed that a reasonably small number of electronic states $\{ \Psi_\gamma^{\mathrm{el}}; \gamma = \alpha,\beta \dots \}$ will form a sufficient expansion. In the CI method, the electronic wave functions may be expressed in a basis of determinants (or of configuration state functions)

$$\Psi_\gamma^{\mathrm{el}} = \sum_\sigma \Phi_\sigma(\underline{r};\underline{R})C_{\sigma\gamma}(\underline{R}) , \tag{4}$$

where $\{ \sigma,\tau \dots \}$ are labels for a complete expansion. The coefficients $\{ C_{\sigma\gamma} \}$ are solutions to the secular problem

$$\underline{H}\underline{C} = \underline{C}\underline{E}^{\mathrm{el}} , \tag{5}$$

where

$$\underline{H} = \{ \langle \Phi_\sigma | H^{\mathrm{el}} \Phi_\tau \rangle \} \tag{6}$$

and $\{ \Phi_\sigma \}$ are orthonormalized functions, such as Slater determinants formed from Hartree-Fock orbitals. An explicit dependence on the nuclear coordinates $\underline{R}$ arises because these coefficients as well as the expansion coefficients (not shown) of the Φ's in terms of the primitive atomic orbital (AO) basis are different for each nuclear arrangement. An implicit $\underline{R}$ dependence of $\underline{\Phi}$ results from the nuclear-centered nature of the AO basis. The best solution for a given AO basis is obtained when the "full CI problem" is solved; that is, the sum in Eq. (4) (and, thus, the dimension of H) is over all possible determinants (excitations) within the basis. However, in practice, the CI problem is almost always truncated.

For simplicity, we examine the form of the matrix elements of the nuclear Hamiltonian for the case of a diatomic molecule. These couplings involve derivatives of the electronic wave functions with respect to the single internuclear coordinate R, $\langle \Psi_\alpha | \partial\Psi_\beta/\partial R \rangle$, and $\langle \Psi_\alpha | \partial^2\Psi_\beta/\partial R^2 \rangle$, where we have dropped the superscript on Ψ^{el}. In the CI framework the first derivative is given by

$$\left\langle \Psi_\alpha \middle| \frac{\partial}{\partial R} \Psi_\beta \right\rangle = \sum_\sigma C_{\alpha\sigma}^\dagger \frac{\partial}{\partial R} C_{\sigma\beta} + \sum_{\sigma,\tau} C_{\alpha\sigma}^\dagger \left\langle \Phi_\sigma \middle| \frac{\partial}{\partial R} \Phi_\tau \right\rangle C_{\tau\beta} , \tag{7}$$

where we use the convention that the derivative operator may not operate beyond the ket of an integral.

It is well known that the coefficient derivative in the first term become large in regions of avoided crossings (between states of the same symmetry). This might cause difficulties for a numerical evaluation scheme. If so, it is expected that the matrix elements of the Hamiltonian would be more well behaved than the coefficients, so that numerical methods based on an exact Hellmann-Feynman-like relation (see the Appendix)

$$\sum_\sigma C_{\alpha\sigma}^\dagger \frac{\partial'}{\partial R} C_{\sigma\beta} = (E_\beta - E_\alpha)^{-1} \sum_{\sigma,\tau} C_{\alpha\sigma}^\dagger \left[\frac{\partial}{\partial R} H_{\sigma\tau} \right] C_{\tau\beta} \tag{8}$$

could be used. In this notation, the derivative operator must stop at the right parenthesis, and E_β is a specific element of $\underline{E}^{\mathrm{el}}$. Although Eq. (8) is valid for any wave function satisfying Eq. (5), this approach is cumbersome since obtaining accurate energies requires the dimension of $\underline{H}$ to be large; e.g., the basis of Eq. (4) might consist of a given set of determinants and all single and double excitations from that set.

The integral in the second term is zero for $\sigma \neq \tau$ if Φ_σ and Φ_τ differ by more than one orbital, and for $\sigma = \tau$ if the Φ's are real. Some treatments have assumed that these terms vary slowly with R and have neglected them. In fact, however, they can be of a magnitude comparable to the first term.[9] When the Φ's are chosen to be Hartree-Fock determinants, the derivatives in the second term can be expressed in terms of quantities used in and obtained from the coupled perturbed Hartree-Fock (CPHF) method,[12,13] which is commonly applied for the determination of energy gradients. Alternatively, they have been obtained by numerical[9] or,

in some cases, analytical[7,11] means. For the purposes of the present paper, we shall assume that the derivatives of the form in the second term are available and refer to them as standard or configuration derivatives.

The second derivatives are more complex. Direct differentiation of Eq. (4) leads to the expression

$$\left\langle \Psi_\alpha \left| \frac{\partial^2}{\partial R^2} \Psi_\beta \right\rangle = \sum_\sigma C^\dagger_{\alpha\sigma} \frac{\partial^2}{\partial R^2} C_{\sigma\beta} + 2 \sum_{\sigma,\tau} C^\dagger_{\alpha\sigma} \left\langle \Phi_\sigma \left| \frac{\partial}{\partial R} \Phi_\tau \right\rangle \frac{\partial}{\partial R} C_{\tau\beta} + \sum_{\sigma,\tau} C^\dagger_{\alpha\sigma} \left\langle \Phi_\sigma \left| \frac{\partial^2}{\partial R^2} \Phi_\tau \right\rangle C_{\tau\beta} \right. \right. \right. \right. . \quad (9)$$

An alternate formulation is

$$\left\langle \Psi_\alpha \left| \frac{\partial^2}{\partial R^2} \Psi_\beta \right\rangle = \frac{\partial}{\partial R} \left[\left\langle \Psi_\alpha \left| \frac{\partial}{\partial R} \Psi_\beta \right\rangle \right| \right. - \left\langle \left[\frac{\partial}{\partial R} \Psi_\alpha \right] \left| \frac{\partial}{\partial R} \Psi_\beta \right\rangle \right. , \quad (10)$$

where the first term would be obtained numerically. If the full CI problem is solved, the second term can be expanded by insertion of the resolution of the identity

$$1 = \sum_\sigma |\Psi_\sigma\rangle\langle\Psi_\sigma| = \sum_\gamma |\Psi_\gamma\rangle\langle\Psi_\gamma| + \sum_\mu |\Psi_\mu\rangle\langle\Psi_\mu| \quad (11)$$

(where the subscripts $\{\mu,\nu\ldots\}$ indicate members of the complement to $\{\alpha,\beta\ldots\}$) to obtain an expression entirely in terms of first-derivative matrix elements[14]:

$$\left\langle \Psi_\alpha \left| \frac{\partial^2}{\partial R^2} \Psi_\beta \right\rangle = \frac{\partial}{\partial R} \left[\left\langle \Psi_\alpha \left| \frac{\partial}{\partial R} \Psi_\beta \right\rangle \right| \right. + \sum_\sigma \left\langle \Psi_\alpha \left| \frac{\partial}{\partial R} \Psi_\sigma \right\rangle \left\langle \Psi_\sigma \left| \frac{\partial}{\partial R} \Psi_\beta \right\rangle \right. \right. . \quad (12)$$

Otherwise this formula is only approximate. Note that it requires additional first derivatives

$$\left\{ \left\langle \Psi_\alpha \left| \frac{\partial}{\partial R} \Psi_\mu \right\rangle \right\} ,$$

i.e., couplings between the basis states of interest and those "not of interest." The effect of truncation of this sum might be particularly severe because the first term of Eq. (10) includes the second. Thus, for an approximation to Eq. (12), the intended cancellation might be incomplete. This would cause spurious contributions from the first term to remain.

III. DERIVATIVE MATRIX ELEMENTS IN THE CANONICAL VAN VLECK FORMALISM

In the past few years methods for the determination of potential energy surfaces have envolved, such as direct CI,[15] unitary group CI,[16] single-state many-body perturbation theory (MBPT),[17,18] multiconfiguration SCF (MCSCF),[19] and MCSCF + CI.[19] For many applications MBPT has several advantages over the CI approaches. However, a perturbative treatment based on a single (SCF) determinant is restricted to the lowest state of a given symmetry. It may even be expected to encounter difficulties for that state in regions of avoided crossings, where more than one configuration is important. In addition, this method is not well suited for many applications involving open shells or multiple bonds. One solution to these problems is the canonical Van Vleck approach to quasidegenerate perturbation theory.[20]

When the canonical Van Vleck formalism is implemented via a diagrammatic expansion,[21] the energies obtained from approximate solutions of Eq. (3) will be size extensive,[22,23] unlike energies of non-full-CI calculations. In addition, perturbation theory provides a means of decreasing the size of the Hamiltonian matrix, which must be diagonalized, and a prescription for obtaining increasingly accurate (and, in principle, exact) results.

In this formalism, the (exact) correlated electronic state of interest are given by

$$\Psi_\gamma = \sum_\delta U(\underline{R}) \Phi_\delta(\underline{r};\underline{R}) D_{\delta\gamma}(\underline{R}) , \quad (13)$$

where the basis for expansion has been restricted to a selected set of states $\{\Phi_\delta\}$ corresponding to the states of interest and referred to as the model space. The $\underline{R}$ dependence will not be indicated in subsequent equations. The $\{D_{\delta\gamma}\}$ are the eigenvectors of the effective Hamiltonian:

$$\mathcal{H}_{\text{eff}} \underline{D} = \underline{D} \underline{E}^{\text{el}} , \quad (14)$$

and $\{U|\Phi_\delta\rangle\}$ are the perturbed (improved) model functions. U is the unitary decoupling operator

which transforms the Hamiltonian operator H to block diagonal form $\mathscr{H}$. In principle, the exact eigenvalues will be obtained because the effects of the complementary states will be contained in U. In practice, U will be determined such that the transformed Hamiltonian operator

$$\mathscr{H}=U^{\dagger}H^{\rm el}U \tag{15}$$

is block diagonal through a certain order. Then the effective Hamiltonian $\underline{\mathscr{H}}_{\rm eff}$, formed of matrix elements of $\mathscr{H}$, $\{\langle\Phi_\alpha|\mathscr{H}\Phi_\beta\rangle\}$, will be diagnonalized.

Actually, an order-by-order prescription for $\underline{\mathscr{H}}_{\rm eff}$ is given, and U is not explicity calculated. However, for comparative and derivational purposes, the formulation of the wave functions may be examined. Inserting the resolution of the identity in the form

$$1=\sum_{\sigma}|\Phi_\sigma\rangle\langle\Phi_\sigma| =\sum_{\gamma}|\Phi_\gamma\rangle\langle\Phi_\gamma|+\sum_{\mu}|\Phi_\mu\rangle\langle\Phi_\mu| \tag{16}$$

into Eq. (13), we can see that Ψ_γ may be written

$$\Psi_\gamma=\sum_{\sigma,\delta}|\Phi_\sigma\rangle\langle\Phi_\sigma|U\Phi_\delta\rangle D_{\delta\gamma}\,. \tag{17}$$

Comparing Eqs. (4) and (17) we find the relation between the full CI coefficients and the exact (infinite-order) effective Hamiltonian eigenvectors:

$$C_{\sigma\gamma}=\sum_{\delta}\langle\Phi_\sigma|U\Phi_\delta\rangle D_{\delta\gamma}\,. \tag{18}$$

Starting from Eq. (13), we find (since U is unitary) that the first derivatives are given by

$$\left\langle\Psi_\alpha\left|\frac{\partial}{\partial R}\Psi_\beta\right.\right\rangle=\sum_{\gamma}D^{\dagger}_{\alpha\gamma}\frac{\partial}{\partial R}D_{\gamma\beta} +\sum_{\gamma,\delta}D^{\dagger}_{\alpha\gamma}\mathscr{G}'_{\gamma\delta}D_{\delta\beta}\,, \tag{19}$$

where

$$\mathscr{G}'_{\gamma\delta}\equiv\left\langle\Phi_\gamma\left|U^{\dagger}\frac{\partial}{\partial R}U\Phi_\delta\right.\right\rangle. \tag{20}$$

$\mathscr{G}'$ can be thought of as matrix elements in the original Φ basis of a transformed derivative operator, or as derivative matrix elements in the basis of perturbed model functions $U\Phi$.

With the reduced dimensions of this approach it should be practical to calculate the first term of Eq. (19) by the analog to Eq. (8):

$$\sum_{\gamma}D^{\dagger}_{\alpha\gamma}\frac{\partial}{\partial R}D_{\gamma\beta}=(E_\beta-E_\alpha)^{-1}\sum_{\gamma,\delta}D^{\dagger}_{\alpha,\gamma}\left[\frac{\partial}{\partial R}\mathscr{H}_{\gamma\delta}\right]D_{\delta\beta}\,. \tag{21}$$

Again, this expression is an exact equality (at any order) because of Eq. (14). However, the exact couplings will only be obtained [from Eq. (19), optionally incorporating Eq. (21)] when the infinite-order effective Hamiltonian is used. Although the summations in these equations run over only the model-space dimensions, the effort of evaluating the couplings is hidden in the determination of $\underline{\mathscr{G}}'$. The expansion of this term will be examined in detail in Sec. IV. We note that only the lower triangular parts of $\underline{\mathscr{G}}'$ and $\partial\underline{\mathscr{H}}_{\rm eff}/\partial R$ need be calculated since $\underline{\mathscr{G}}'$ is anti-Hermitian and $\underline{\mathscr{H}}_{\rm eff}$ is Hermitian.

The matrix elements of the second-derivative operator obtained by direct differentiation are

$$\left\langle\Psi_\alpha\left|\frac{\partial^2}{\partial R^2}\Psi_\beta\right.\right\rangle=\sum_{\gamma}D^{\dagger}_{\alpha\gamma}\frac{\partial^2}{\partial R^2}D_{\gamma\beta}+2\sum_{\gamma,\delta}D^{\dagger}_{\alpha\gamma}\mathscr{G}'_{\gamma\delta}\frac{\partial}{\partial R}D_{\delta\beta}+\sum_{\gamma,\delta}D^{\dagger}_{\alpha\gamma}\mathscr{G}''_{\gamma\delta}D_{\delta\beta}\,, \tag{22}$$

where

$$\mathscr{G}''_{\gamma\delta}=\left\langle\Phi_\gamma\left|U^{\dagger}\frac{\partial^2}{\partial R^2}U\Phi_\delta\right.\right\rangle. \tag{23}$$

Equation (22) can be expressed alternatively [by substituting Eq. (13) into Eq. (10)] as

$$\left\langle\Psi_\alpha\left|\frac{\partial^2}{\partial R^2}\Psi_\beta\right.\right\rangle=\frac{\partial}{\partial R}\left\langle\Psi_\alpha\left|\frac{\partial}{\partial R}\Psi_\beta\right.\right\rangle-\left\{\sum_{\gamma}\left[\frac{\partial}{\partial R}D^{\dagger}_{\alpha\gamma}\right]\frac{\partial}{\partial R}D_{\gamma\beta}+\sum_{\gamma,\delta}\left[\left[\frac{\partial}{\partial R}D^{\dagger}_{\alpha\gamma}\right]\mathscr{G}'_{\gamma\delta}D_{\delta\beta}-D^{\dagger}_{\alpha\gamma}\mathscr{G}'_{\gamma\delta}\frac{\partial}{\partial R}D_{\delta\beta}\right]\right.$$
$$\left.-\sum_{\gamma,\delta}D^{\dagger}_{\alpha\gamma}\left[\sum_{\epsilon}\mathscr{G}'_{\gamma\epsilon}\mathscr{G}'_{\epsilon\delta}+\sum_{\mu}\mathscr{G}'_{\gamma\mu}\mathscr{G}'_{\mu\delta}\right]D_{\delta\beta}\right\}. \tag{24}$$

Equation (12) could be used, truncated to a sum over γ only (since the remaining states are not determined

in the effective Hamiltonian method), but the previously stated criticism of this procedure would apply. The second derivative of the coefficients in Eq. (22) can be alternatively obtained by similar techniques. We write it as

$$\sum_{\gamma} D^{\dagger}_{\alpha\gamma}\frac{\partial^2}{\partial R^2}D_{\gamma\beta}=\frac{\partial}{\partial R}\left[\sum_{\gamma} D^{\dagger}_{\alpha\gamma}\frac{\partial}{\partial R}D_{\gamma\beta}\right]-\sum_{\gamma}\left[\frac{\partial}{\partial R}D^{\dagger}_{\alpha\gamma}\right]\frac{\partial}{\partial R}D_{\gamma\beta}\,, \tag{25}$$

where the first term is to be obtained numerically. Inserting the identity into the second term and substituting Eq. (21) gives

$$\sum_{\gamma} D^{\dagger}_{\alpha\gamma}\frac{\partial^2}{\partial R^2}D_{\gamma\beta}=\frac{\partial}{\partial R}\left[(E_\beta-E_\alpha)^{-1}\sum_{\gamma,\delta} D^{\dagger}_{\alpha\gamma}\left[\frac{\partial}{\partial R}\mathscr{H}_{\gamma\delta}\right]D_{\delta\beta}\right]$$

$$+\sum_{\gamma,\delta,\epsilon,\zeta,\eta}(E_\delta-E_\alpha)^{-1}D^{\dagger}_{\alpha\gamma}\left[\frac{\partial}{\partial R}\mathscr{H}_{\gamma\zeta}\right]D_{\zeta\delta}(E_\beta-E_\delta)^{-1}D^{\dagger}_{\delta\epsilon}\left[\frac{\partial}{\partial R}\mathscr{H}_{\epsilon\eta}\right]D_{\eta\beta}\,. \tag{26}$$

The latter process can also be applied to the second term of Eq. (24). The choice between Eqs. (22) and (24) is then further influenced by observing that Eq. (24) requires the additional matrix elements $\{\mathscr{G}'_{\gamma\mu}\}$, while Eq. (22) calls for $\mathscr{G}''$ matrix elements. These off-diagonal $\mathscr{G}'$ matrix elements can be obtained analogously to the model-space diagonal block of $\mathscr{G}'$; however, there will, in general, be many more of them. The perturbative determination of $\mathscr{G}'$ and $\mathscr{G}''$ will be given in Sec. IV.

IV. PERTURBATIVE EXPANSIONS

The first-derivative matrix elements in the effective Hamiltonian formalism are prescribed by Eq. (19). The coefficient derivatives (first term) can be calculated numerically or from derivatives of $\mathscr{H}_{\rm eff}$ via Eq. (21). In the latter case, an ordered evaluation scheme emerges. In the canonical Van Vleck method it is convenient to define the transformation U by

$$U=e^{G}\,, \tag{27}$$

with

$$G=-G^{\dagger}\,. \tag{28}$$

Then, through third order, the effective Hamiltonian is given by[20]

$$\begin{aligned}
&\mathscr{H}^{(0)}_{\gamma\delta}=\delta_{\gamma\delta}E^0_\gamma\,,\\
&\mathscr{H}^{(1)}_{\gamma\delta}=\langle\Phi_\gamma|V\Phi_\delta\rangle\,,\\
&\mathscr{H}^{(2)}_{\gamma\delta}=\tfrac{1}{2}\langle\Phi_\gamma|[V,G^{(1)}]\Phi_\delta\rangle\,,\\
&\mathscr{H}^{(3)}_{\gamma\delta}=\tfrac{1}{2}\langle\Phi_\gamma|[V,G^{(2)}]\Phi_\delta\rangle\,,
\end{aligned} \tag{29}$$

where

$$G^{(0)}=0\,,$$

$$G^{(1)}=\sum_{\gamma}\{R^0_\gamma VP_\gamma-P_\gamma VR^0_\gamma\}\,, \tag{30}$$

$$G^{(2)}=\sum_{\gamma}\{R^0_\gamma[V,G^{(1)}]P_\gamma-P_\gamma[V,G^{(1)}]R^0_\gamma\}\,,$$

and

$$\begin{aligned}
&H^{\rm el}=H^0+V\,,\\
&H^0\Phi_\gamma=E^0_\gamma\Phi_\gamma\,,\\
&P_\gamma=|\Phi_\gamma\rangle\langle\Phi_\gamma|\,,\\
&R^0_\gamma=\sum_{\mu}\frac{|\Phi_\mu\rangle\langle\Phi_\mu|}{(E^0_\gamma-E^0_\mu)}\,.
\end{aligned} \tag{31}$$

It should be noted that G has no block diagonal (D) parts:

$$G_D=\sum_{\gamma,\delta}|\Phi_\gamma\rangle\langle\Phi_\gamma|G\Phi_\delta\rangle\langle\Phi_\delta|+\sum_{\mu,\nu}|\Phi_\mu\rangle\langle\Phi_\mu|G\Phi_\nu\rangle\langle\Phi_\nu|=0\,. \tag{32}$$

Thus G is completely specified by its off-diagonal part G_X:

$$G_X=\sum_{\gamma,\mu}\{|\Phi_\gamma\rangle\langle\Phi_\gamma|G\Phi_\mu\rangle\langle\Phi_\mu|+|\Phi_\mu\rangle\langle\Phi_\mu|G\Phi_\gamma\rangle\langle\Phi_\gamma|\}\,. \tag{33}$$

It is then straightforward to see that the derivatives of $\mathscr{H}_{\text{eff}}$ involve only derivatives of the two-electron integrals and the (zeroth-order) orbital energies:

$$\frac{\partial}{\partial R}\mathscr{H}^{(0)}_{\gamma\delta}=\delta_{\gamma\delta}\frac{\partial}{\partial R}E^0_\gamma\,,$$

$$\frac{\partial}{\partial R}\mathscr{H}^{(1)}_{\gamma\delta}=\frac{\partial}{\partial R}(\langle\Phi_\gamma|V\Phi_\delta\rangle)\,,$$

$$\frac{\partial}{\partial R}\mathscr{H}^{(2)}_{\gamma\delta}=\frac{1}{2}\frac{\partial}{\partial R}\left[\sum_\mu\langle\Phi_\gamma|V\Phi_\mu\rangle\langle\Phi_\mu|V\Phi_\delta\rangle[(E^0_\gamma-E^0_\mu)^{-1}+(E^0_\delta-E^0_\mu)^{-1}]\right], \tag{34}$$

$$\frac{\partial}{\partial R}\mathscr{H}^{(3)}_{\gamma\delta}=\frac{1}{2}\frac{\partial}{\partial R}\left[\sum_{\mu,\nu}\left[\frac{\langle\Phi_\gamma|V\Phi_\mu\rangle\langle\Phi_\mu|V\Phi_\nu\rangle\langle\Phi_\nu|V\Phi_\delta\rangle}{(E^0_\gamma-E^0_\mu)(E^0_\gamma-E^0_\nu)}+\frac{\langle\Phi_\gamma|V\Phi_\mu\rangle\langle\Phi_\nu|V\Phi_\mu\rangle\langle\Phi_\mu|V\Phi_\delta\rangle}{(E^0_\delta-E^0_\nu)(E^0_\delta-E^0_\mu)}\right]\right.$$
$$\left.-\sum_{\mu,\epsilon}\left[\frac{\langle\Phi_\gamma|V\Phi_\mu\rangle\langle\Phi_\mu|V\Phi_\epsilon\rangle\langle\Phi_\epsilon|V\Phi_\delta\rangle}{(E^0_\delta-E^0_\mu)(E^0_\epsilon-E^0_\mu)}+\frac{\langle\Phi_\gamma|V\Phi_\epsilon\rangle\langle\Phi_\epsilon|V\Phi_\mu\rangle\langle\Phi_\mu|V\Phi_\delta\rangle}{(E^0_\epsilon-E^0_\mu)(E^0_\gamma-E^0_\mu)}\right]\right].$$

These derivatives may be determined by the CPHF method as implemented by Pople and co-workers.[12]

$\mathscr{L}'$ may also be examined in an ordered fashion. When U is expanded, $\mathscr{L}'$ may be given by a Hausdorf expansion:

$$\mathscr{L}'_{\gamma\delta}=\left\langle\Phi_\gamma\left|\left[\frac{\partial}{\partial R}+\left[\frac{\partial}{\partial R},G\right]+\frac{1}{2}\left[\left[\frac{\partial}{\partial R},G\right],G\right]+\dots\right]\Phi_\delta\right\rangle, \tag{35}$$

where the derivative operator is allowed to work all the way through to the ket. Then we find

$$\mathscr{L}'_{\gamma\delta}=\left\langle\Phi_\gamma\left|\frac{\partial}{\partial R}\Phi_\delta\right\rangle+\left\langle\Phi_\gamma\right|\left[\left[\frac{\partial G}{\partial R}\right]_D+\frac{1}{2}\left[\left[\frac{\partial G}{\partial R}\right]_X,G_X\right]+\frac{1}{6}\left[\left[\left[\frac{\partial G}{\partial R}\right]_D,G_X\right],G_X\right]\right.$$
$$\left.+\frac{1}{24}\left[\left[\left[\left[\frac{\partial G}{\partial R}\right]_X,G_X\right],G_X\right],G_X\right]+\dots\right]\Phi_\delta\right\rangle. \tag{36}$$

When G is expanded by order we find the low orders of $\mathscr{L}'$ to be

$$\mathscr{L}'^{(0)}_{\gamma\delta}=\left\langle\Phi_\gamma\left|\frac{\partial}{\partial R}\Phi_\delta\right\rangle\right.,$$

$$\mathscr{L}'^{(1)}_{\gamma\delta}=\left\langle\Phi_\gamma\left|\left[\frac{\partial}{\partial R}G^{(1)}\right]_D\Phi_\delta\right\rangle\right., \tag{37}$$

$$\mathscr{L}'^{(2)}_{\gamma\delta}=\left\langle\Phi_\gamma\right|\left[\left[\frac{\partial}{\partial R}G^{(2)}\right]_D+\frac{1}{2}\left[\left[\frac{\partial}{\partial R}G^{(1)}\right]_X,G^{(1)}\right]\right]\Phi_\delta\,,$$

$$\mathscr{L}'^{(3)}_{\gamma\delta}=\left\langle\Phi_\gamma\right|\left[\left[\left[\frac{\partial}{\partial R}G^{(3)}\right]_D+\frac{1}{2}\left[\left[\frac{\partial}{\partial R}G^{(1)}\right]_X,G^{(2)}\right]+\frac{1}{2}\left[\left[\frac{\partial}{\partial R}G^{(2)}\right]_X,G^{(1)}\right]\right.$$
$$\left.+\frac{1}{6}\left[\left[\left[\frac{\partial}{\partial R}G^{(1)}\right]_D,G^{(1)}\right],G^{(1)}\right]+\dots\right]\Phi_\delta\right\rangle.$$

Thus, by multiplying Eqs. (34) and (37) by the appropriate eigenvector components, prescribed by Eqs. (19)–(21), the coupling matrix elements can be obtained to an order consistent with that of the effective

Hamiltonian. Explicit contruction of the wave functions is unncessary.

The transition from the notation above, involving operator derivatives, to the basic expressions is straightforward, although fairly complex. However, a shortcut is available for those terms involving the diagonal block components, such as the leading terms above. Since $G_D=0$,

$$\frac{\partial}{\partial R}\langle\Phi_\gamma|G\Phi_\delta\rangle=0\,,$$

$$\frac{\partial}{\partial R}\langle\Phi_\mu|G\Phi_\nu\rangle=0\,, \tag{38}$$

and, therefore,

$$\left\langle\Phi_\gamma\left|\left[\frac{\partial}{\partial R}G\right]_D\Phi_\delta\right\rangle=-\left\{\left\langle\left[\frac{\partial}{\partial R}\Phi_\gamma\right]\middle|G\Phi_\delta\right\rangle+\left\langle\Phi_\gamma\middle|G\frac{\partial}{\partial R}\Phi_\delta\right\rangle\right\},$$

$$\left\langle\Phi_\mu\left|\left[\frac{\partial}{\partial R}G\right]_D\Phi_\nu\right\rangle=-\left\{\left\langle\left[\frac{\partial}{\partial R}\Phi_\mu\right]\middle|G\Phi_\nu\right\rangle+\left\langle\Phi_\mu\middle|G\frac{\partial}{\partial R}\Phi_\nu\right\rangle\right\}. \tag{39}$$

These equations are valid for each order. For example, at first order

$$\mathscr{G}'^{(1)}_{\gamma\delta}=-\sum_\mu\left[\frac{\left\langle\left[\frac{\partial}{\partial R}\Phi_\gamma\right]\middle|\Phi_\mu\right\rangle\langle\Phi_\mu|V\Phi_\delta\rangle}{(E^0_\delta-E^0_\mu)}-\frac{\langle\Phi_\gamma|V\Phi_\mu\rangle\left\langle\Phi_\mu\middle|\frac{\partial}{\partial R}\Phi_\delta\right\rangle}{(E^0_\gamma-E^0_\mu)}\right]. \tag{40}$$

The integrals $\{\langle\Phi_\gamma|V\Phi_\mu\rangle\}$ are the same ones required for $\mathscr{H}^{(2)}_{\rm eff}$, and the derivative matrix elements are a subset of the standard ones used in Eq. (7). In this form, considering the derivative operator as a one-electron operator, $\mathscr{G}'^{(1)}$ can be easily diagrammed, as will be demonstrated in Sec. V. The nested derivatives involving $(\partial G/\partial R)_D$ may be expressed similarly.

However, terms with $(\partial G/\partial R)_X$ must be handled directly, substituting and differentiating the components of Eqs. (30) and (31):

$$\begin{aligned}\mathscr{G}'^{(2)}_{\gamma\delta}=&-\left\langle\left[\frac{\partial}{\partial R}\Phi_\gamma\right]\middle|G^{(2)}\Phi_\delta\right\rangle-\left\langle\Phi_\gamma\middle|G^{(2)}\frac{\partial}{\partial R}\Phi_\delta\right\rangle\\
&-\tfrac{1}{2}\sum_\mu\left[\sum_\epsilon\frac{\left\langle\Phi_\gamma\middle|\frac{\partial}{\partial R}\Phi_\epsilon\right\rangle\langle\Phi_\epsilon|V\Phi_\mu\rangle}{(E^0_\epsilon-E^{0)}_\mu}+\frac{\partial}{\partial R}\left[\frac{\langle\Phi_\gamma|V\Phi_\mu\rangle}{(E^0_\gamma-E^0_\mu)}\right]\right]\frac{\langle\Phi_\mu|V\Phi_\delta\rangle}{(E^0_\delta-E^0_\mu)}\\
&+\tfrac{1}{2}\sum_\mu\frac{\langle\Phi_\gamma|V\Phi_\mu\rangle}{(E^0_\gamma-E^0_\mu)}\left[\sum_\epsilon\frac{\langle\Phi_\mu|V\Phi_\epsilon\rangle\left\langle\left[\frac{\partial}{\partial R}\Phi_\epsilon\right]\middle|\Phi_\delta\right\rangle}{(E^0_\epsilon-E^0_\mu)}+\frac{\partial}{\partial R}\left[\frac{\langle\Phi_\mu|V\Phi_\delta\rangle}{(E^0_\delta-E^0_\mu)}\right]\right]\\
&+\sum_{\mu,\nu}\frac{\langle\Phi_\gamma|V\Phi_\mu\rangle\left\langle\Phi_\mu\middle|\frac{\partial}{\partial R}\Phi_\nu\right\rangle\langle\Phi_\nu|V\Phi_\delta\rangle}{(E^0_\gamma-E^0_\mu)(E^0_\delta-E^0_\nu)}\,.\end{aligned} \tag{41}$$

Although this result is fairly complicated, the terms involving the two-electron integral and energy derivatives are the same ones required for $\partial\mathscr{H}^{(2)}_{\rm eff}/\partial R$ [in Eq. (34)]. The remaining terms of $\mathscr{G}'^{(2)}$ can be diagrammed similarly to the first-order terms, although there are quite a number of them.

The $\mathscr{G}''$ matrix elements called for in Eq. (22) can also be examined in an ordered fashion by converting from U to G:

$$\mathscr{G}''_{\gamma\delta}=\left\langle\Phi_\gamma\left|\left\{\frac{\partial^2}{\partial R^2}+\left[\frac{\partial^2}{\partial R^2},G\right]+\frac{1}{2}\left[\left[\frac{\partial^2}{\partial R^2},G\right],G\right]+\ldots\right\}\Phi_\delta\right\rangle. \tag{42}$$

Then, expanding G by orders and collecting terms we obtain

$$\mathscr{G}''^{(0)}_{\gamma\delta} = \left\langle \Phi_\gamma \left| \frac{\partial^2}{\partial R^2} \Phi_\delta \right\rangle \right.,$$

$$\mathscr{G}''^{(1)}_{\gamma\delta} = \left\langle \Phi_\gamma \left| \left[\frac{\partial^2}{\partial R^2} G^{(1)} \right]_D \Phi_\delta \right\rangle \right. + 2 \left\langle \Phi_\gamma \left| \left[\frac{\partial}{\partial R} G^{(1)} \right] \frac{\partial}{\partial} R \Phi_\delta \right\rangle \right., \tag{43}$$

$$\mathscr{G}''^{(2)}_{\gamma\delta} = \left\langle \Phi_\gamma \left| \left[\frac{\partial^2}{\partial R^2} G^{(2)} \right]_D \Phi_\delta \right\rangle \right. + 2 \left\langle \Phi_\gamma \left| \left[\frac{\partial}{\partial R} G^{(2)} \right] \frac{\partial}{\partial R} \Phi_\delta \right\rangle \right. + \left\langle \Phi_\gamma \left| \left[\frac{\partial}{\partial R} G^{(1)} \right]^2 \Phi_\delta \right\rangle \right.$$
$$+ \tfrac{1}{2} \left\langle \Phi_\gamma \left| \left[\left[\frac{\partial^2}{\partial R^2} G^{(1)} \right] \Phi_\delta \right\rangle \right. + \left\langle \Phi_\gamma \left| \left[\left[\frac{\partial}{\partial R} G^{(1)} \right] \frac{\partial}{\partial R} \Phi_\delta \right\rangle \right. \right. \right. .$$

Examples of the evaluation of $\underline{\mathscr{G}}'$ and $\underline{\mathscr{G}}''$ in terms of orbitals are given in Sec. V.

V. DIAGRAMMATIC REPRESENTATION

We present an orbital formulation of the nonadiabatic couplings between electronic states obtained from a diagrammatic implementation of canonical Van Vleck perturbation theory, illustrated for the model space chosen in Ref. (21), which consists of a Hartree-Fock determinant plus selected single and double excitations. The effective Hamiltonian matrix elements have been given both formally[20] and diagrammatically.[21] These diagrams are useful for showing which subsets of integrals are required for evaluation of the matrix elements and (as in ordinary MBPT calculations) for providing size-extensive approximations and efficient algorithms for their evaluation. The derivatives of these matrix elements required for the evaluation of the coefficient derivative part of the nonadiabatic couplings using Eq. (21) will be obtained via CPHF, as mentioned earlier. The terms in $\underline{\mathscr{G}}'$ can be diagrammed using the one-electron nature of the derivative operator working on a Slater determinant. Examination of the derivatives of $\underline{\mathscr{G}}'^{(0)}$, i.e., the standard configuration derivatives

$$\left\{ \left\langle \Phi_\gamma \left| \frac{\partial}{\partial R} \Phi_\delta \right\rangle \right. \right\},$$

in the conventional, second-quantized, and diagrammatic forms serves as a convenient introduction to the many-body techniques employed herein.

It is well known that the configuration derivatives in Eq. (36) [or Eq. (7)] are zero if γ and δ (or σ and τ) are identical and $\underline{\Phi}$ is real, or if Φ_γ and Φ_δ differ by more than one orbital. For example, let Φ_γ and Φ_δ be singly excited determinants, which may be expressed in terms of annihilation and creation operators (indicated by orbital labels, appropriately daggered) working on the Hartree-Fock determinant Φ_0:

$$|\Phi_\gamma\rangle = a^\dagger i \,|\Phi_0\rangle \,, \tag{44}$$
$$|\Phi_\delta\rangle = b^\dagger j \,|\Phi_0\rangle \,,$$

where a, i, b, and j, refer to specific one-electron spin orbitals (with $\{i,j,k\ldots\}$ and $\{a,b,c,\ldots\}$ labeling occupied and virtual orbitals, respectively). Then the matrix element is represented conventionally by

$$\left\langle \Phi_\gamma \left| \frac{\partial}{\partial R} \Phi_\delta \right\rangle \right. = \left\langle \mathscr{A}\{1,2,\ldots,(n-2),a,j\} \left| \frac{\partial}{\partial R} \mathscr{A}\{1,2,\ldots,(n-2),i,b\} \right\rangle \right. , \tag{45}$$

where orbital $a(b)$ has replaced orbital $i(j)$. Since $i,j \neq \{1,2\ldots(n-2),a,b\}$,

$$\left\langle \Phi_\gamma \left| \frac{\partial}{\partial R} \Phi_\delta \right\rangle \right. = -\delta_{ab} \left\langle j \left| \frac{\partial}{\partial R} i \right\rangle \right. + \delta_{ij} \left\langle a \left| \frac{\partial}{\partial R} b \right\rangle \right. . \tag{46}$$

The sign of the first term arises from the permutation of orbitals required to match up the remaining orbitals when $i \neq j$. When $i = j$, no rearrangement is necessary (second term). Again, the diagonal matrix elements are zero if $\underline{\Phi}$ is real. In second quantization, we respresent $\partial/\partial R$ as a one-electron operator:

$$\frac{\partial}{\partial R} \equiv \sum_{s,t} q_{st} s^\dagger t \ , \tag{47}$$

where

$$q_{st} = \left\langle s \left| \frac{\partial}{\partial R} t \right. \right\rangle . \tag{48}$$

Then, following the usual procedures (and indicating only the orbitals which differ from those in Φ_0)

$$\begin{aligned} \left\langle i^\dagger a \left| \frac{\partial}{\partial R} b^\dagger j \right. \right\rangle &= \sum_{s,t} q_{st} \langle i^\dagger a s^\dagger t b^\dagger j \rangle \\ &= \delta_{ij} q_{ab} - \delta_{ab} q_{ji} + \delta_{ab} \delta_{ij} \sum_s q_{ss} \\ &= \delta_{ij} \left\langle a \left| \frac{\partial}{\partial R} b \right. \right\rangle - \delta_{ab} \left\langle j \left| \frac{\partial}{\partial R} i \right. \right\rangle . \end{aligned} \tag{49}$$

The nonzero configuration derivatives within the chosen model space are shown digrammatically in Fig. 1. In these diagrams an open dot represents the differential operator, which (because of the orbital product form of the model functions) acts as one-electron operator. Thus, each open dot must have one vector (a particle or hole line) entering and one leaving. Particle (hole) lines are oriented from right to left (left to right). The terms required are specified diagrammatically by forming all possible connections of the bra and ket model-state vertices with the differential operator. The bras and kets are indicated by diamonds with equal numbers of specifically labeled particle and hole lines (the so-called "open" lines) which describe the model states with reference to the Hartree-Fock determinant. The algebraic expressions are regained diagrammatically by interpreting the derivative interaction symbol as ⟨outgoing vector | $\partial/\partial R$ | incoming vector⟩ with a sign factor $(-1)^{l+h}$, where l indicates the number of loops and h the number of hole lines. Thus the two terms of Eq. (46) are represented by the SE | SE diagram of Fig. 1 and its particle-hole reversed (phr) diagram. Since the integrals in Eq. (46) involve two orbitals of the same type (occupied or virtual), the entering and leaving vectors of the differential operator go in the same direction.

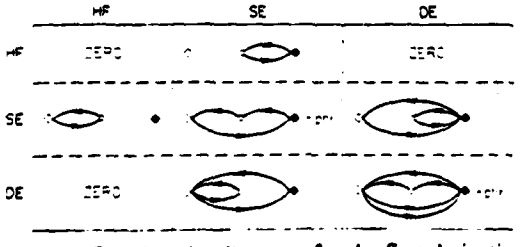

FIG. 1. Zeroth-order diagrams for the first derivative part $\mathcal{L}'$ of the nonadiabatic coupling matrix elements.

The derivative parts of the $\mathcal{L}'^{(1)}$ terms in Eq. (40) are diagrammed and derived similarly. The usual two-electron interactive perturbation V [represented by a solid dot and referred to as V^N in Ref. (21)] in the right-hand part of the first term must have two vectors entering and two leaving. Figure 2 shows all of the types of diagrams which occur in the evaluation of this term for a model space consisting of the Hartree-Fock determinant plus selected singly and double excited determinants. The diagrams for the second term are obtained by time reversal (TR) (left-right mirror imaging) of the ones shown. The off-diagonal block diagrams will come from TR of their conjugate blocks; e.g., TR(SE|DE) yields the DE|SE diagrams. We note that the DE|SE terms in the figure can have triply excited intermediate states (whereas the SE|DE terms cannot) because of the ordering of the two operators. Of course the opposite holds when the order is reversed.

The diagrams in Fig. 2 may be derived algebraically in the following manner. Let us examine the case of a SE|SE (single-excitation diagonal block) matrix element. Take the definitions in Eq. (44) and let Φ_μ be a single excitation

$$|\Phi_\mu\rangle = c^\dagger k \, |\Phi_0\rangle \ . \tag{50}$$

Then

$$\left\langle \Phi_\gamma \left| \frac{\partial}{\partial R} \Phi_\mu \right. \right\rangle = -\delta_{ac} \left\langle k \left| \frac{\partial}{\partial R} i \right. \right\rangle + \delta_{ik} \left\langle a \left| \frac{\partial}{\partial R} c \right. \right\rangle . \tag{51}$$

Next, we determine that

$$\langle \Phi_\mu | \, V \Phi_\delta \rangle = -\langle bj | \, | ck \rangle \ , \tag{52}$$

since $\delta_{bc}\delta_{jk}$ is not allowed (i.e., Φ_μ must not be a model state). The combination of Eqs. (51) and (52) yields two types of terms

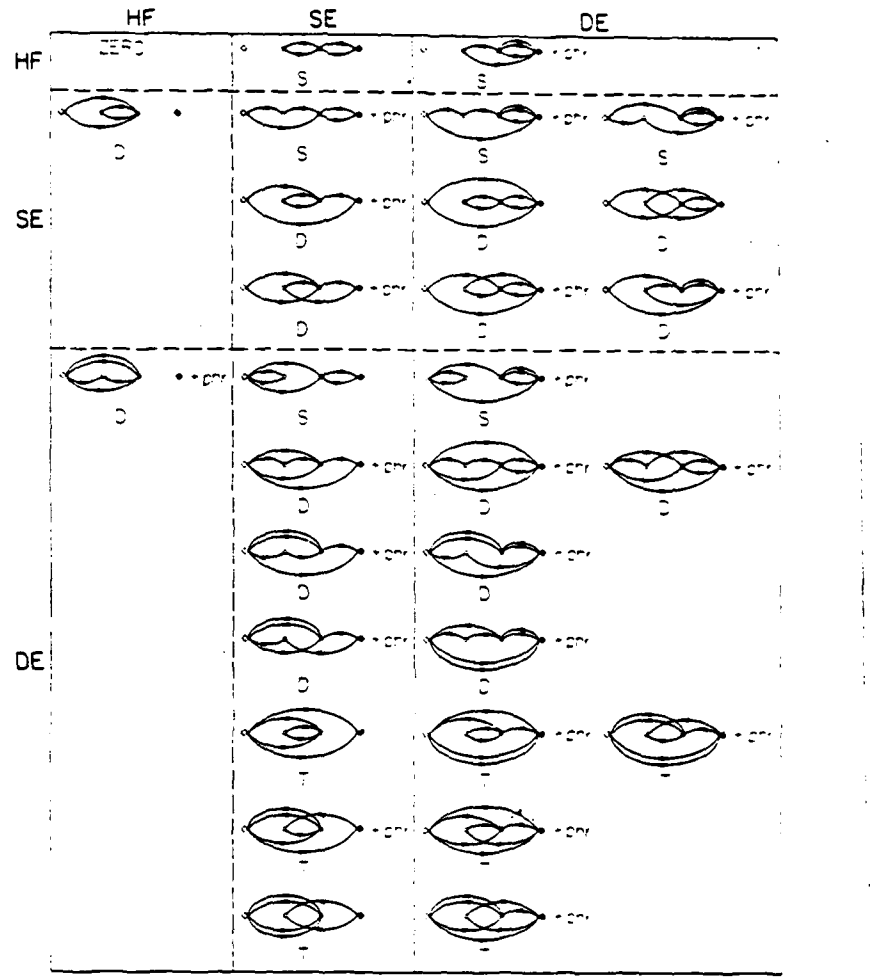

FIG. 2. First-order diagrams for the first-derivative part $\mathcal{L}'$ of the nonadiabatic coupling matrix elements.

$$\sum_{\mu}^{SE}\left\langle\Phi_\gamma\left|\frac{\partial}{\partial R}\Phi_\mu\right.\right\rangle\langle\Phi_\mu|V\Phi_\delta\rangle=\sum_k\left\langle k\left|\frac{\partial}{\partial R}i\right.\right\rangle\langle aj||bk\rangle-\sum_c\left\langle a\left|\frac{\partial}{\partial R}c\right.\right\rangle\langle cj||bi\rangle\,, \tag{53}$$

which are graphically given by the first SE|SE diagram of Fig. 2 and its phr. The remaining orbital summation corresponds in the diagram to the vector *not* touching a model-state vertex (indicated by a diamond).

Similarly, if Φ_μ is a double excitation

$$|\Phi_\mu\rangle=c^\dagger d^\dagger lk\,|\Phi_0\rangle\,, \tag{54}$$

then

$$\left\langle\Phi_\gamma\left|\frac{\partial}{\partial R}\Phi_\mu\right.\right\rangle=\tfrac{1}{4}\left\langle\mathcal{A}\{1,2,\ldots,(n-3),a,k,l\}\left|\frac{\partial}{\partial R}\mathcal{A}\{1,2,\ldots,(n-3),i,c,d\}\right.\right\rangle \tag{55}$$

may be reduced to

$$\left\langle\Phi_\gamma\left|\frac{\partial}{\partial R}\Phi_\mu\right.\right\rangle=\tfrac{1}{4}\delta_{i(kl)}\delta_{a(cd)}\left\langle(lk)\left|\frac{\partial}{\partial R}(dc)\right.\right\rangle\,, \tag{56}$$

where the notation

$$\delta_{i(kl)}\,|\,(lk)\rangle = \delta_{ik}\,|\,l\rangle - \delta_{il}\,|\,k\rangle \tag{57}$$

is used. Taken together with

$$\langle\Phi_\gamma\,|\,V\Phi_\delta\rangle = \delta_{j(kl)}\langle(lk)b\,|\,|\,cd\rangle + \delta_{b(cd)}\langle(dc)j\,|\,|\,kl\rangle\ , \tag{58}$$

Eq. (56) gives

$$\sum_{\mu}^{DE}\left\langle\Phi_\gamma\left|\frac{\partial}{\partial R}\Phi_\mu\right.\right\rangle\langle\Phi_\mu\,|\,V\Phi_\delta\rangle = -\delta_{ij}\sum_{e,m}\left\langle m\left|\frac{\partial}{\partial R}e\right.\right\rangle\langle mb\,|\,|\,ae\rangle + \delta_{ab}\sum_{m,e}\left\langle m\left|\frac{\partial}{\partial R}e\right.\right\rangle\langle ej\,|\,|\,im\rangle$$
$$+\sum_{e}\left\langle j\left|\frac{\partial}{\partial R}e\right.\right\rangle\langle ib\,|\,|\,ae\rangle - \sum_{m}\left\langle m\left|\frac{\partial}{\partial R}b\right.\right\rangle\langle aj\,|\,|\,im\rangle\ . \tag{59}$$

The first two terms of Eq. (59) correspond to the second diagram (in Fig. 2) and it phr. The last two are represented by the remaining SE|SE digram and its phr.

The second-derivative matrix elements may be derived similarly. From the form in Eq. (43) we substitute for $G^{(n)}$ and obtain at low order

$$\mathcal{G}''^{(0)}_{\gamma\delta} = \left\langle\Phi_\gamma\left|\frac{\partial^2}{\partial R^2}\Phi_\delta\right.\right\rangle, \tag{60}$$

$$\mathcal{G}''^{(1)}_{\gamma\delta} \sum_{\mu}\left\langle\Phi_\gamma\left|\frac{\partial^2}{\partial R^2}\Phi_\mu\right.\right\rangle\frac{\langle\Phi_\gamma\,|\,V\Phi_\delta\rangle}{(E^0_\delta - E^0_\mu)} + 2\left\langle\Phi_\gamma\left|\frac{\partial}{\partial R}\Phi_\mu\right.\right\rangle\frac{\partial}{\partial R}\left[\frac{\langle\Phi_\mu\,|\,V\Phi_\delta\rangle}{(E^0_\delta - E^0_\mu)}\right] + \frac{\langle\Phi_\gamma\,|\,V\Phi_\mu\rangle}{(E^0_\gamma - E^0_\mu)}\left\langle\Phi_\mu\left|\frac{\partial^2}{\partial R^2}\Phi_\delta\right.\right\rangle .$$

The complexity of successive terms grows rapidly; the second-order part consist of 17 terms.

Let us convert the zeroth-order contribution to orbital form. In second quantization we represent $\partial^2/\partial R^2$ by $\partial/\partial R$ operating twice:

$$\frac{\partial^2}{\partial R^2} = \sum_{s,t,u,v}\left\langle s\left|\frac{\partial}{\partial R}t\right.\right\rangle s^\dagger t\left\langle u\left|\frac{\partial}{\partial R}v\right.\right\rangle u^\dagger v\ . \tag{61}$$

Then we find for single excitations, for example, that

$$\left\langle\Phi_\gamma\left|\frac{\partial^2}{\partial R^2}\Phi_\delta\right.\right\rangle = -\delta_{ab}\delta_{ij}\sum_{s,u}^{occ}\left\langle s\left|\frac{\partial}{\partial R}u\right.\right\rangle\left\langle u\left|\frac{\partial}{\partial R}s\right.\right\rangle - \delta_{ab}\delta_{ij}\sum_{s}^{occ}\left\langle\left[\frac{\partial}{\partial R}s\right]\right|\left.\frac{\partial}{\partial R}s\right\rangle$$
$$+2\delta_{ab}\sum_{s}^{occ}\left\langle s\left|\frac{\partial}{\partial R}i\right.\right\rangle\left\langle j\left|\frac{\partial}{\partial R}s\right.\right\rangle + \delta_{ab}\left\langle\left[\frac{\partial}{\partial R}j\right]\right|\left.\frac{\partial}{\partial R}i\right\rangle$$
$$-2\delta_{ij}\sum_{s}^{occ}\left\langle s\left|\frac{\partial}{\partial R}b\right.\right\rangle\left\langle a\left|\frac{\partial}{\partial R}s\right.\right\rangle - \delta_{ij}\left\langle\left[\frac{\partial}{\partial R}a\right]\right|\left.\frac{\partial}{\partial R}b\right\rangle$$
$$-2\left\langle a\left|\left[\frac{\partial}{\partial R}b\right]\right.\right\rangle\left\langle j\left|\frac{\partial}{\partial R}i\right.\right\rangle + 2\left\langle a\left|\frac{\partial}{\partial R}i\right.\right\rangle\left\langle j\left|\frac{\partial}{\partial R}b\right.\right\rangle\ . \tag{62}$$

These terms are prescribed diagrammatically by the SE|SE block of Fig. 3. Diagrammatically, the necessary terms consist simply of all possible proper connections of the SE bra and ket with two derivative operator symbols. Note that the intermediate states here can be model-space states since they are part of the resolution of the identity in the form

$$1 = \sum_{t}|\,t\rangle\langle t\,|\ . \tag{63}$$

The factors of 2 on the last two terms of Eq. (62) arise diagrammatically when it is observed that the last two diagrams are equivalent, as are the third from the last and its phr. The remaining diagrams are only

reconcilable with Eq. (62) after combining the terms with matching delta functions. This is accomplished by inserting the resolution of the identity into the even numbered terms, and separating the sums over occupied and virtual orbitals; e.g.,

$$-\delta_{ab}\delta_{ij}\sum_{s}^{\text{occ}}\left[\sum_{u}^{\text{occ}}\left\langle s\left|\frac{\partial}{\partial R}u\right.\right\rangle\left\langle u\left|\frac{\partial}{\partial R}s\right.\right\rangle+\left\langle\left|\frac{\partial}{\partial R}s\right.\right|\left.\frac{\partial}{\partial R}s\right\rangle\right] \tag{64}$$

$$=-\delta_{ab}\delta_{ij}\sum_{k}\left[\sum_{l}\left\langle k\left|\frac{\partial}{\partial R}l\right.\right\rangle\left\langle l\left|\frac{\partial}{\partial R}k\right.\right\rangle+\sum_{l}\left\langle\left|\frac{\partial}{\partial R}k\right.\right|\left.l\right\rangle\left\langle l\left|\frac{\partial}{\partial R}k\right.\right\rangle$$

$$+\sum_{c}\left\langle\left|\frac{\partial}{\partial R}k\right.\right|\left.c\right\rangle\left\langle c\left|\frac{\partial}{\partial R}k\right.\right\rangle\Bigg].$$

The first two terms cancel leaving

$$-\delta_{ab}\delta_{ij}\sum_{k,c}\left\langle\left|\frac{\partial}{\partial R}k\right.\right|\left.c\right\rangle\left\langle c\left|\frac{\partial}{\partial R}k\right.\right\rangle, \tag{65}$$

which then corresponds exactly to the first SE|SE diagram. The other two diagrams are obtained similarly. Comparison with a conventional derivation is straightforward, and uses the anti-Hermitian property of $\partial/\partial R$; e.g.,

$$\left\langle\left|\frac{\partial}{\partial R}a\right.\right|\left.\frac{\partial}{\partial R}b\right\rangle=-\left\langle a\left|\frac{\partial^2}{\partial R^2}b\right.\right\rangle. \tag{66}$$

The elementary second derivative terms

$$\left\{\left\langle\Phi_\gamma\left|\frac{\partial^2}{\partial R^2}\Phi_\delta\right.\right\rangle\right\},$$

which are similar to the $\underline{\mathcal{G}}''^{(0)}$ matrix elements, are the only additional component necessary to evaluate the first-order $\underline{\mathcal{G}}''$ terms. The integral and energy (first) derivatives are the same ones already used in Eqs. (34) and (41), but this time they are multiplied by $\underline{\mathcal{G}}'^{(0)}$-like terms. These terms are the ones required for $\underline{\mathcal{G}}'^{(1)}$ in Eq. (40). $\underline{\mathcal{G}}''^{(2)}$ will require second derivatives of the two-electron integrals, but these are also available.[12]

If the nuclear Schrödinger equation is to be solved exactly, either (1) the couplings must be calculated in the coordinate system in which the scattering problem is to be solved, which is not the usual case, or (2) a complementary set of coupling matrix elements of similar one-electron operators must be provided to enable a transformation of coordinates.[3] The diagrams presented in this paper are sufficient in either case. As derivatives with respect to various coordinates are called for, one-electron equations analogous to Eq. (47) may be defined. However, the diagrams required will be

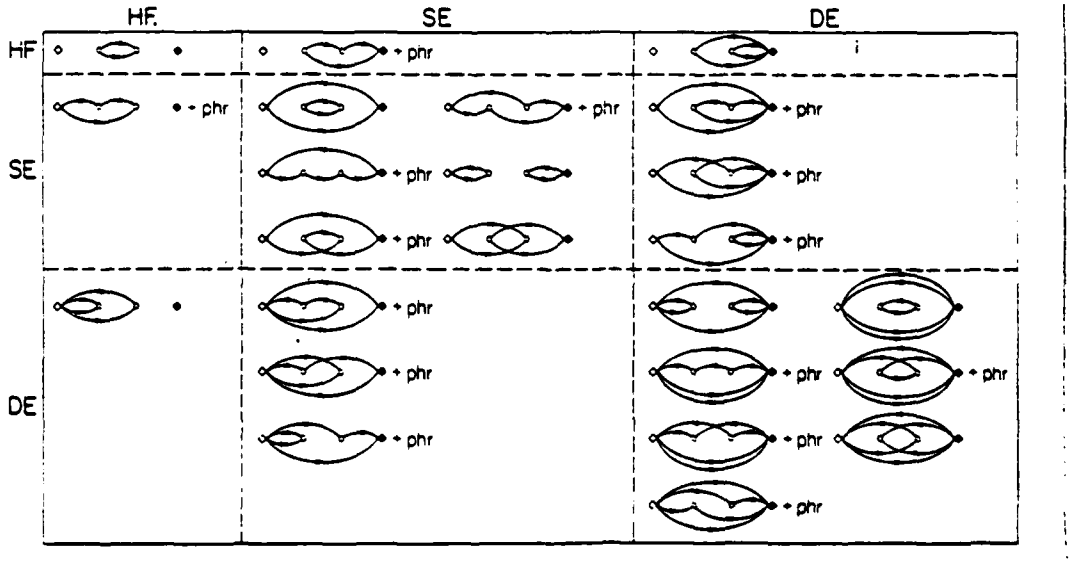

FIG. 3. Zeroth-order diagrams for the second derivative part $\underline{G}''$ of the nonadiabatic coupling matrix elements.

the same for any one-electron operator. A complementary set of couplings may be obtained in the same fashion. Similarly, cross-term matrix elements arising in the transformation can be evaluated using the second-derivative diagrams if the two one-electron interactions are appropriately labeled.

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APPENDIX: AN EXACT MATRIX HELLMANN-FEYNMAN RELATION

Write the eigenvalue problem in the chosen model space

$$\underline{H}\underline{B}=\underline{B}\underline{E} \tag{A1}$$

(with $\underline{E}$ diagonal) as

$$\underline{B}^{\dagger}\underline{H}\underline{B}=\underline{E} \ . \tag{A2}$$

($\underline{H}\underline{B}$ can be $\underline{H}\underline{C}$ of $\mathscr{H}_{\text{eff}}\underline{D}$ from the text.) Then differentiate each side of Eq. (A2) with respect to R (representing this by a prime symbol):

$$(\underline{B}^{\dagger})'\underline{H}\underline{B}+\underline{B}^{\dagger}\underline{H}'\underline{B}+\underline{B}^{\dagger}\underline{H}\underline{B}'=\underline{E}' \ . \tag{A3}$$

Using Eq. (A1) and reorganizing, we obtain

$$\underline{B}^{\dagger}\underline{H}'\underline{B}=\underline{E}'-(\underline{B}^{\dagger})'\underline{B}\underline{E}-\underline{E}\underline{B}^{\dagger}\underline{B}' \ . \tag{A4}$$

From differentiating the normalization equation

$$\underline{B}^{\dagger}\underline{B}=\underline{1} \ , \tag{A5}$$

we can see that

$$(\underline{B}^{\dagger})'\underline{B}=-\underline{B}^{\dagger}\underline{B}' \ . \tag{A6}$$

Realizing that $\underline{E}$ and thus $\underline{E}_z'$ are diagonal, we obtain from Eq. (A6) and the off-diagonal part of Eq. (A4)

$$\{\underline{B}^{\dagger}\underline{B}'\}_{\alpha\beta}=\frac{\{\underline{B}^{\dagger}\underline{H}'\underline{B}_{\alpha\beta}\}}{(E_{\beta}-E_{\alpha})} \quad (\alpha\neq\beta) \ . \tag{A7}$$

When $\underline{B}$ is real,

$$B^{\dagger}_{\alpha\gamma}=B_{\gamma\alpha} \ . \tag{A8}$$

Then using Eq. (A8) in Eq. (A6) gives

$$\sum_{\gamma}(B^{\dagger})'_{\alpha\gamma}B_{\gamma\alpha}=-\sum_{\gamma}B_{\gamma\alpha}(B^{\dagger}_{\alpha\gamma})' \ , \tag{A9}$$

so that

$$\{\underline{B}^{\dagger}\underline{B}'\}_{\alpha\alpha}=0 \ . \tag{A10}$$

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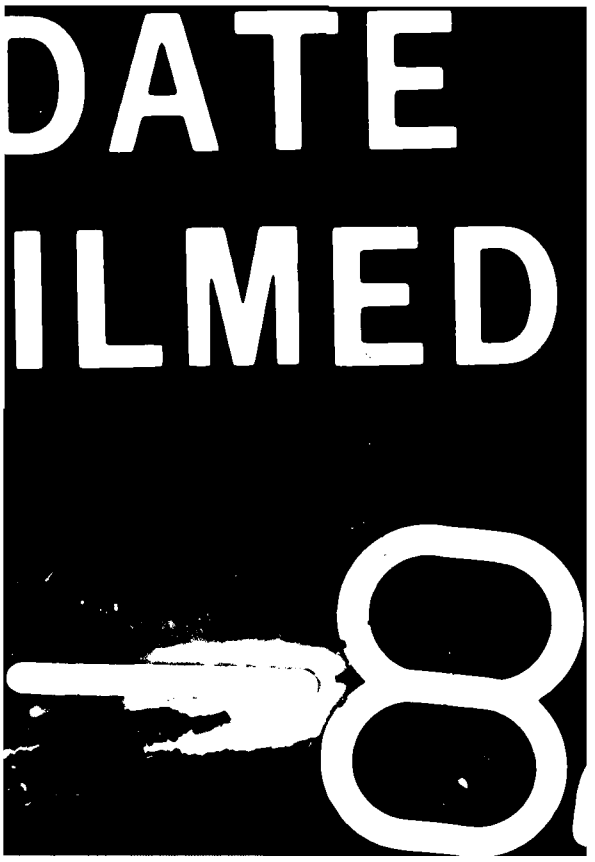
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