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Exchange perturbation theory. I. General definitions and relations[*]

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We define a class of primitive functions which are *least distorted* from the unsymmetrized function F^0, a product of atomic or other group functions, in the limit that the interactions between the groups have been turned off. These primitive functions have the property that at least one Schrödinger eigenfunction may be obtained from them by symmetry projection. It has been shown elsewhere that these functions satisfy a transformed Schrödinger equation in which the interactions between groups are screened. The screened potential is regarded as a perturbation and the corresponding Rayleigh-Schrödinger perturbation equations are derived. It is shown that a number of inequivalent, but equally valid energy expressions may be defined in terms of the primitive functions. Only when the primitive function is calculated exactly to infinite order will the different energy expressions all yield the same numerical value. It is suggested that this provides a check on the accuracy of approximate primitive functions.

I. INTRODUCTION

The relatively small interaction energies between atoms, molecules, and other electronic groups should be most easily understood and calculated by use of perturbation methods. Although considerable effort has been invested to this end,[1] one cannot say that it has proven to be the case. The fundamental source of difficulty has been the indistinguishability of electrons. In a series of papers of which this is the first, we shall focus on circumventing and turning to our advantage the problems which arise from electron indistinguishability. By the approach we have adopted we have gained new insights into exchange perturbation theories as well as new equations.

A principal criticism of the use of perturbation methods to calculate molecular wave functions and energies, is that by standard methods perturbation calculations require the evaluation of the same sets of integrals as variational calculations, but are less accurate unless carried to high order.[2] The traditional response to this criticism has been that the perturbation approach offers greater physical insight into the interaction process. Recently, however, it has been suggested that the application of the configuration-interaction method to systems having more than a few electrons can be made more tractable by use of what are essentially perturbation methods.[3] If this proves to be the case, the criticism we mentioned will no longer be applicable.

The exchange symmetry of electrons has been more a source of confusion than a barrier to the development of perturbation theories of the interactions between many electron systems. The basic problem is that there is no limit to the number of such theories which might be developed and, thus, no chance that one theory can be demonstrated computationally to be *the most accurate*.[4] In fact, calculations on H_2^+ (Ref. 5) and H_2 (Ref. 6) show that one can expect comparable accuracy from several of the proposed theories. In a sense, this is a satisfactory situation.[7] We shall show, however, that it is possible to develop exchange perturbation theory (EPT) so that one gains new insights into the theory.

The classic problem of EPT is to develop a method by which one can accurately calculate the interaction energy of two atoms at both small and large nuclear separations. Faced with this problem for the first time, the simplest approach is to ignore the electronic exchange symmetry in the following manner[8]: Assign electrons $1, 2, \ldots, N_a$ to atom a, electrons $N_a+1, N_a+2, \ldots, N_a+N_b$ to atom b. Let $\hat{h}_a$ be the electronic Hamiltonian of a, $\hat{h}_b$ that of b. The molecular electronic Hamiltonian $\hat{H}$ can be broken into a zeroth-order Hamiltonian $\hat{H}_1 = \hat{h}_a + \hat{h}_b$ and a perturbation $\hat{V}_1 = \hat{H} - \hat{H}_1$. The zeroth-order wave function F^0, a product of one eigenfunction of $\hat{h}_a$ and one of $\hat{h}_b$, does not have the exchange symmetry characteristic of an eigenfunction of $\hat{H}$. One can apply the Rayleigh-Schrödinger perturbation theory to determine the eigenfunctions of $\hat{H}_1 + \lambda\hat{V}_1$.[9] This is called the polarization EPT.[1] When carried to infinite order, it yields in the limit $\lambda = 1$ one eigenfunction of $\hat{H}$ with the appropriate exchange symmetry for each F^0 *if the series converges*.[10]

There are several things wrong with the polarization EPT. Firstly, it is very inaccurate for H_2^+ and H_2 when the interaction energy is calculated through third order.[5,6] Secondly, the sum of the zeroth- and first-order functions does not have the symmetry that an eigenfunction of $\hat{H}$ should have. One can rectify this by symmetry-projecting the sum.[11] In the case of H_2^+, one obtains in this way quite accurate interaction energies for both the $1s\sigma_g$ and $2p\sigma_u$ states from the same sum of zerothand first-order functions.[5] For H_2, one projects out both a singlet and a triplet Σ function each of which also gives quite accurate interaction energies.[6] The problem with this success is that one expects a good approximation in these cases only to the ground-state energy *if the expansion converges*.[10] If the expansion does not converge, justification must be found for symmetry projection. One concludes that if one wants to calculate intermolecular energies by perturbation methods and understand what one is doing, one must deal carefully with electron indistinguishability.

The most popular starting point[1] for the development of perturbation theories incorporating exchange is to assert that one seeks to determine a primitive wave function F, i.e., a function which is not an eigenfunction of $\hat{H}$, but from which one may obtain by symmetry projection one or more eigenfunctions of $\hat{H}$. The function F is supposed to be related to an eigenfunction F^0 of $\hat{H}_1$. The equation which F satisfies is chosen to guarantee that at least one symmetry projection of F is an eigenfunction of $\hat{H}$. The complementary projection of F is defined arbitrarily. Thus, an unlimited number of EPT's can be developed.[4]

Our first contribution to the EPT problem is to define F so that it is *least distorted* from F^0 in a very particular sense. The definition may be applied without reference to the perturbation equations. Because F is least distorted from F^0, we infer that F differs from F^0 only in ways essential to the interaction between systems. We assume this to be true to each order in the perturbation. By our approach the perturbation is not $\hat{V}_1$ but $\hat{V}_1$ *screened* by a nonlocal potential.

The starting point for our development of EPT is a recently demonstrated property of the Schrödinger equation. It has been shown[12,13] that operators may be added to the Schrödinger Hamiltonian to obtain an effective Hamiltonian whose eigenfunctions are primitive wave functions. The effective Hamiltonian can be chosen so that these primitive wave functions are *least distorted* from F^0. We call these primitive functions localized wave functions (LW). The LW equations have been solved by the configuration-interaction method for both H_2^+ and H_2.[14,15]

In Sec. II we review the properties of the LW equations and their solutions. An important point to recognize is that we have a set of distinct LW equations, all expressible in the same form and all having eigenfunctions which are least distorted from F^0 under specific constraints. In Sec. III we derive the perturbation expansion of the LW and its eigenvalue in a form applicable to all types of LW's.

The physically interesting energies, the eigenvalues of $\hat{H}$, are discussed at length in Sec. IV because we have more than one expression for them. This arises from the exchange symmetry and is common to EPT's. Because there is no unique energy expression, there is no unique perturbation expansion of the energy. We argue that this is a virtue of EPT.

Our conclusions and the program of research we are carrying out on EPT's are outlined in the last section.

II. LOCALIZED WAVE FUNCTIONS

There is a spectrum of localized-wave-function (LW) equations. They differ in the degree to which the interactions between electronic groups are screened and in the degree to which their solutions are distorted from a product of atomic or, more generally, electronic group functions. We consider explicitly here two extreme types of LW's. We first define them, then present the equations from which they may be determined without knowledge of the eigenfunctions of $\hat{H}$.

Let $\hat{H}$ be the nonrelativistic Hamiltonian of an N-electron system in the Born-Oppenheimer approximation. Let $\Psi^{\mu}_{\alpha i}$ be an eigenfunction of $\hat{H}$. The superscript μ specifies the multiplicity, the irreducible representation (IR) of the symmetric group and of the point group to which $\Psi^{\mu}_{\alpha i}$ belongs. The subscript i specifies the z component of the total spin and the rows of the IR's to which the function belongs. The different energy states having the same μ and i are distinguished by the subscript α.

In what follows the symmetry projection operators $\hat{e}^{\mu}_{ii}$ and the related shift operators $\hat{e}^{\mu}_{ij}$ are used. (Note that we have changed our original notation[13] by substituting $\hat{e}$ for $\hat{\rho}$.) These are the elements of a matric basis for the irreducible representations[16] of the group of operators which commute with $\hat{H}$. They have the important property that

$$\hat{e}^{\mu}_{ij}\hat{e}^{\nu}_{kl}=\delta_{\mu\nu}\delta_{jk}\hat{e}^{\mu}_{il}\,. \tag{1}$$

Note that $\hat{e}^{\nu}_{kl}\Psi^{\mu}_{\alpha i}=\delta_{\mu\nu}\delta_{il}\Psi^{\mu}_{\alpha k}$ is a consequence of (1).

Imagine that an N-electron molecule is made up of groups of electrons: atoms, ions, shells, etc. Assign each electron to a specific group. Let $\hat{h}_a$ be the Hamiltonian of group a when all interactions between groups have been turned off. Let $\hat{H}_1=\sum_a \hat{h}_a$. Let ϕ_a satisfy $\hat{h}_a\phi_a=E_a\phi_a$. Then for $F^0=\prod_a \phi_a$ and $\epsilon^0=\sum_a E_a$ one has $\hat{H}_1F^0=\epsilon^0F^0$. Let $\hat{V}_1=\hat{H}-\hat{H}_1$.

We define one type of LW in the following manner. Consider the requirement that the N-electron function G satisfy

$$\epsilon = \langle G|\hat{H}_1|G\rangle / \langle G|G\rangle = \text{extremal}. \tag{2}$$

If we impose no constraints on G, we find $G = F^0$. If, however, we introduce for one μ and i the constraint

$$\hat{e}^{\mu}_{ii}G = \Psi^{\mu}_{\alpha i}\langle\Psi^{\mu}_{\alpha i}|G\rangle \tag{3}$$

and require (2) to be satisfied, then G will differ from F^0, but only in ways essential to satisfying (3). In this sense G is *least distorted* from F^0 under the constraint (3). Clearly, one could impose more constraints on G. The constraint (3) is the least restrictive we have been able to apply in defining an LW. It is essentially the same constraint that is imposed in the Eisenschitz-London EPT.[8]

The most restrictive constraint we have imposed on an LW, call it F, is that for all μ and i, with α independent of i,

$$\hat{e}^{\mu}_{ii}F = \Psi^{\mu}_{\alpha i}\langle\Psi^{\mu}_{\alpha i}|F\rangle \quad \text{for } all\ \mu\,. \tag{4}$$

We require that (2) be satisfied with F substituted for G and that (4) be satisfied. Thus, F will differ from F^0 only in ways essential to satisfying the constraints (4). It is also least distorted from F^0, although we expect it to be more distorted than G, since more constraints have been imposed. The constraints (4) correspond to those used by Hirschfelder and Silbey.[17] Note that in (4) μ ranges over all possible values, including those which do not satisfy the Pauli principle.

We have used two symbols, G and F, to distinguish the LW which satisfies the constraint (3) from that which satisfies (4). It is possible to adopt constraints intermediate in number to (3) and (4), e.g., that (4) be satisfied only for the physically allowed μ's. One expects the so-defined LW to differ more from F^0 than does G, but less than does F. The perturbation equations that we develop in this paper are applicable whether one imposes the constraints (3) or (4), or constraints of an intermediate degree of severity.

It has been proven[3] that if one solves

$$(\hat{H}_1 + \hat{V}_1 - \hat{Q}\hat{V}_1\hat{Q})G = \epsilon G \tag{5a}$$

for G with

$$\hat{Q} = M\hat{e}^{\mu}_{ii}|G\rangle\langle G|\hat{e}^{\mu}_{ii} + 1 - \hat{e}^{\mu}_{ii}\,, \tag{5b}$$

$$M^{-1} = \langle G|\hat{e}^{\mu}_{ii}|G\rangle \neq 0\,, \tag{5c}$$

then

$$\hat{e}^{\mu}_{ii}G = \Psi^{\mu}_{\alpha i}\langle\Psi^{\mu}_{\alpha i}|G\rangle\,. \tag{6}$$

The solution to (5) is the same G which was defined by (2) and (3).[13] Note that $\hat{e}^{\nu}_{jj}G$ is proportional to one eigenfunction of $\hat{H}$ only if $\nu = \mu$ and $j = i$, where μ and i are used in (5b).

One can prove[19] that if one solves

$$(\hat{H}_1 + \hat{V}_1 - \hat{Q}\hat{V}_1\hat{Q})F = \epsilon F \tag{7a}$$

for F with

$$\hat{e}^{\nu} = \sum_j \hat{e}^{\nu}_{jj}\,, \tag{7b}$$

$$\hat{Q} = \sum_{\nu} M_{\nu}^{-1}\hat{e}^{\nu}|F\rangle\langle F|\hat{e}^{\nu}\,, \tag{7c}$$

$$M_{\nu}^{-1} = \langle F|\hat{e}^{\nu}|F\rangle\,, \tag{7d}$$

then for all ν and j,

$$\hat{e}^{\nu}_{jj}F = \Psi^{\nu}_{\alpha j}\langle\Psi^{\nu}_{\alpha j}|F\rangle \tag{8}$$

and for each ν, α is independent of j. The solution to (7) can be shown[13,15] to be the same F that was defined by the condition (2) and the constraints (4). Note that the sum in (7b) extends over all IR's, including those which do *not* satisfy the Pauli principle.

It can be seen by comparing Eqs. (5) and (7), that these two LW equations differ only in the way in which the projection operator $\hat{Q}$ is constructed. For other types of LW's, there will be corresponding $\hat{Q}$'s. Thus in developing the perturbation expansions for LW's we can work with Eq. (5a), taking into consideration that $\hat{Q}$ depends on the perturbation through the LW, but not using the particular definition of $\hat{Q}$ given in (5b) or (7b). In this way we obtain perturbation expansions valid for all types of LW's. They may be specialized to a particular type of LW by using the explicit form for $\hat{Q}$, as will be illustrated in the following two papers.

The G, ϵ, and $\hat{Q}$ used in Eqs. (5) could be labeled by μ and i since they depend on them. The F, ϵ, and $\hat{Q}$ used in Eqs. (7) do not depend on these labels. A label could be attached which would link G or F to the ground- or various excited-state F^0's. We prefer to remember that such labels should be used, rather than clutter up the equations.

The eigenvalue ϵ which appears in Eq. (5a) is neither the electronic energy nor the interaction energy. To calculate these energies one uses (6) or (8). They imply that

$$\hat{H}\hat{e}^{\mu}_{ii}G = E^{\mu}_{\alpha}\hat{e}^{\mu}_{ii}G\,. \tag{9}$$

It follows from this and $\hat{H} = \hat{H}_1 + \hat{V}_1$, that

$$E^{\mu}_{\alpha} - \epsilon^0 = \langle F^0|\hat{V}_1\hat{e}^{\mu}_{ii}|G\rangle\langle F^0|\hat{e}^{\mu}_{ii}|G\rangle^{-1}. \tag{10}$$

The interaction energy might thus be calculated without having to calculate separately E^{μ}_{α} and ϵ^0.

In both of the LW equations (5a) and (7a), the combination $\hat{V}_1 - \hat{Q}\hat{V}_1\hat{Q}$ occurs. The interpretation of $\hat{Q}\hat{V}_1\hat{Q}$ is that it is a nonlocal potential which *screens* $\hat{V}_1$.[13] The definition of $\hat{Q}$ by (7c), is, as a consequence of (8), equivalent to

$$\hat{Q}=\sum_{\nu}|\Phi_{\alpha}^{\nu}\rangle\langle\Phi_{\alpha}^{\nu}|\,, \tag{7c$'$}$$

where each Φ_{α}^{ν} is a normalized linear combination of the $\Psi_{\alpha j}^{\nu}$, the coefficients having been chosen to satisfy (2). The $\hat{Q}$ defined by (5b) is equivalent to

$$\hat{Q}=|\Psi_{\alpha i}^{\mu}\rangle\langle\Psi_{\alpha i}^{\mu}|+1-\hat{e}_{ii}^{\mu}\,. \tag{5b$'$}$$

One can see that the latter $\hat{Q}$ is more nearly equal to the identity operator than is the former, and therefore, when the latter is used in $\hat{V}_1-\hat{Q}\hat{V}_1\hat{Q}$, the resultant potential more nearly vanishes. The screened potential $\hat{V}_1-\hat{Q}\hat{V}_1\hat{Q}$ distorts F^0 into G or F. It is a weaker perturbation than $\hat{V}_1$, the perturbation usually considered in developing EPT's.

A detailed study of LW's will be published in due course by one of us.

III. PERTURBATION EXPANSION FOR LOCALIZED WAVE FUNCTIONS

We apply the Rayleigh-Schrödinger perturbation theory to the solution of the LW equation by regarding $\hat{V}_1-\hat{Q}\hat{V}_1\hat{Q}$ as a perturbation to $\hat{H}_1$. The effect of the perturbation is to distort F^0 into G. [Note that from this point on, unless otherwise noted, we use G for both the LW defined by (2) and (3), and that defined by (2) and (4).] Because G is least distorted from F^0, we expect that to each order in the perturbation, G will contain only those contributions essential to converting F^0 into a function from which at least one eigenfunction of $\hat{H}$ may be symmetry-projected.

We introduce an expansion parameter λ into the LW equation:

$$\{\hat{H}_1+\lambda[\hat{V}_1-\hat{Q}(\lambda)\hat{V}_1\hat{Q}(\lambda)]\}\,G(\lambda)=\epsilon(\lambda)G(\lambda)\,. \tag{11}$$

Note that G, $\hat{Q}$, and ϵ now depend on λ. Only for $\lambda=1$ can $\hat{e}_{ii}^{\mu}G(\lambda)$ be an eigenfunction of $\hat{H}$, a point discussed at length in Sec. IV. We assume that $G(\lambda)$, $\epsilon(\lambda)$, and $\hat{Q}(\lambda)$ are analytic functions of λ for $|\lambda|\leqslant 1$, i.e.,

$$G(\lambda)=F^0+\lambda G^{(1)}+\lambda^2G^{(2)}+\cdots\,, \tag{12}$$

$$\epsilon(\lambda)=\epsilon^0+\lambda\epsilon^{(1)}+\lambda^2\epsilon^{(2)}+\cdots\,, \tag{13}$$

$$\hat{Q}(\lambda)=\hat{Q}^{(0)}+\lambda\hat{Q}^{(1)}+\lambda^2\hat{Q}^{(2)}+\cdots\,. \tag{14}$$

The equations determining the $G^{(n)}$ and $\epsilon^{(n)}$ follow from (11), whereas the $\hat{Q}^{(n)}$ are determined by Eqs. (5b) and (5c) or related equations, e.g., by (7b)-(7d).

Whether one defines $Q(\lambda)$ by (5b)-(5c) or (7b)-(7d), $Q(\lambda)$ is a projection operator which satisfies

$$\hat{Q}(\lambda)G(\lambda)=G(\lambda)\,. \tag{15}$$

This permits the simplification of (11) to

$$\{\hat{H}_1+\lambda[1-\hat{Q}(\lambda)]\hat{V}_1\}\,G(\lambda)=\epsilon(\lambda)G(\lambda)\,. \tag{16}$$

From Eq. (15) it follows that

$$(\hat{1}-\hat{Q}^{(0)})G^{(n)}=\hat{Q}^{(1)}G^{(n-1)}+\hat{Q}^{(2)}G^{(n-2)}+\cdots+\hat{Q}^{(n)}F^{(0)}\,. \tag{17}$$

This relationship is used in simplifying expressions for some of the $\epsilon^{(n)}$.

The derivation from (16) of the hierarchy of perturbation equations is straightforward. Alternative expressions for the $\epsilon^{(n)}$ can be derived from Eq. (2). The intermediate normalization condition $\langle F^0|G^{(n)}\rangle=0$ for $n\geqslant 1$ has been used. The first few equations are

$$\hat{H}_1F^0=\epsilon^0F^0\,, \tag{18}$$

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

$$(\hat{H}_1-\epsilon^0)G^{(1)}=-(1-\hat{Q}^{(0)})\hat{V}_1F^0\,, \tag{19b}$$

$$\epsilon^{(2)}=-\langle G^{(1)}|(1-\hat{Q}^{(0)})\hat{V}_1|F^0\rangle=\langle G^{(1)}|\hat{H}_1-\epsilon^0|G^{(1)}\rangle\,, \tag{20a}$$

$$(\hat{H}_1-\epsilon^0)G^{(2)}=(\epsilon^{(2)}+\hat{Q}^{(1)}\hat{V}_1)F^0-(1-\hat{Q}^{(0)})\hat{V}_1G^{(1)}\,, \tag{20b}$$

$$\begin{aligned}\epsilon^{(3)}&=2\,\mathrm{Re}\{-\langle G^{(1)}|(1-\hat{Q}^{(0)})\hat{V}_1|G^{(1)}\rangle\\&\qquad+\langle G^{(1)}|\hat{Q}^{(1)}\hat{V}_1|F^0\rangle\}\\&=2\,\mathrm{Re}\langle G^{(1)}|\hat{H}_1-\epsilon^0|G^{(2)}\rangle\,,\end{aligned} \tag{21}$$

$$\begin{aligned}\epsilon^{(4)}&=\langle G^{(2)}|\hat{H}_1-\epsilon^0|G^{(2)}\rangle+\epsilon^{(2)}\langle G^{(1)}|G^{(1)}\rangle\\&\quad+2\,\mathrm{Re}\{-\langle G^{(1)}|(1-\hat{Q}^{(0)})\hat{V}_1|G^{(2)}\rangle\\&\quad+\langle G^{(1)}|\hat{Q}^{(1)}\hat{V}_1|G^{(1)}\rangle+\langle G^{(1)}|\hat{Q}^{(2)}\hat{V}_1|F^0\rangle\}\,.\end{aligned} \tag{22}$$

Note that (15) and (16) imply that $\epsilon(\lambda)$ is real. Also, we need F^0 and $G^{(1)}$ to evaluate $\epsilon^{(3)}$; and F^0, $G^{(1)}$, and $G^{(2)}$ to evaluate $\epsilon^{(4)}$. We have been unable to eliminate $G^{(3)}$ from our expressions for $\epsilon^{(5)}$. It appears that if we know G through order n, we can calculate ϵ only through $n+2$ order.

The LW EPT equations given above do not involve the ambiguities in order[18] which are a common characteristic of EPT's. This is because not even in the limit $\lambda=1$ does $\hat{H}_1+\lambda[\hat{V}_1-\hat{Q}(\lambda)\hat{V}_1\hat{Q}(\lambda)]$ commute with $\hat{e}_{ii}^{\mu}$. Use of the relation $[\hat{H}_1, e_{ii}^{\mu}]=[\hat{e}_{ii}^{\mu},\hat{H}_1]$ in our equations does not alter the order of a term because $\hat{V}_1$ is not by itself the perturbation.

IV. ENERGY EXPRESSIONS

Although there is no ambiguity in the orders for the perturbation expansion of an LW, there is no unique expansion of the electronic energy. This is not alone due to $[\hat{H}_1,\hat{e}_{ii}^{\mu}]=[\hat{e}_{ii}^{\mu},\hat{V}_1]$.[18] It is because it is quite easy to write down inequivalent expressions for E_{α}^{μ} as a function of λ. We have no reason to prefer one of these expressions to all others.

Inequivalent expressions for E^{μ}_{α} in LW EPT can exist because of the noncommutation of $\hat{H}_1+\lambda\hat{V}_1$ and $\hat{e}^{\mu}_{ii}$ for $\lambda\neq 1$ [18] and because one is not compelled in the LW EPT to identify any term in Eq. (16) with E^{μ}_{α}. There is no term in the LW equation itself which depends only on E^{μ}_{α}. One can obtain E^{μ}_{α} from $G(1)$ because it has been proven[13] that $\hat{e}^{\mu}_{ii}G(1)$ is an eigenfunction of $\hat{H}=\hat{H}_1+\hat{V}_1$. For $\lambda\neq 1$, $\hat{e}^{\mu}_{ii}G(\lambda)$ is not an eigenfunction of $\hat{H}_1+\lambda\hat{V}_1$. If we want E^{μ}_{α} as a function of λ, we have to define it.

In the other EPT's that have been based on primitive functions,[1] an energy $E^{\mu}(\lambda)$ has been defined by

$$\hat{e}^{\mu}_{ii}[\hat{H}_1+\lambda\hat{V}_1-E^{\mu}(\lambda)]G(\lambda)=0 \tag{23a}$$

such that

$$E^{\mu}(1)=E^{\mu}_{\alpha}\,. \tag{23b}$$

We show below that our $G(\lambda)$ satisfies (23a) if $E^{\mu}(\lambda)$ is appropriately defined. In the limit that $\lambda=1$, (23a) implies that $\hat{e}^{\mu}_{ii}G(1)$ is an eigenfunction of $\hat{H}_1+\hat{V}_1$. We can use Eqs. (23) to define $E^{\mu}(\lambda)$ in the LW EPT, but it is only one of many possible definitions.

To derive (23a) for LW's, operate on Eq. (16) from the left with $\hat{e}^{\mu}_{ii}$ to obtain

$$\hat{e}^{\mu}_{ii}(\hat{H}_1+\lambda\hat{V}_1)G(\lambda)=\hat{e}^{\mu}_{ii}[\epsilon(\lambda)+\lambda\hat{Q}(\lambda)\hat{V}_1]G(\lambda)\,. \tag{24}$$

When $Q(\lambda)$ is defined by Eqs. (5b) and (5c),

$$\hat{e}^{\mu}_{ii}\hat{Q}(\lambda)=\langle G(\lambda)|\,\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle^{-1}\,\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle\,\langle G(\lambda)|\hat{e}^{\mu}_{ii}\,.$$

Thus, (24) is equivalent to (23a) if we set

$$E^{\mu}(\lambda)=\epsilon(\lambda)+\lambda\langle G(\lambda)|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle^{-1}\langle G(\lambda)|\hat{e}^{\mu}_{ii}\hat{V}_1|G(\lambda)\rangle\rangle\,. \tag{25}$$

In a similar manner, when $Q(\lambda)$ is defined by Eqs. (7b)–(7d), one can show that (23a) is satisfied when $E^{\mu}(\lambda)$ is defined by

$$E^{\mu}(\lambda)=\epsilon(\lambda)+\lambda\langle F(\lambda)|\hat{e}^{\mu}|F(\lambda)\rangle\rangle^{-1}\,\langle F(\lambda)|\hat{e}^{\mu}\hat{V}_1|F(\lambda)\rangle\rangle\,.$$

This definition is identical to (25) for one-dimensional irreducible representations.

We show in the following two papers that $E^{\mu}(\lambda)$ as defined by (25) has the following properties:

$$E^{\mu}(0)=\epsilon^0\,, \tag{26a}$$

$$E^{\mu}(1)=E^{\mu}_{\alpha}\,, \tag{26b}$$

$$\left[\frac{dE^{\mu}(\lambda)}{d\lambda}\right]_{\lambda=0}=E^{\mu(1)}_{\mathrm{HL}}=\langle F^0|\hat{e}^{\mu}_{ii}|F^0\rangle^{-1}\langle F^0|\hat{e}^{\mu}_{ii}\hat{V}_1|F^0\rangle\,, \tag{26c}$$

where $E^{\mu(1)}_{\mathrm{HL}}$ is the Heitler-London correction to ϵ^0 as an approximation to E^{μ}_{α}. If $E^{\mu}(\lambda)$ were the only function we could define which satisfied (26a)–(26c), we would argue that $E^{\mu}(\lambda)$ is the unique energy function that one wants.

We can define other $E^{\mu}(\lambda)$'s which satisfy (26a)–(26c). The conditions (26a)–(26c) are not very difficult to satisfy. It is equivalent to asking how many smooth curves $f(x)$ can be drawn which intersect at $x=0$ and $x=1$, and which have the same slope at $x=0$. There are an unlimited number of such curves.

We derive other expressions for $E^{\mu}(\lambda)$ with the help of

$$\begin{aligned}\lim_{\lambda=1}(\hat{H}_1+\lambda\hat{V}_1)\hat{e}^{\mu}_{ii}G(\lambda)&=\lim_{\lambda=1}\hat{e}^{\mu}_{ii}(\hat{H}_1+\lambda\hat{V}_1)G(\lambda)\\&=E^{\mu}_{\alpha}\lim_{\lambda=1}\hat{e}^{\mu}_{ii}G(\lambda)\,.\end{aligned} \tag{27}$$

Three $E(\lambda)$'s which satisfy (26a)–(26c) (see papers II and III) are

$${}^{\mathrm{I}}E^{\mu}(\lambda)=\langle F^0|(\hat{H}_1+\lambda\hat{V}_1)\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle\,\langle F^0|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle^{-1}\,, \tag{28}$$

$${}^{\mathrm{II}}E^{\mu}(\lambda)=\langle F^0|\hat{e}^{\mu}_{ii}(\hat{H}_1+\lambda\hat{V}_1)|G(\lambda)\rangle\rangle\,\langle F^0|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle^{-1}\,, \tag{29}$$

$${}^{\mathrm{III}}E^{\mu}(\lambda)=\langle G(\lambda)|(\hat{H}_1+\lambda\hat{V}_1)\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle\,\langle G(\lambda)|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle^{-1}\,. \tag{30}$$

It follows from (23a) that ${}^{\mathrm{II}}E^{\mu}(\lambda)$ must be identical to the $E^{\mu}(\lambda)$ defined in (25). By the same reasoning, if we had defined a fourth $E^{\mu}(\lambda)$ to be

$$\langle G(\lambda)|\hat{e}^{\mu}_{ii}(\hat{H}_1+\lambda\hat{V}_1)|G(\lambda)\rangle\rangle\,\langle G(\lambda)|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle^{-1}$$

it would have been identical to ${}^{\mathrm{II}}E(\lambda)$. Since we are interested in $E^{\mu}(\lambda)$ in the limit $\lambda=1$, it appears to be a matter of personal preference whether one uses (28), (29), (30), or some other expression as the definition of $E^{\mu}(\lambda)$. The common tie between these expressions is that they all satisfy (26a) and (26b).

We can easily invent more complicated expressions for $E^{\mu}(\lambda)$, e.g., by starting from

$$\lim_{\lambda=1}e^{\hat{H}_1+\lambda\hat{V}_1}\hat{e}^{\mu}_{ii}G(\lambda)=\hat{e}^{\mu}_{ii}G(1)\,e^{E^{\mu}_{\alpha}}\,.$$

A definition based on this identity is

$$E^{\mu}(\lambda)=\ln[\,\langle F^0|e^{\hat{H}_1+\lambda\hat{V}_1}\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle\,\langle F^0|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle^{-1}]\,.$$

This $E^{\mu}(\lambda)$ satisfies Eqs. (26a)–(26c). We do not consider this definition further because it is unnecessarily complicated.

One could argue that ${}^{\mathrm{III}}E^{\mu}(\lambda)$ should be preferred because for $\lambda=1$ it is the expectation value of $\hat{H}_1+\lambda\hat{V}_1$ calculated with $\hat{e}^{\mu}_{ii}G(\lambda)$. The argument, of course, is that for a first-order error in $G(1)$ one can expect the error in ${}^{\mathrm{III}}E^{\mu}(\lambda)$ to be second order. However, if we want to have an $E^{\mu}(\lambda)$ which is an expectation value for $\lambda<1$, we should use

$$\begin{aligned}{}^{\mathrm{IV}}E^{\mu}(\lambda)=&\langle G(\lambda)|\hat{e}^{\mu}_{ii}(\hat{H}_1+\lambda\hat{V}_1)\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle\\&\times\langle G(\lambda)|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\rangle^{-1}\,.\end{aligned} \tag{31}$$

In papers II and III we show that ${}^{\mathrm{IV}}E^{\mu}(\lambda) \neq {}^{\mathrm{III}}E^{\mu}(\lambda)$ and that ${}^{\mathrm{IV}}E^{\mu}(\lambda)$ satisfies neither (26a) nor (26c). We do not believe that ${}^{\mathrm{IV}}E^{\mu}(\lambda)$ is an improvement over the energy expressions defined in (28)–(30).

It occurred to us that one might define a unique $E^{\mu}(\lambda)$ by modifying our approach to EPT. Why not introduce an operator $\Theta(\lambda)$ such that $\Theta(\lambda)G(\lambda)$ is an eigenfunction of $\hat{H}_1 + \lambda\hat{V}_1$, and then develop the whole perturbation theory from

$$(\hat{H}_1 + \lambda\hat{V}_1)\hat{\Theta}(\lambda)G(\lambda) = E(\lambda)\hat{\Theta}(\lambda)G(\lambda) . \qquad (32)$$

We want $\hat{\Theta}(0) = 1$ and $\hat{\Theta}(1) = e^{\mu}_{ii}$, but for intermediate values of λ we shall have to use (32) to determine $\hat{\Theta}(\lambda)$. However, (32) is the only equation we have from which to determine $G(\lambda)$, $\hat{\Theta}(\lambda)$, and $E(\lambda)$. Since $G(\lambda)$ and $\hat{\Theta}(\lambda)$ occur in this equation in the combination $\hat{\Theta}(\lambda)G(\lambda)$, we might as well substitute $\Phi(\lambda) = \hat{\Theta}(\lambda)G(\lambda)$ and just determine $\Phi(\lambda)$. If we do this, we are back to using the polarization EPT. We explained in Sec. I why the polarization EPT was unsatisfactory.

It is possible that the $E^{\mu}(\lambda)$ defined in (28)–(31) only look like different functions. In the following two papers we show in fact that ${}^{\mathrm{III}}E^{\mu}(\lambda) = {}^{\mathrm{II}}E^{\mu}(\lambda)$, but that ${}^{\mathrm{I}}E^{\mu}(\lambda)$, ${}^{\mathrm{II}}E^{\mu}(\lambda)$, and ${}^{\mathrm{IV}}E^{\mu}(\lambda)$ are unequal for $\lambda < 1$ because they have different expansions in powers of λ.

Since there is no unique, preferred expression for $E(\lambda)$, one can attach no special significance to the coefficients in the power-series expansions of ${}^{\mathrm{I}}E^{\mu}(\lambda)$, ${}^{\mathrm{II}}E^{\mu}(\lambda)$, and ${}^{\mathrm{IV}}E^{\mu}(\lambda)$. We believe that one should not expand these expressions in power series in λ. Firstly, λ is not a small, physically meaningful parameter. We are interested only in $\lambda = 1$. Secondly, what one is essentially doing in developing these expansions, is approximating the normalizing effect of $\langle F^0|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle$ or $\langle G(\lambda)|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle$. Why introduce an unnecessary approximation into the energy expressions?

We suggest that one use $F^0 + \lambda G^{(1)} + \cdots + \lambda^n G^{(n)}$ in ${}^{\mathrm{I}}E^{\mu}(\lambda)$, ${}^{\mathrm{II}}E^{\mu}(\lambda)$, and ${}^{\mathrm{IV}}E^{\mu}(\lambda)$. One then has approximate expressions for these energies which are of the form of one polynomial in λ divided by a second. This, of course, is just the sort of approximation that one gets by applying the method of Padé approximants to a power-series expansion, a procedure that has been applied to EPT energy expressions.[22]

We suggest also that it is an advantage to have two or more distinct expressions for $E^{\mu}(\lambda)$ which are equal for $\lambda = 1$ only if the expansion of $G(\lambda)$ is summed to infinite order. One can readily verify that with $G(1)$ approximated by $F^0 + G^{(1)} + \cdots + G^{(n)}$, one has ${}^{\mathrm{IV}}E^{\mu}(1) = {}^{\mathrm{III}}E^{\mu}(1) = {}^{\mathrm{II}}E^{\mu}(1) \neq {}^{\mathrm{I}}E^{\mu}(1)$. Thus, using this approximation, if ${}^{\mathrm{II}}E^{\mu}(1)$ is quite different from ${}^{\mathrm{I}}E^{\mu}(1)$, we know that we have not carried our calculations to sufficiently high order. Unfortunately, if the approximate ${}^{\mathrm{II}}E^{\mu}(1)$ and ${}^{\mathrm{I}}E^{\mu}(1)$ are equal, we cannot be sure that we have an accurate approximation to the energy.

V. DISCUSSION

The EPT outlined in this paper is based on the use of a primitive function G which is defined so that it is least distorted from F^0, a product of the wave functions for noninteracting atoms (ions, groups). Such functions should be particularly amenable to calculation by perturbation methods since they differ from F^0 only in ways essential to satisfying the constraint $\hat{e}^{\mu}_{ii}G = \Psi^{\mu}_{\alpha i}\langle\Psi^{\mu}_{\alpha i}|G\rangle$. The least-distortion requirement does not, however, exhaust the options available. One can develop EPT's in which the primitive functions satisfy the least-distortion requirement, but are consistent with other quite distinct requirements. This point will be clarified in the following two papers.

We have made the customary assumption that the zeroth-order Hamiltonian $\hat{H}_1$ is the sum of atomic Hamiltonians. This may not be a practical choice for systems containing atoms other than hydrogen since we do not generally know the eigenfunctions of $\hat{H}_1$. Work is in progress here on the application of the theory to diatomic systems such as LiH and He_2 using configuration-interaction methods. This should show us how practical the usual choice of $\hat{H}_1$ is.

A more practical approach would be to make $\hat{H}_1$ the sum of approximate atomic Hamiltonians in which electron correlation has been omitted, e.g., each atomic Hamiltonian could be a sum of the one-electron Fock operators for the atom. A more sophisticated approach would be to use the nonorthogonal group-function Hamiltonians proposed elsewhere.[22] In this case the only contribution to the first-order primitive function will be from dispersion interactions between the atoms. Investigations along these lines have also been initiated here.

The role of the numerical studies that we have carried out and will carry out is to provide further insight into the properties of the two extreme forms of LW EPT: one based on the constraint (3), the other on (4). In previous calculations[5,6] only the first-order functions have been evaluated, the idea being that it is not practical to go beyond first order. However, if one uses a configuration-interaction approach to the perturbation expansion, it is quite easy to go beyond first order. By going beyond first order, one can see if the expansions are convergent in a practical sense.

Our calculations should not be expected to show that one EPT is better than another. For this purpose other criteria have to be used.[4,23] We shall consider such criteria in the following papers in arguing that one type of LW EPT is to be preferred for some problems, another type for other problems.

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