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NEW PARTITIONING PERTURBATION THEORY:

III. APPLICATIONS TO ELECTRON EXCHANGE

BY

Phillip R. Certain and Joseph O. Hirschfelder

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page

2 should be $\gamma_{A_{ij}}$ in equation

5 middle page, should be $\gamma_{\Psi_{ij}}(N)$

6 third line replace "inhomogeneity" by "the right hand side of Eq. (7)".

8 seventh line from bottom, should be $\gamma_{A_{ij}}$.

9 three lines below (15), the (10) should be (11).

10 line above (18) should read: "is the lowest root of the 3x3 secular equation."

three lines below (18), change (6) to (9a).

13 two lines above (23), should read: "real positive constants".

14 Eq. (26) should have $\tilde{f}_a$ in place of f_a (3 times).

15 in (29) and (31) should be $\tilde{e}'_k$.

16 for $j = 13$ should be $r_b^2 \cos\theta_b$.

17 Eq. (34) close bracket to read $(R^3/12)$.

Eq. (35) should be $(\tilde{e}'_k + \tilde{e}'_\ell)^{-1}$.

Eq. (36) should be $\exp(-r_{a1} - r_{a2})$ and omit the extra exponential.

18 Heading should be α_{ij} in place of γ_{ij}; also α_{ij} in table. The 2,10 entry should be $r_{a2}^2 + r_{b1}^2$.

22 second line should be "intramolecular"

24 should read: "D. M. Chipman".

NEW PARTITIONING PERTURBATION THEORY:

III. APPLICATIONS TO ELECTRON EXCHANGE*

by

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ABSTRACT

A new partitioning perturbation technique provides a rigorous derivation and generalization of the Hirschfelder-Silbey formalism for treating electron exchange problems. A new method of solving the first order perturbation equation is introduced. The first order wave function is the sum of the polarization function which describes van der Waals correlations and an exchange function which introduces ionic terms. The exchange function is determined variationally for both the ground state $H + H^+$ and $H + H$ interactions. In the many electron case, the first order equation reduces to a set of one and two electron equations.

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I. Introduction.

In a companion paper[1] (which we shall refer to as I), a partitioning formalism was developed for treating electron exchange, as well as degenerate and almost degenerate, perturbations. In the present paper, it is shown that this procedure can be greatly simplified by the use of symmetry considerations.

The essential idea is to construct, by perturbation methods, a finite basis set for the expansion of the wavefunction. The basis is defined to have small hamiltonian matrix elements coupling the basis with any function which is orthogonal to the basis. The energy and properly symmetrized wavefunction are obtained by diagonalizing the hamiltonian in the finite basis. The advantage of this procedure is that the basis functions are not required to have the symmetry of the total wavefunction, but simply form a basis for a reducible representation of the symmetry group of the hamiltonian. This approach to exchange perturbation theory leads to a generalization of the Hirschfelder-Silbey (HS) formalism[2], which is analogous to the DE-FOP-VIM generalization of the Modified Kirtman (MK) proceduce[1].

We have separated our first order equation into a polarization equation which describes van der Waals correlations and an exchange equation which introduces ionic terms into the wavefunction. For both H_2^+ and H_2 we have determined a variational approximation to the exchange function. For many electron systems we have shown that the first order equation is equivalent to a set of one and two electron equations. For problems involving multi-configurational interactions, the treatment here must be modified although the formalism in I is applicable.

There are many ways in which our treatment can take electron spins into consideration. However, our formulation is well suited to "spin-free quantum chemistry"[3] in which our wave functions would be spatial functions having symmetry with respect to electron permutations corresponding to a Young diagram conjugate to the Young diagram of its associated spin function. In a forthcoming article, Matsen and Junker[4] will incorporate our treatment into the spin-free quantum chemistry.

II. General Formulation

Let us consider the determination of the energy levels of a hamiltonian H, to which there corresponds a symmetry group G of order g. Later we will specialize the discussion the case where H is a molecular electronic hamiltonian and G is a permutation group. The eigenfunctions of H may be made to be simultaneously eigenfunctions of the projectors $^{\gamma}A_{kk}$ $(1 \leq k \leq n_\gamma;\ 1 \leq \gamma \leq \ell)$ associated with the γ-th irreducible representation $\Gamma^{(\gamma)}$ of dimension n_γ. If $D_{ij}^{(\gamma)}(R)$ denotes the matrix of the operator O_R, belonging to G, in $\Gamma^{(\gamma)}$, then

$$A_{ij} = \frac{n_\gamma}{g} \sum_R D_{ij}^{(\gamma)*}(R)\ O_R .$$

One way to compute the eigensolutions of H is to set up and diagonalize an infinite secular equation with a complete set of functions. As in Appendix A of I we follow the Van Vleck-Kirtman[5] approach in considering such a set split into two classes, $\Psi^{(o)}$ and $\chi^{(o)}$. Special attention is given to $\Psi^{(o)}$, which we assume to be the symmetry components of a single primitive function $\phi^{(o)}$.

The elements of $\Psi^{(o)}$ are given by

$$ {}^{\gamma}\Psi_{ij}^{(o)} = {}^{\gamma}A_{ij}\ \phi^{(o)} \ ; \ 1 \leq i,j \leq n_{\gamma} \ ; \ 1 \leq \gamma \leq \ell \ . $$

If the set of functions $0_R\ \phi^{(o)}$ is linearly dependent, some of the ${}^{\gamma}\Psi_{ij}^{(o)}$ vanish and are, of course, omitted from $\Psi^{(o)}$. We assume that $\phi^{(o)}$ is an eigenfunction of an unperturbed hamiltonian $H^{(o)}$ with nondegenerate energy $\epsilon^{(o)}$. However we do not assume that $H^{(o)}$ commutes with G, hence, the $\Psi^{(o)}$ are not eigenfunctions of $H^{(o)}$. The elements of $\Psi^{(o)}$ are orthogonal by symmetry.

The remaining infinite set of functions $\chi^{(o)}$ is assumed, without loss of generality, to be orthonormal and orthogonal to $\Psi^{(o)}$. No other assumptions need be made regarding $\chi^{(o)}$.

Of course, we cannot diagonalize the matrix of H in the infinite set $\Psi^{(o)} + \chi^{(o)}$ and, in fact, we would like to limit ourselves just to the set $\Psi^{(o)}$. However, $\Psi^{(o)}$ is connected to $\chi^{(o)}$ in the secular equation by the matrix $\langle \Psi^{(o)} | H-E | \chi^{(o)} \rangle$, which is not necessarily negligible. Thus, we transform the initial basis to a new basis

$$ \Psi^{(N)} = \Psi^{(o)} + \lambda \Psi^{(1)} + \ldots + \lambda^N \Psi^{(N)} \ , $$

$$ \chi^{(N)} = \chi^{(o)} + \lambda \chi^{(1)} + \ldots + \lambda^N \chi^{(N)} \ . $$

Here λ is a formal perturbation parameter whose numerical value is unity. The functions $\Psi^{(n)}$, $\chi^{(n)}$ are chosen so as to make the overlap and hamiltonian matrix elements connecting $\Psi^{(N)}$ and

$\chi^{(N)}$ vanish through terms $O(\lambda^N)$. Then

$$\langle \Psi^{(N)} | H-E | \chi^{(N)} \rangle = O(\lambda^{N+1}) \qquad (1)$$

If the set $\chi^{(N)}$ is ignored and the energies determined by the secular equation

$$\langle \Psi^{(N)} | H-E | \psi^{(N)} \rangle = 0 , \qquad (2)$$

the resulting eigenvalues are accurate through $O(\lambda^{2N+1})$. Thus, our method consists of solving Eq. (1) for the $\psi^{(N)}$ by a perturbation expansion, and then solving the secular equation (2) to obtain approximate energies and wavefunctions. However, we do not solve Eq. (2) by perturbation methods since it is a finite determinant and can be diagonalized easily by other methods. Thus we do not produce a perturbation expansion for the energy and wavefunction.

The functions $\chi^{(N)}$ are obtained by Schmidt orthogonalizing $\chi^{(o)}$ to $\Psi^{(N)}$, and the $\psi^{(N)}$ are chosen so that

$$\langle {}^{r}\Psi_{ij}^{(N)} | H | \chi^{(N)} \rangle = O(\lambda^{N+1}). \qquad (3)$$

We assume the existence of primitive functions ${}^{r}\Phi_j^{(N)}$ such that

$${}^{r}\Psi_{ij}^{(N)} = {}^{r}A_{ij}\, {}^{r}\Phi_j^{(N)}$$

and

$${}^{r}\Phi_j^{(N)} = \phi^{(o)} + \lambda\, {}^{r}\phi_j^{(1)} + \ldots + \lambda^N\, {}^{r}\phi_j^{(N)}.$$

then, due to the commutivity of H and ${}^{\nu}A_{jj}$, Eq. (3) becomes

$$\langle H\, {}^{\nu}\Phi_j^{(N)} \mid {}^{\nu}A_{jj}\, \chi^{(N)} \rangle = o(\lambda^{N+1}). \tag{4}$$

We now introduce λ into H as $H = H^{(o)} + \lambda V$. The solution of Eq. (4) is

$$(H^{(o)} + \lambda V)\, {}^{\nu}\Phi_j^{(N)} = \sum_R {}^{\nu}\mathcal{E}_{jR}^{(N)}\, O_R\, {}^{\nu}\Phi_j^{(N)} + o(\lambda^{N+1}) \tag{5}$$

where the ${}^{\nu}\mathcal{E}_{jR}(N)$ are, as yet, undetermined numbers. This results follows since ${}^{\nu}A_{ij}\, O_R = \sum_k {}^{\nu}A_{kj}\, D_{ki}^{(N)}(R)$ and $\chi(N)$ is orthogonal to all ${}^{\nu}\Psi_{ij}(N)$.

The equations for the components ${}^{\nu}\phi_j^{(k)}$ are obtained by resolving Eq. (5) into different orders in λ. Thus,

$$(H^{(o)} - \epsilon^{(o)})\, \phi^{(o)} = 0, \tag{6}$$

$$(H^{(o)} - \epsilon^{(o)})\, {}^{\nu}\phi_j^{(1)} + V\, \phi^{(o)} = \sum_R {}^{\nu}\mathcal{E}_{jR}^{(1)}\, O_R\, \phi^{(o)}, \tag{7}$$

$$(H^{(o)} - \epsilon^{(o)})\, {}^{\nu}\phi_j^{(N)} + V\, \phi^{(N-1)} = \sum_{\ell=1}^{N} \sum_R {}^{\nu}\mathcal{E}_{jR}^{(\ell)}\, O_R\, \phi^{(N-\ell)} \tag{8}$$

The solution of the zeroth order equation is assumed known.

We shall consider in detail here only the first order equation, since practical calculations are limited at present to solving this equation. Assuming the functions $O_R\, \phi^{(o)}$ to be linearly independent, Eq. (7) involves $g+1$ unknown quantities: the function ${}^{\nu}\phi_j^{(1)}$ and

the constants ${}^{\gamma}\mathcal{E}_{jk}^{(1)}$ clearly, one equation is not sufficient to determine all of them uniquely. A further relation is provided by mathematical consistency, the inhomogeneity must be orthogonal to $\phi^{(o)}$. Hence,

$$\langle \phi^{(o)} | v | \phi^{(o)} \rangle = \sum_R {}^{\gamma}\mathcal{E}_{jR}^{(1)} \langle \phi^{(o)} | O_R | \phi^{(o)} \rangle . \quad (9)$$

A solution ${}^{\gamma}\phi_j^{(1)}$ can be obtained as an implicit function of any set of ${}^{\gamma}\mathcal{E}_{jR}^{(1)}$ which satisfy Eq. (9). This is analogous to the almost degenerate perturbation theory, and we shall use the methods of I as a guide in deriving relations to fix the ${}^{\gamma}\mathcal{E}_{jR}^{(1)}$.

One method discussed in I is to use normalization conditions to determine the arbitrary constants. This leads to the modified Kirtman (MK) treatment, in which the first order wavefunction is required to be orthogonal to all zeroth order wavefunctions. For the electron exchange problem, Kirtman[6] has proposed the analogous requirement $\langle \phi^{(o)} | O_R | {}^{\gamma}\phi_j^{(1)} \rangle = 0$. A similar, but more attractive, condition is $\langle O_R \phi^{(o)} | H^{(o)} - \epsilon^{(o)} | {}^{\gamma}\phi_j^{(1)} \rangle = 0$, which is used in the Hirschfelder-Silbey (HS) approach[2]. This latter condition has the properties that the energy through first order agrees with the Heitler-London result so that the first order energy is obtained by the zeroth order wavefunction[2]. Furthermore, in the HS theory the ${}^{\gamma}\phi_j^{(1)}$ and ${}^{\gamma}\mathcal{E}_{jR}^{(1)}$ are independent of γ and j. Thus, the same primitive function is used to obtain all states which can arise from $\phi^{(o)}$.

In the present paper, we shall generalize the HS procedure

and fix the unknown constants by a variational method analogous to the DE-FOP-VIM formalism discussed in I. This has the advantage of providing the best energy values for the lowest states of particular symmetries obtainable from Eq. (2) with N = 1. As we shall see, as a result of this variation, the HS concept of a single primitive function for all states is destroyed.

The most general solution of Eq. (7) and (9) is

$$ {}^{\nu}\phi_j^{(1)} = \hat{\phi}^{(1)} + \sum_R{}' {}^{\nu}c_{jR}^{(1)}\, \omega_R^{(1)} + {}^{\nu}\alpha_j^{(1)} \phi^{(o)}, \qquad (10) $$

Here the prime means that the identity permutation is omitted, and ${}^{\nu}\alpha_j^{(1)}$ is a variational constant introduced to optimize the component of $\phi^{(o)}$ in ${}^{\nu}\phi_j^{(1)}$. The $\hat{\phi}^{(1)}$ is orthogonal to $\phi^{(o)}$ and satisfies the polarization equation

$$ (H^{(o)} - \epsilon^{(o)})\, \hat{\phi}^{(1)} + (V - \langle \phi^{(o)} | V | \phi^{(o)} \rangle)\, \phi^{(o)} = 0 \qquad (11) $$

This is the first order equation in an unsymmetrical Rayleigh-Schrodinger expansion of the eigensolutions of H. The $\omega_R^{(1)}$ satisfy the exchange equations

$$ (H^{(o)} - \epsilon^{(o)})\, \omega_R^{(1)} - (O_R - \langle \phi^{(o)} | O_R | \phi^{(o)} \rangle)\, \phi^{(o)} = 0, \qquad (12) $$

and $\langle \omega_R^{(1)} | \phi^{(o)} \rangle = 0$. The $\omega_R^{(1)}$ provide a correction to $\hat{\phi}^{(1)}$ due to symmetry. Note that neither $\hat{\phi}^{(1)}$ nor $\omega_R^{(1)}$ depends on ν or j.

Since ${}^{\nu}\alpha_j^{(1)}$ and ${}^{\nu}c_{jR}^{(1)}$ are independent variational constants, the ${}^{\nu}\Psi_{ij}(1)$ are linear variation functions in the set ${}^{\nu}A_{ij}\, \phi^{(o)}$, ${}^{\nu}A_{ij}\, \hat{\phi}^{(1)}$, ${}^{\nu}A_{ij}\, \omega_R^{(1)}$. The secular equation (2) is equivalent

to the expanded determinant

$$0 = \begin{vmatrix} \langle \phi^{(0)} | H-E | {}^{\nu}A_{ij}\phi^{(0)} \rangle & \langle \phi^{(0)} | H-E | {}^{\nu}A_{ij}\hat{\phi}^{(1)} \rangle & \langle \phi^{(0)} | H-E | {}^{\nu}A_{ij}\omega_R^{(1)} \rangle \\ \langle \hat{\phi}^{(1)} | H-E | {}^{\nu}A_{ij}\phi^{(0)} \rangle & \langle \hat{\phi}^{(1)} | H-E | {}^{\nu}A_{ij}\hat{\phi}^{(1)} \rangle & \langle \hat{\phi}^{(1)} | H-E | {}^{\nu}A_{ij}\omega_R^{(1)} \rangle \\ \langle \omega_R^{(1)} | H-E | {}^{\nu}A_{ij}\phi^{(0)} \rangle & \langle \omega_R^{(1)} | H-E | {}^{\nu}A_{ij}\hat{\phi}^{(1)} \rangle & \langle \omega_R^{(1)} | H-E | {}^{\nu}A_{ij}\omega_R^{(1)} \rangle \end{vmatrix} \tag{13}$$

The maximum dimension of this secular equation is $g^2(g+1)$. Only the roots which evolve from the roots of the zeroth order equation $|\langle \phi^{(0)} | H-E | {}^{\nu}A_{ij}\phi^{(0)} \rangle| = 0$ have meaning, however.

Finally, we remark that this variational method, has meaning only in low order perturbation theory. This is because in infinite order, the exact solution ${}^{\nu}\Phi_j$ of Eq. (5) is a linear combination of degenerate eigenfunctions ${}^{\nu}\Psi_k$, $1 \leq k \leq n_\nu$, of H corresponding to energy, say, ${}^{\nu}E$. The ${}^{\nu}\Phi_j$ depends on the ${}^{\nu}\mathcal{E}_{jR}$ only through the coefficients of the ${}^{\nu}\Psi_k$. Hence,

$$\langle A_{ij}\,{}^{\nu}\Phi_j | H | {}^{\nu}A_{ik}\,{}^{\nu}\Phi_k \rangle = {}^{\nu}E \langle {}^{\nu}A_{ij}\,{}^{\nu}\Phi_j | {}^{\nu}A_{ik}\,{}^{\nu}\Phi_k \rangle,$$

so that the roots of the secular equation (2) do not depend on the ${}^{\nu}\mathcal{E}_{jR}$.

III. APPLICATIONS TO ELECTRON EXCHANGE IN H_2 AND H_2^+.

For electron exchange problems H is the molecular electronic hamiltonian and G is the permutation group of electron labels. All wavefunctions that we consider are spatial wavefunctions.

Let us consider the interaction of two ground state hydrogen atoms, which results in the molecular singlet $^1\Sigma_g^+$ (^1E, $^1\Psi$) and triplet $^3\Sigma_u^+$ (^3E, $^3\Psi$). Here G consists of the identity and P_{12}, the transposition of electron labels. The projectors corresponding to the singlet and triplet irreducible representations are $^1A = \frac{1}{2}(1+P_{12})$ and $^3A = \frac{1}{2}(1-P_{12})$, respectively.

The zeroth order primitive function is $\phi^{(o)} = a_o(1)b_o(2)$, where a_o, b_o are 1s orbitals centered on the two nuclei, a and b. Hence,

$$H^{(o)} = h_a(1) + h_b(2) \tag{14}$$

and

$$V = H-H^{(o)} = R^{-1}+r_{12}^{-1} -r_{a2}^{-1} -r_{b1}^{-1} \tag{15}$$

where $h_a = -\frac{1}{2}\nabla^2 - r_a^{-1}$ and similarly for h_b. The unperturbed energy is $\epsilon^{(o)} = 2e_o = -1$ Hartree.

The polarization equation (10) has been solved to high accuracy by variational methods by Hirschfelder and Löwdin[7] and by Kolos.[8] The primary effect of $\phi^{(1)}$ is to introduce correlations between the electrons which give rise to van der Waals interactions.

The exchange function $\omega^{(1)}$ is orthogonal to $a_o(1)b_o(2)$ and satisfies the equation (12),

$$(h_a(1)-e_o + h_b(2)-e_o)\,\omega^{(1)} = b_o(1)a_o(2) - S_{oo}^2\, a_o(1)b_o(2), \tag{16}$$

where S_{oo} is the overlap between a_o and b_o. The $\omega^{(1)}$ provides

a correction to $\hat{\phi}^{(1)}$ due to the Pauli principle. Since $\omega^{(1)}$ is a new function appearing in our theory, we consider the solution of Eq. (16) in detail below.

The singlet and triplet wave functions, accurate through first order, are given by

$$^{i}\Psi_{(1)} = {}^{i}A\,\phi^{(o)} + \alpha_i\,{}^{i}A\,\hat{\phi}^{(1)} + \beta_i\,{}^{i}A\,\omega^{(1)}, \quad i=1 \text{ or } 3, \tag{17}$$

where α_i, β_i are variational constants. It follows that the energies are the lowest roots of the two 3x3 secular equations

$$0 = \begin{vmatrix} \langle \phi^{(o)} | H - {}^{i}E | {}^{i}A\,\phi^{(o)} \rangle & \langle \phi^{(o)} | H - {}^{i}E | {}^{i}A\,\hat{\phi}^{(1)} \rangle & \langle \phi^{(o)} | H - {}^{i}E | {}^{i}A\,\omega^{(1)} \rangle \\ \langle \hat{\phi}^{(1)} | H - {}^{i}E | {}^{i}A\,\phi^{(o)} \rangle & \langle \hat{\phi}^{(1)} | H - {}^{i}E | {}^{i}A\,\hat{\phi}^{(1)} \rangle & \langle \hat{\phi}^{(1)} | H - {}^{i}E | {}^{i}A\,\omega^{(1)} \rangle \\ \langle \omega^{(1)} | H - {}^{i}E | {}^{i}A\,\phi^{(o)} \rangle & \langle \omega^{(1)} | H - {}^{i}E | {}^{i}A\,\hat{\phi}^{(1)} \rangle & \langle \omega^{(1)} | H - {}^{i}E | {}^{i}A\,\omega^{(1)} \rangle \end{vmatrix} \tag{18}$$

The recent application[9] of the HS procedure to H_2^+ gives an indication of the accuracy to be expected from our treatment. The energies labelled $^{i}E(1,\lambda)$ in Tables V and VI of Ref. (6) correspond, in the present treatment, to the lowest roots of the 2x2 secular equation resulting from the basis ${}^{i}A\,\phi^{(o)}$ and ${}^{i}A(\hat{\phi}^{(1)} + \beta\,\omega^{(1)})$, where β is fixed and taken to be the Heitler-London exchange energy. The resulting energies are quite accurate in the region of the van der Waals minimum of the triplet state, although at shorter distances the error increases. Allowing β to vary so as to minimize the energy (as in our treatment) improves the results. We have not repeated the calculations, however, since our

primary interest at present is in characterizing the exchange function $\omega^{(1)}$. Although $\omega^{(1)}$ is implicit in the function ${}^{g}\chi + {}^{u}\chi$ of Ref. (9), the form of the basis which was used makes a meaningful extraction of $\omega^{(1)}$ impossible. Thus we have obtained $\omega^{(1)}$ by solving Eq. (12) variationally.

The interaction of a ground state hydrogen atom with a proton to form the $1s\,\sigma_g$ and $2p\,\pi_u$ states of H_2^+ provides a very similar example of electron exchange. In this case, one electron is being exchanged between the two nuclei, as contrasted to the H_2 case where the two electrons are being interchanged. The H_2^+ example has been studied by McQuarrie and Hirschfelder[10] who used the HS treatment together with the Unsöld approximation for the exchange function. In this case: $\phi^{(o)} = a_o$, $H^{(o)} = h_a$, $V = R^{-1} - r_b^{-1}$, and $\epsilon^{(o)} = e_o = -\frac{1}{2}$ Hartree. The polarization function $\hat{\phi}^{(1)}$ has been expressed in closed form by Dalgarno and Lewis.[11,10] The exchange function $\omega_a^{(1)}$ is orthogonal to a_o and satisfies the equation

$$(h_a - e_o)\,\omega_a^{(1)} = b_o - S_{oo}\,a_o \tag{19}$$

The two states are characterized by the projectors ${}^{g}A = (1 + I)/2$ and ${}^{u}A = (1 - I)/2$ respectively where I is the inversion operator. Otherwise the analysis is the same as for the H_2: Eq. (17) gives the wave function through the first order and Eq. (18) gives the energy through the third order. The resulting energy is in good agreement with the exact energies for separations greater than 4 Bohr radii.[10]

IV. The Exchange Functions for H_2 and H_2^+ .

The equations, (16) and (19), for the exchange functions appear deceptively simple! These equations correspond to first order perturbation equations in which the $\omega^{(1)}$ plays the role of the first order wave function. For H_2 , the perturbation potential is $-\exp(r_{a1} + r_{b2} - r_{b1} - r_{a2})$; for H_2^+ , it is $-\exp(r_a - r_b)$. In neither case does the equation separate in ellipsoidal coordinates.

The Unsöld approximation gives $\omega^{(1)}(H_2)$ proportional to $b_o(1)a_o(2)$ and $\omega^{(1)}(H_2^+)$ proportional to b_o . In both cases, ${}^1A\,\omega^{(1)}$ would be proportional to $\phi^{(o)}$. Thus, in the Unsöld approximation, the β_i in Eq. (17) can be set equal to zero and the row and column involving the $\omega^{(1)}$ can be omitted from the secular equation (18) without affecting the energy ${}^1E$. This approximation is very interesting but it is not sufficiently accurate to determine the exchange energy, especially at large separations.

In order to obtain a more accurate approximation for $\omega^{(1)}$, let us make spectral expansions in terms of the complete set of eigenfunctions of h_a and h_b . If

$$(h_a - e_o - e'_k)\, a_k = 0 \quad \text{and} \quad (h_b - e_o - e'_\ell)\, b_\ell = 0 \,, \tag{20}$$

then

$$\omega^{(1)}(H_2) = \sum_{k\neq 0} \sum_{\ell \neq 0} \frac{a_k(1) b_\ell(2) \langle a_k | b_o \rangle \langle b_\ell | a_o \rangle}{e'_k + e'_\ell}$$

$$+ S_{oo}\left[\omega_a^{(1)}(1) b_o(2) + a_o(1)\omega_b^{(1)}(2)\right] \tag{21}$$

where $\omega_a^{(1)}$ and $\omega_b^{(1)} = I\omega_a^{(1)}$ are the exchange functions for H_2^+,

$$\omega_a^{(1)}(H_2^+) = \sum_{k\neq 0} a_k \langle a_k | b_0 \rangle (e_k')^{-1} \qquad (22)$$

The double summation in Eq. (21) can be factored into the product of one electron summations by making use of a mathematical identity which has previously been used for the calculation of atomic polarizabilities, van der Waals coefficients, etc.[12] If e_k' and e_ℓ' are real constants, then it follows from the residue theorem that

$$\frac{1}{e_k' + e_\ell'} = \frac{1}{2\pi}\int_0^\infty \left[\frac{1}{e_k' + iu} + \frac{1}{e_k' - iu}\right]\left[\frac{1}{e_\ell' + iu} + \frac{1}{e_\ell' - iu}\right] du \qquad (23)$$

Thus,

$$\omega^{(1)}(H_2) = \frac{1}{2\pi}\int_0^\infty [f_a(1) + f_a^*(1)][f_b(2) + f_b^*(2)]\, du + S_{oo}\,[\omega_a^{(1)}(1)b_o(2) + a_o(1)\omega_b^{(1)}(2)] \qquad (24)$$

where the function $f_b = I f_a$ and f_a is orthogonal to a_o and satisfies the equation

$$(h_a - e_o + iu) f_a = b_o - S_{oo} a_o \qquad (25)$$

Comparing Eqs. (19) and (25), it is clear that $\omega_a^{(1)}(H_2^+) = f_a$ when $u = 0$. Thus, $\omega^{(1)}(H_2)$ is obtained by solving the one-electron

two-center equation (25) and performing the quadrature indicated in Eq. (24).

Since it does not appear possible to obtain an exact solution for f_a, it is expedient to use variational methods to obtain an approximate solution. If $\tilde{f}_a$ is a trial function and $J[\tilde{f}_a]$ is the functional,[13]

$$J[\tilde{f}_a] = \langle \tilde{f}_a^* \mid h_a - e_o + iu \mid f_a \rangle - \langle f_a^* \mid b_o - S_{oo} a_o \rangle - \langle b_o - S_{oo} a_o \mid f_a \rangle \quad , \tag{26}$$

then the variational approximation to f_a is given as an extremum point of $J[\tilde{f}_a]$. If f_a is a linear variational function, then increasing the size of the basis set yields a better bound to $J[\tilde{f}_a]$.

For $u = 0$, the $J[\tilde{\omega}_a^{(1)}]$ is the Hylleraas functional for a ground state hydrogen atom perturbed by the potential $-\exp(r_a - r_b)$. Since the Hylleraas functional gives an upper bound to the second order energy for a system in its ground state, $J[\tilde{\omega}_a^{(1)}] \geq J[\omega_a^{(1)}]$. If $\hat{\omega}_a^{(1)}$ is the function $\tilde{\omega}_a^{(1)}$ which minimizes J, then $J[\hat{\omega}_a^{(1)}] = -\langle b_o - S_{oo} a_o \mid \hat{\omega}_a^{(1)} \rangle \geq J[\omega_a^{(1)}]$.

We have taken as our basis set $\theta_1, \ldots, \theta_{14}$ the Slater type orbitals: $(1s_a)$, $(1s_b)$, $(2s_a)$, $(3s_a)$, $(4s_a)$, $(2p_a)$, $(3p_a)$, $(4p_a)$, $(2s_b)$, $(3s_b)$, $(4s_b)$, $(2p_b)$, $(3p_b)$, and $(4p_b)$ where

$$\begin{aligned} (ns) &= [2^{2n-1}/(2n)!\pi\,]^{1/2}\; r^{n-1} \exp(-r) \\ (np) &= [2^{2n-1}\,3/(2n)!\pi\,]^{1/2}\; r^{n-1} \cos\theta \exp(-r) \quad . \end{aligned} \tag{27}$$

The first step is to form a set of 14 linear combinations of the Slater orbitals[14]

$$\chi_k = \sum_{j=1}^{14} \theta_j D_{jk} \tag{28}$$

which are orthonormal and diagonalize h_a,

$$\begin{aligned} \langle \chi_k | \chi_\ell \rangle &= \delta_{k\ell} \\ \langle \chi_k | h_a - e_o | \chi_\ell \rangle &= e'_k \delta_{k\ell} \end{aligned} \tag{29}$$

χ_1 is taken to be $(1s_a)$. Thus,

$$\tilde{f}_a = \sum_{k=2}^{14} c_k \chi_k \tag{30}$$

The c_k which minimize $J[\tilde{f}_a]$ are

$$c_k = (e'_k + iu)^{-1} \langle \chi_k | b_o - S_{oo} a_o \rangle \tag{31}$$

Thus, the variational approximation to $\omega_a^{(1)}(H_2^+)$ is

$$\hat{\omega}_a^{(1)} = \sum_{k=2}^{14} (\tilde{e}'_k)^{-1} \langle \chi_k | b_o - S_{oo} a_o \rangle \chi_k \tag{32}$$

or, expressing the χ_k in terms of the Slater-type orbitals,

$$\hat{\omega}_a^{(1)} = \sum_j f_j F_j(r_b) \exp(-r_b) + \sum_i g_i G_i(r_a) \exp(-r_a) \tag{33}$$

In Table I, the functions $F_j(r_b)$ and $G_i(r_a)$ are given together with the coefficients f_j and g_i calculated at internuclear separations

Table I. The Variational Approximation to the Exchange Function $\omega_a^{(1)}(H_2^+)$. See Eq. (33).

j	$F_j(r_b)$	f_j			
		$(R/a_o)=4$	6	8	10
2	1	+.37619	+.34366	+.32522	+.31477
9	r_b	+.37593	+.33184	+.31935	+.31324
10	r_b^2	+.03757	+.02970	+.01825	+.01197
11	r_b^3	-.00267	-.00161	-.00034	+.00015
12	$r_b\cos\theta_b$	+.00899	-.00279	+.00017	+.00189
13	$r_b\cos\theta_b$	+.03369	+.02373	+.00955	+.00350
14	$r_b^3\cos\theta_b$	-.00412	-.00164	+.00044	+.00090
i	$G_i(r_a)$	g_i			
		$(R/a_o)=4$	6	8	10
1	1	-.28686	-.09913	-.02777	-.00709
3	r_a	-.04440	-.01735	-.00405	+.00037
4	r_a^2	+.00716	+.01115	+.00247	-.00053
5	r_a^3	-.00174	-.00120	+.00011	+.00029
6	$r_a\cos\theta_a$	+.06611	+.00950	+.00263	+.00204
7	$r_a^2\cos\theta_a$	+.02126	+.01919	+.00305	-.00135
8	$r_a^3\cos\theta_a$	-.00476	-.00215	+.00056	+.00070

of R = 4, 6, 8 and 10 Bohr radii. In the limit as R becomes large,[15]

$$\omega_a^{(1)} = (4\pi)^{-1/2} [1 + r_b] \exp(-r_b)$$

$$- (\pi)^{-1/2} [(R^3/12 + (R^2/2) + (5R/4) + (5/4)] \exp(-R - r_a) \tag{34}$$

At smaller separations, other terms become important.

Now let us consider the variational approximation to $\omega^{(1)}(H_2)$. Using (31), (30) and (23), the integral in Eq. (24) becomes

$$\sum_{k=2}^{14} \sum_{\ell=2}^{14} (e'_k+e'_\ell)^{-1} \langle \chi_k | {}^{b}_{o}-S_{oo}{}^{a}_{o} \rangle \langle \chi_\ell | {}^{b}_{o}-S_{oo}{}^{a}_{o} \rangle \chi_k(1) \chi_\ell(2) \tag{35}$$

and Eq. (28) can be used to express the χ's in terms of the Slater-type orbitals. Thus, we obtain $\omega^{(1)}(H_2)$ as the sum of four types of terms:

$$\omega^{(1)}(H_2) = E(r_{b1},r_{a2}) \exp(-r_{b1} -r_{a2})$$

$$+ C(r_{a1},r_{b2}) \exp(-r_{a1} -r_{b2})$$

$$+ I(r_{a1},r_{a2}) \exp(-r_{a1},r_{a2}) \exp(-r_{a1} -r_{a2}) \tag{36}$$

$$+ I(r_{b1},r_{b2}) \exp(-r_{b1} - r_{b2})$$

Here $E(r_{b1},r_{a2})$ corresponds to electron exchange terms; $C(r_{a1},r_{b2})$ corresponds to coulomb-type terms; and $I(r_{a1},r_{a2})$ and $I(r_{b1},r_{b2})$ correspond to ionic terms. Tables II, III, and IV give the leading terms in these functions at separations of 4, 6, 8 and 10 Bohr radii.

Table II. Leading Electron Exchange Terms in $\omega^{(1)}(H_2)$.

Here $E(r_{b1},r_{a2}) = A_{22} \sum_{i \leq j} E_{ij}(r_{b1},r_{a2})\ \gamma_{ij}$. See Eq. (36).

ij	$E_{ij}(r_{b1},r_{a2})$	ij			
		$R/a_o)=4$	6	8	10
2,2	1	+1.0000	+1.0000	+1.0000	+1.0000
9,9	$r_{a2}r_{b1}$	+ .9940	+ .9214	+ .9046	+ .8980
2,9	$r_{a2}+r_{b1}$	+ .8086	+ .7664	+ .7518	+ .7457
9,10	$r_{a2}r_{b1}(r_{a2}+r_{b1})$	- .1563	- .1511	- .1542	- .1566
2,10	$r_a^2+r_{b1}^2$	- .1252	- .1249	- .1311	- .1353
10,10	$r_{a2}^2 r_{b1}^2$	+ .0810	+ .0725	+ .0664	+ .0633
9,12	$r_{a2}r_{b1}(r_{a2}\cos\theta_{a2}+r_{b1}\cos\theta_{b1})$	+ .0256	+ .0204	+ .0098	+ .0045
2,12	$r_{a2}^2\cos\theta_{a2}+r_{b1}^2\cos\theta_{b1}$	+ .0149	+ .0142	+ .0062	+ .0020
	A_{22}	+ .062450	+ .059155	+ .057435	+ .056482

Table III. Leading Coulomb-type Terms in $\omega^{(1)}(H_2)$.

Here $C(r_{a1},r_{b2}) = S_{oo}^2 \sum_{i \leq j} C_{ij}(r_{a1},r_{b2})\beta_{ij}$. See Eq. (36).

ij	$C_{ij}(r_{a1},r_{b2})$	β_{ij}			
		R=4	6	8	10
11	1	-1.2704	-1.7168	-2.17	-2.53
16	$r_{a1}\cos\theta_{a1}+r_{b2}\cos\theta_{b2}$	+ .1182	+ .0789	+ .08	- .08
13	$r_{a1}+r_{b2}$	- .0875	- .1249	- .15	- .50
66	$r_{a1}r_{b2}\cos\theta_{a1}\cos\theta_{b2}$	+ .0200	+ .0122	+ .08	+ .86
33	$r_{a1}r_{b2}$	+ .0104	+ .0392	+ .20	+1.69
14	$r_{a1}^2+r_{b2}^2$	+ .0138	+ .0784	+ .10	+ .28
17	$r_{a1}^2\cos\theta_{a1}+r_{b2}^2\cos\theta_{b2}$	+ .0565	+ .1402	+ .12	+ .22
37	$r_{a1}r_{b2}^2\cos\theta_{b2}+r_{a1}^2r_{b2}\cos\theta_{a1}$	- .0055	- .0716	- .13	-1.16
36	$r_{a1}r_{b2}(\cos\theta_{b2}+\cos\theta_{a1})$	- .0066	+ .0079	+ .12	+1.16
34	$(r_{a1}r_{b2}^2+r_{a1}^2r_{b2})$	- .0034	- .0247	- .12	-1.09
47	$r_{a1}^2r_b^2(\cos\theta_{b2}+\cos\theta_{a1})$	+ .0021	- .0035	+ .08	+ .77
46	$r_{a1}^2r_{b2}\cos\theta_{b2}+r_{a1}r_{b2}^2\cos\theta_{a1}$	- .0007	- .0046	- .07	- .77
67	$(r_{a1}^2r_{b2}+r_{a1}r_{b2}^2)\cos\theta_{a1}\cos\theta_{b2}$	+ .0008	- .0018	- .07	- .85
77	$r_{a1}^2r_{b2}^2\cos\theta_{a1}\cos\theta_{b2}$	+ .0043	+ .0292	+ .08	+ .86
	S_{oo}^2	+ .035820	+ .002218	+ .0001035	+ .000004051

Table IV. Leading Ionic Terms in $\omega^{(1)}(H_2)$. Here

$$I(r_{a1},r_{a2}) = S_{oo}^2 \sum_{i \le j} I_{ij}(r_{a1},r_{a2})\, \gamma_{ij} .$$ See Eq. (36).

Although $\gamma_{6,12}$ is small, it is given here because it is mentioned in the text.

ij	$I_{ij}(r_{a1},r_{a2})$	γ_{ij}			
		R=4	6	8	10
1,2	1	+.3783	+.9959	+3.98	+25.18
1,9	r_{a2}	+.3529	+.8268	+2.76	+ 8.89
1,10	r_{a2}^2	+.1470	+.3687	+ .80	- 1.41
6,9	$r_{a2}r_{a1}\cos\theta_{a1}$	+.1117	+.0373	- .65	- 1.69
2,6	$r_{a1}\cos\theta_{a1}$	+.0845	-.0783	-2.08	-23.23
2,3	r_{a1}	-.0813	-.5212	-4.67	-49.51
3,9	$r_{a1}r_{a2}$	-.0641	-.3246	-2.17	-12.97
1,13	$r_{a2}^2\cos\theta_{a2}$	+.0576	+.1114	+ .07	- 0.63
2,7	$r_{a1}^2\cos\theta_{a1}$	+.0126	+.4017	+2.67	+23.81
2,4	r_{a1}^2	+.0262	+.3274	+2.74	+29.78
7,9	$r_{a1}^2 r_{a2}\cos\theta_{a1}$	-.0077	+.2786	+1.41	+ 4.35
6,12	$r_{a1}r_{a2}\cos\theta_{a1}\cos\theta_{a2}$	+.0000	-.0121	-0.08	- 0.91
	S_{oo}^2	+.035820	+.002218	+.0001035	+.000004051

The exchange terms remain very nearly constant over a wide range of separations and

$$E(r_{b1},r_{a2}) \approx 0.057[\ 1 + 0.9\ r_{b1}r_{a2} + 0.75\ (r_{b1} + r_{a2})] \qquad (37)$$

At small separations, the only appreciable coulombic-type term is proportional to $a_o(1)b_o(2)$. But at large separations, a large number of terms contribute to $C(r_{a1},r_{b2})$. Similarly, the composition of the ionic terms varies a great deal with the separation and the leading terms at one separation may contribute very little at another separation. Since $I(r_{b1},r_{b2}) = I\ I(r_{a1},r_{a2})$, the ionic terms with two electrons on nucleus b are the same as those for two electron on a . The ionic terms enter naturally in our approach due to the two center character of Eq. (16). It is surprising that the ionic coefficient $\gamma_{6,12}$ corresponding to $2p_a(1)2p_a(2)$ is so small since Alexander and Salem[16] found that the addition of this term to the Heitler-London wave function greatly improved the exchange energy for R=8 Bohr radii. However, much significance cannot be placed on any one term since $\omega^{(1)}(H_2)$ is such a mixture of a large number of non-orthogonal functions. Alexander and Salem also found that $2p_a(1)2p_b(2)$, the leading dipole-dipole term in $\hat{\phi}^{(1)}$, greatly improved the exchange energy. This corresponds to the fact that $\hat{\phi}^{(1)}$, as well as the $\omega^{(1)}$, is involved in the determination of the exchange energy.

V. Extension to Many-Electron Systems.

The case of H_2 is, of course, a particularly simple one. To be useful, our methods must be extended to interactions involving many electrons.

We have in mind that the zeroth order primitive function will be a simple product of atomic or molecular orbitals. This introduces intermolecular perturbations due to the incorrect description of the separated molecules, as well as the intermolecular perturbations. However, this is beside our main point here, which is to show that Eq. (12), which potentially contains complicated exchange terms due to many electron permutation operators, can be solved in terms of one and two electron equations. Thus, to avoid the complications which arise when the exact eigensolutions of the separated molecules are unknown, consider the interaction of N ground state hydrogen atoms.

The zeroth order primitive function is

$$\phi^{(o)} = a_o(1)b_o(2) \ldots n_o(N) , \tag{38}$$

and the group G is the permutation group on the N electron labels. Corresponding to $\phi^{(o)}$ is

$$H^{(o)} = h_a(1) + h_b(2) + \ldots + h_n(N) , \tag{39}$$

and

$$V = V_{ab}(1,2) + V_{ac}(1,3) + \ldots , \tag{40}$$

where

$$V_{ab} = r_{12}^{-1} + R_{ab}^{-1} - r_{a2}^{-1} - r_{b1}^{-1} \tag{41}$$

and $\epsilon^{(o)} = Ne_o$. The solution to the polarization equation (11) is

$$\hat{\phi}^{(1)} = \varphi_{ab}(1,2) \frac{\phi^{(o)}}{a_o(1)b_o(2)} + \varphi_{ac}(1,3) \frac{\phi^{(o)}}{a_o(1)c_o(3)} + \ldots , \tag{42}$$

where

$$(h_a(1)-e_o+h_b(2)-e_o)\,\varphi_{ab} + [\,V_{ab} - (V_{ab})_{oo}\,]\,a_o(1)b_o(2) = 0\ . \qquad (43)$$

Here $(V_{ab})_{oo} = \langle a_o(1)b_o(2) \mid V_{ab} \mid a_o(1)b_o(2) \rangle$. Eq. (43) is the polarization equation for H_2 . The exchange equation (12) is a coupled k-electron equation if $\mathcal{O}_R$ permutes the labels of k electrons. However, we can generalize the mathematical identity, Eq. (23). If $c_1, c_2, \ldots, c_k$ are any set of real positive constants,

$$(c_1+c_2+\ldots c_k)^{-1} = (\pi)^{1-k} \int_{-\infty}^{\infty} du_1 \ldots \int_{-\infty}^{\infty} \frac{du_k \quad c_1 c_2 \ldots c_k \; \delta(u_1+u_2+\ldots+u_k)}{(c_1^2+u_1^2)(c_2^2+u_2^2)\ldots(c_k^2+u_k^2)} \qquad (44)$$

Eq. (44) allows the reduction of Eq. (12) for $\omega_R^{(1)}$ to a set of one electron equations of the form of Eq. (25).

VI. Summary.

The extension to exchange perturbation problems of the formalism developed in I leads to the Hirschfelder-Silbey (HS) perturbation theory if the undetermined constants in the first order equation are chosen to yield the Heitler-London first order energy. A generalization of the HS theory results from choosing the constants by a variational procedure analogous to the DE-FOP-VIM formalism. The first order wave function is the sum of a polarization function, which describes van der Waals correlations, and an exchange function, which introduces ionic terms. In the many electron case the first order equation reduces to a set of one and two electron equations.

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