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may be more important.¹³ The present theory applies to both of these cases, provided the quantity $a/2l_{\sigma}$ is less than unity.

IV. CONCLUSION AND DISCUSSION

We have demonstrated that the solution of the Poisson-Boltzmann equation for a charged cylinder can be approximated uniformly by the solution of the Debye-Hückel equation even when the molality of the electrolyte is low, i.e., when $e\psi/kT\gg1$, provided the cylinder is "moderately charged." However, when the charge on the cylinder exceeds the critical value, making $a/l_{\sigma}>1$, we expect a considerably more complicated result. Tentatively, our feeling is that there will be a strong tendency for counterions to pile up against the cylinder, with ψ dropping off very fast in a short distance. Since $a/2l_{\sigma}$ is proportional to the net charge

¹³ E. J. Verwey and J. Th. G. Overbeek, *Theory of the Stability* of Lyophobic Colloids (Elsevier Publ. Co., New York, 1948), p. 53. per unit length within a cylinder of radius a, there will be a certain distance a' where the net charge per unit length within the cylinder of radius a' is such that $a'/2l_{a'}=1$. Here $l_{a'}$ is the length based on the net charge within the cylinder. In the neighborhood of this point, we should expect the Bessel function solution to be a good approximation out to infinity.

According to the above description, the rate of increase of the potential ψ as the cylinder is charged suddenly drops when the critical charge is reached. For DNA, the resulting free energy of charging would be considerably less than the value computed using the Debye-Hückel equation. We hope to report concrete results on this and other aspects of the problem in the near future.

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New Type of Molecular Perturbation Treatment*

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A new type of perturbation treatment is developed for molecular problems using a product of atomic or molecular orbitals as the zeroth-order wavefunction. A special feature of this procedure is that all of the quantum states arising from a single electronic configuration are treated simultaneously. The formulas are derived for a general molecular configuration. For the special case of H_2^+ where the 1s atomic orbital leads to both a symmetric and antisymmetric molecular state, our basic equation is

$Ha = \frac{1}{2}(E_s + E_a)a + \frac{1}{2}(E_s - E_a)b$

where the exact unnormalized wavefunctions for the symmetric and antisymmetric states are $\psi_s = a + b$ and $\psi_a = a - b$, respectively. This basic equation is used to generate a set of perturbation equations, the zeroth order being the Schrödinger equation for a separated hydrogen atom. The interaction of three hydrogen atoms in their ground state is also considered as an example. In general, the energy through the first order agrees with the Heitler-London formalism.

INTRODUCTION

WE are developing a new type of perturbation treatment for molecular problems which uses a product of atomic or molecular orbitals as the zerothorder wavefunction. It differs from standard perturbation schemes¹ in considering simultaneously the energies and wavefunctions of all the quantum states which arise from a particular electron configuration. Our approach should be especially useful in the calculation of intermolecular forces in the intermediate range of separation where the wavefunctions of the interacting molecules overlap slightly. Or, it should be useful in the determination of potential-energy surfaces for use in reaction kinetics. Using products of atomic orbitals

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¹ J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Advances in Quantum Chemistry (Academic Press Inc., New York, 1964), Vol. 1, 255.

to form the zeroth-order wavefunction, we agree with the Heitler-London energy through the first order. Thus, our treatment provides an extension of the Heitler-London formalism to higher orders.

The spin-independent Hamiltonian H of the molecule commutes with a group G (of order g) of transformations R_i :

$$R_i H = H R_i. \tag{1}$$

Usually G is the direct product of the group of electron permutations and the symmetry group of the nuclear framework. Let $D^{(\alpha)}(R_i)_{kj}$ be the kjth matrix element of the α th irreducible unitary representation of the transformation R_i . The dimensionality of the α th irreducible representation is h_{α} .

We choose a zeroth-order unsymmetrized wavefunction $F_1^{(0)}$ (which might be, for example, a product of atomic or molecular orbitals, $F_1^{(0)} = a_1^{(0)} b_2^{(0)} c_3^{(0)} \cdots$). Corresponding to $F_1^{(0)}$ there is a set of zeroth-order wavefunctions $\psi_{kj}^{(0)}(\alpha)$ which are the projections of $F_1^{(0)}$ for every type of symmetry,

$$\psi_{kj}^{(0)}(\alpha) = (h_{\alpha}/g) \sum_{i} D^{(\alpha)}(R_{i})_{jk} * R_{i}F_{1}^{(0)}.$$
 (2a)

According to the completeness theorem for the projection operators,²

$$F_{1}^{(0)} = \sum_{\alpha,k} \psi_{kk}^{(0)}(\alpha).$$
 (3a)

The application of the transformations R_i to the $\psi_{kj}^{(0)}(\alpha)$ produces a linear combination of the h_{α} functions $\psi_{k1}^{(0)}(\alpha)$, $\psi_{k2}^{(0)}(\alpha)$, \cdots .

The zeroth-order eigenfunctions $\Phi_k^{(0)}(\alpha; \mathbf{r}, \mathbf{s})$ which include the spin \mathbf{s} , as well as the spatial coordinates \mathbf{r} , may be written in the form

$$\Phi_{k}^{(0)}(\alpha; \mathbf{r}, \mathbf{s}) = \sum_{j} \psi_{kj}^{(0)}(\alpha; \mathbf{r}) \chi_{j}(\mathbf{s}).$$
(4)

Here the spin functions $\chi_j(\mathbf{s})$ are independent and orthogonal. Not all of the $\Phi_k^{(0)}(\alpha; \mathbf{r}, \mathbf{s})$ satisfy the Pauli exclusion principle. If the $F_1^{(0)}$ is the product of atomic orbitals, then those $\Phi_k^{(0)}(\alpha)$ which satisfy the Pauli exclusion principle are the usual valence bond approximation wavefunctions. The zeroth-order functions $\Phi_k^{(0)}(\alpha)$ correspond to quantum states for the unperturbed system. Under the influence of the perturbations (corresponding to electron-electron interactions, etc.), the $\Phi_k^{(0)}(\alpha)$ and the $\psi_{kj}^{(0)}(\alpha)$ go adiabatically into the exact wavefunctions $\Phi_k(\alpha)$ and $\psi_{kj}(\alpha)$,

and

$$H\psi_{kj}(\alpha) = E_k(\alpha)\psi_{kj}(\alpha).$$
 (5)

 $H\Phi_k(\alpha) = E_k(\alpha)\Phi_k(\alpha)$

Correspondingly, under the influence of the perturbations, the $F_1^{(0)}$ goes adiabatically into a new function F_1 . Thus

$$\psi_{kk}(\alpha) = (h_{\alpha}/g) \sum_{i} D^{(\alpha)}(R_i)_{kk} * R_i F_1 \qquad (2b)$$

and

$$F_1 = \sum_{\alpha,k} \psi_{kk}(\alpha). \tag{3b}$$

Operating on Eq. (3b) by the Hamiltonian H and making use of Eq. (5),

$$HF_1 = \sum_{\alpha,k} E_k(\alpha) \psi_{kk}(\alpha).$$
 (6)

There are two types of electron correlations: the electron correlation built into the F_1 as contrasted to the correlation which results from the projection of F_1 into the proper symmetry type.

The set of functions $F_1, F_2 = R_2F_1, \dots, F_k = R_kF_1, \dots, F_g = R_gF_1$ forms a basis to a reducible representation of the symmetry group G. The functions $\psi_{kj}(\alpha)$ form the corresponding basis to the irreducible representations of the symmetry group. As is well known, the function set F_1, F_2, \dots, F_g is therefore expressible in terms of the $\psi_{kj}(\alpha)$ by means of a nonsingular transformation matrix; or, conversely, the $\psi_{kj}(\alpha)$ may be expressed in terms of the F_1, F_2, \dots, F_g by means of a nonsingular transformation matrix [for example, Eq. (2)].

Applying the operator R_i on Eq. (6) and making use of Eqs. (1) and (2b),

$$HF_{j} = \sum_{\alpha,k} E_{k}(\alpha) \left(h_{\alpha}/g\right) \sum_{t} D^{(\alpha)}(R_{t})_{kk} * R_{j}R_{t}F_{1}.$$
 (7)

Now letting $R_m = R_j R_i$,

$$HF_{j} = \sum_{\alpha,k} E_{k}(\alpha) \left(h_{\alpha}/g\right) \sum_{m} D^{(\alpha)} \left(R_{j}^{-1}R_{m}\right)_{kk} * F_{m}.$$
 (8)

Equation (8) has the form

$$HF_{j} = \sum_{m} A_{jm}F_{m}, \qquad (9)$$

where

$$A_{jm} = \sum_{\alpha,k} E_k(\alpha) (h_{\alpha}/g) D^{(\alpha)} (R_j^{-1} R_m)_{kk}^*.$$
(10)

Thus, we have started with the set of Schrödinger equations [(5)] and derived an equivalent set of coupled equations [(9)] for the set of functions F_{j} . Notice that the diagonal element A_{jj} is given by

$$A_{jj} = \sum_{\alpha,k} E_k(\alpha) (h_{\alpha}/g). \qquad (10')$$

The advantage of the coupled equations is that the zeroth-order approximation to an F_j can be a simple product of either atomic or molecular orbitals. Thus, Eq. (9) provides a rigorous starting point for a molecu-

² See for example, E. P. Wigner, and J. J. Griffin, *Group Theory* (Academic Press Inc., New York, 1959).

lar perturbation scheme where no restrictions are made regarding orbital overlaps.

The perturbation scheme may be derived by expanding the energies and functions F_j in the following manner:

$$F_{j} = \sum_{n=0}^{\infty} F_{j}^{(n)}; \qquad E_{k}(\alpha) = \sum_{n=0}^{\infty} \epsilon_{k}(\alpha)^{(n)}.$$
(11)

The $\epsilon_k(\alpha)^{(0)} = \epsilon^{(0)}$, independent of both α and k. Also

$$A_{jm} = \sum_{n=0}^{\infty} A_{jm}{}^{(n)}, \qquad (12)$$

where

$$A_{jm}{}^{(n)} = \sum_{\alpha,k} \epsilon_k(\alpha){}^{(n)} (h_\alpha/g) D^{(\alpha)} (R_j{}^{-1}R_m)_{kk} *.$$
(13)

We also define

$$H_j F_j^{(0)} = \epsilon^{(0)} F_j^{(0)} \tag{14}$$

and

$$H = H_j + V_j. \tag{15}$$

From Eq. (13) we see that $A_{j1}^{(0)} = \epsilon^{(0)} \delta_{j1}$. We, then, may resolve the fundamental equation (9) into per-

turbation equations

$$[H_j - \epsilon^{(0)}]F_j{}^{(1)} + V_jF_j{}^{(0)} = \sum_m A_{jm}{}^{(1)}F_m{}^{(0)}, \quad (16)$$

$$[H_j - \epsilon^{(0)}]F_j^{(n)} + V_jF_j^{(n-1)} = \sum_m \sum_{k=1}^n A_{jm}^{(k)}F_m^{(n-k)}.$$
 (17)

Hopefully, Eqs. (16) and (17) will be soluble by some standard technique of solving differential equations. However, it should be pointed out that the solution to Eq. (16), for example, can also be found by finding the function $\tilde{F}_{j}^{(1)}$ which extremizes the functional J with respect to variations of $\tilde{F}_{j}^{(1)}$, where

$$J = \langle \tilde{F}_{j}^{(1)} | H_{j} - \epsilon^{(0)} | \tilde{F}_{j}^{(1)} \rangle + 2 \langle \tilde{F}_{j}^{(1)} | V_{j} | F_{j}^{(0)} \rangle - 2 \sum_{m} A_{jm}^{(1)} \langle \tilde{F}_{j}^{(1)} | F_{m}^{(0)} \rangle.$$
(18)

In order to determine the $\epsilon(\alpha)^{(n)}$ and hence the $A_{km}^{(n)}$ we expand $\psi_{kk}(\alpha)$ in the perturbation series

$$\psi_{kk}(\alpha) = \sum_{n=0}^{\infty} \psi_{kk}(\alpha)^{(n)}, \qquad (19)$$

where according to Eq. (2b)

$$\psi_{kk}(\alpha)^{(n)} = (h_{\alpha}/g) \sum_{m} D^{(\alpha)}(R_{m})_{kk} * F_{m}^{(n)}$$
⁽²⁰⁾

or

$$\psi_{kk}(\alpha)^{(n)} = (h_{\alpha}/g) \sum_{i} D^{(\alpha)}(R_{i}^{-1})_{kk} F_{i}^{(n)}, \qquad (21)$$

so that

$$\langle \psi_{kk}(\alpha)^{(n)} | H | \psi_{kk}(\alpha)^{(n')} \rangle = (h_{\alpha}/g)^{2} \sum_{t,t'} D^{(\alpha)} (R_{t}^{-1})_{kk}^{*} D^{(\alpha)} (R_{t'})_{kk} \langle R_{t}F_{1}^{(n)} | H | R_{t'}F_{1}^{(n')} \rangle$$

$$= (h_{\alpha}/g) \sum_{m} D^{(\alpha)} (R_{m})_{kk} \langle R_{m}F_{1}^{(n)} | H | F_{1}^{(n')} \rangle.$$

$$(22)$$

But from Eq. (5),

$$E_{k}(\alpha) = \langle \psi_{kk}(\alpha) | H | \psi_{kk}(\alpha) \rangle / \langle \psi_{kk}(\alpha) | \psi_{kk}(\alpha) \rangle.$$
(23)

Substituting Eqs. (19) and (22) into (23),

$$E_{k}(\alpha) = \left[\sum_{n,n'} \sum_{m} D^{(\alpha)}(R_{m})_{kk} \langle F_{m}^{(n)} | H | F_{1}^{(n')} \rangle\right] / \left[\sum_{n,n'} \sum_{m} D^{(\alpha)}(R_{m})_{kk} \langle F_{m}^{(n)} | F_{1}^{(n')} \rangle\right].$$
(24)

Here $HF_1^{(n')} = H_1F_1^{(n')} + V_1F_1^{(n')}$. Expanding Eq. (24) into terms of different orders, and making use of Eq. (16), we obtain relations for the different orders of $\epsilon_k(\alpha)^{(n)}$, and hence the $A_{j1}^{(n)}$. As in the usual Rayleigh-Schrödinger perturbation theory, a knowledge of F_j through the *n*th order suffices to determine the $\epsilon_k(\alpha)$ through the (2n+1)th order.

We obtained the following explicit formulas:

$$\epsilon_{k}(\alpha)^{(1)} = \left[\sum_{j} D^{(\alpha)}(R_{j})_{kk} \langle F_{j}^{(0)} | V_{1} | F_{1}^{(0)} \rangle / \sum_{j} D^{(\alpha)}(R_{j})_{kk} \langle F_{j}^{(0)} | F_{1}^{(0)} \rangle \right]$$
(25)

and

$$\epsilon_{k}(\alpha)^{(2)} = \frac{\sum_{j} D^{(\alpha)}(R_{j})_{kk} \left[\langle F_{j}^{(0)} \mid V_{1} - \epsilon_{k}(\alpha)^{(1)} \mid F_{1}^{(1)} \rangle + \sum_{m} A_{1m}^{(1)} \langle F_{j}^{(1)} \mid F_{m}^{(0)} \rangle - \epsilon_{k}(\alpha)^{(1)} \langle F_{j}^{(1)} \mid F_{1}^{(0)} \rangle \right]}{\sum_{j} D^{(\alpha)}(R_{j})_{kk} \langle F_{j}^{(0)} \mid F_{1}^{(0)} \rangle}.$$
 (26)

Also

$$\epsilon_{k}(\alpha)^{(3)} = \frac{\sum_{j} D^{(\alpha)}(R_{j})_{kk} \left[\langle F_{j}^{(1)} \mid V_{1} - \epsilon_{k}(\alpha)^{(1)} \mid F_{1}^{(1)} \rangle - 2\epsilon_{k}(\alpha)^{(2)} \langle F_{j}^{(0)} \mid F_{1}^{(1)} \rangle \right]}{\sum_{j} D^{(\alpha)}(R_{j})_{kk} \langle F_{j}^{(0)} \mid F_{1}^{(0)} \rangle}.$$
(27)

(38)

EXAMPLE: H₂+

Consider the hydrogen molecule ion. For this case

$$H = K - r_a^{-1} - r_b^{-1}, \qquad (28)$$

where K is the kinetic-energy operator and r_a is the distance from the electron to Center a. Now, consider the two lowest energy states of the system (the symmetric ${}^{2}\Sigma_{a}^{+}$ and the antisymmetric ${}^{2}\Sigma_{u}^{+}$). We write

$$\psi_{s}(\Sigma_{a}^{+}) = (1/N_{s})(\phi_{a} + \phi_{b}),$$

$$\psi_{a}(\Sigma_{u}^{+}) = (1/N_{a})(\phi_{a} - \phi_{b}),$$
 (29)

where ϕ_a is a function centered on Center *a* and ϕ_b is a function centered on b; these functions are related to one another by a reflection plane perpendicular to the molecular axis and passing through the midpoint of the molecule. We form the function F_1 by choosing $F_1 = \phi_a$. In a similar manner we can choose $F_2 = \sigma_v F_1 = \phi_b$ (where σ_r is the reflection in the vertical plane).

Using Eq. (9) we find

$$HF_{1} = \frac{1}{2} [E_{s}(\Sigma_{g}^{+}) + E_{a}(\Sigma_{u}^{+})]F_{1} + \frac{1}{2} [E_{s}(\Sigma_{g}^{+}) - E_{a}(\Sigma_{u}^{+})]F_{2}. \quad (30)$$

We can, of course, derive an exactly analogous equation for F_2 , by replacing F_1 by F_2 in Eq. (30). Now, write $H = H_1 + V_1 (= H_2 + V_2)$, where

$$H_1 = K - r_a^{-1},$$

$$V_1 = -r_b^{-1},$$
 (31)

and H_2 and V_2 are found from H_1 and V_1 by interchanging r_a and r_b . We write, from Eq. (13)

$$F_{1} = \sum_{n=0}^{\infty} F_{1}^{(n)},$$

$$E_{\epsilon}(\Sigma_{g}^{+}) = \sum_{n=0}^{\infty} \epsilon_{\epsilon}^{(n)},$$

$$E_{a}(\Sigma_{u}^{+}) = \sum_{n=0}^{\infty} \epsilon_{a}^{(n)}.$$
(32)

Substituting Eqs. (31) and (32) into Eq. (30), we find [compare Eqs. (16) and (17)]

$$(H_1 - \epsilon^{(0)}) F_1^{(0)} = 0, \qquad (33a)$$

$$(H_{1} - \epsilon^{(0)})F_{1}^{(1)} + (V_{1} - \epsilon_{s}^{(1)})F_{1}^{(0)}$$

= $\frac{1}{2}(\epsilon_{s}^{(1)} - \epsilon_{a}^{(1)})(F_{2}^{(0)} - F_{1}^{(0)})$ (33b)
$$(H_{-} - \epsilon^{(0)})F_{-}^{(n)} + (V_{-} - \epsilon^{(1)})F_{-}^{(n-1)}$$

$$= \frac{1}{2} \left(\epsilon_{s}^{(1)} - \epsilon_{a}^{(1)} \right) \left(F_{2}^{(n-1)} - F_{1}^{(n-1)} \right) \\ + \frac{1}{2} \sum_{m=2}^{n} \left[\left(\epsilon_{s}^{(m)} + \epsilon_{a}^{(m)} \right) F_{1}^{(n-m)} + \left(\epsilon_{s}^{(m)} - \epsilon_{a}^{(m)} \right) F_{2}^{(n-m)} \right].$$
(33c)

Thus, by solving the differential equations of each order, we can solve the Schrödinger equation. Notice that the zeroth-order equation is that of the hydrogen atom, showing that $\epsilon^{(0)}$ and $F_1^{(0)}$ (or $F_2^{(0)}$) are the eigenvalue and eigenfunction of the ground-state hydrogen atom. Also, the first-order equation (33b) is different from those obtained from other perturbation schemes. Using Eq. (25) and Eqs. (33), we find that

> $\langle F_{2}^{(0)} | H_{1} - \epsilon^{(0)} | F_{1}^{(1)} \rangle = 0.$ (34)

Using the condition that the first-order wavefunction determines the third-order energy, we find

$$\langle F_{2}^{(0)} | H_{1} - \epsilon^{(0)} | F_{1}^{(2)} \rangle = 0,$$
 (35)

$$\langle F_{2}^{(0)} | H_{1} - \epsilon^{(0)} | F_{1}^{(3)} \rangle + \langle F_{2}^{(1)} | H_{1} - H_{2} | F_{1}^{(2)} \rangle = 0.$$
 (36)

In a similar manner, we find that to nth order (n even)

$$\sum_{m=0}^{j_{1}} \langle F_{2}^{(m)} | H_{1} - H_{2} | F_{1}^{(n-m)} \rangle = 0.$$
 (37)

For *n* odd, replace the $\frac{1}{2}n$ in the upper limit of the sum by $\frac{1}{2}(n-1)$.

The wavefunction of zeroth order is just the simple molecular orbital function; however, the first-order function is not the same as either the first-order function obtained from the perturbation treatment using molecular orbitals,3 or the first-order function obtained from an unsymmetric perturbation treatment starting from atomic orbitals.⁴ The first-order equation (33b) is not separable in any of the conventional coordinate systems because of the $F_2^{(0)}$ on the right-hand side. Therefore, another method of solution must be employed.

One method would be to solve Eq. (18) for this special case, that is solve

 $\delta J = 0$,

where

$$J = \langle \tilde{F}_{1}^{(1)} | H_{1} - \epsilon^{(0)} | \tilde{F}_{1}^{(1)} \rangle + \langle \tilde{F}_{1}^{(1)} | V_{1} - \epsilon_{\epsilon}^{(1)} | F_{1}^{(0)} \rangle + \langle F_{1}^{(0)} | V_{1} - \epsilon_{\epsilon}^{(1)} | \tilde{F}_{1}^{(1)} \rangle - \frac{1}{2} (\epsilon_{s}^{(1)} - \epsilon_{a}^{(1)}) \langle \tilde{F}_{1}^{(1)} | (F_{2}^{(0)} - F_{1}^{(0)}) \rangle - \frac{1}{2} (\epsilon_{s}^{(1)} - \epsilon_{a}^{(1)}) \langle (F_{2}^{(0)} - F_{1}^{(0)}) | \tilde{F}_{1}^{(1)} \rangle.$$
(39)

Obviously, extremizing J with respect to arbitrary variations in $\tilde{F}_1^{(1)}$ will produce a solution of Eq. (33b). One may also solve Eq. (38) in a finite basis set and obtain solutions within that set.

The orbitals F_1 and F_2 which we generate will have nodes at both Nuclei a and b, and hence will not be the "unique orbitals" of Harriss and Frost.⁵ This is clear from the nodal structure of Eq. (33b).

⁸ W. D. Lyon, R. L. Matcha, W. A. Sanders, W. J. Meath, and

W. D. Lyon, R. L. Matcha, W. A. Sanders, W. J. Meath, and J. O. Hirshfelder, J. Chem. Phys. 43, 1095 (1965).
 W. D. Lyon, W. A. Sanders, and J. O. Hirschfelder, J. Chem. Phys. 45, 1075 (1966); A. Dalgarno and N. Lynn, Proc. Roy. Soc. (London) A70, 223 (1957); P. D. Robinson, *ibid.* A71, 828 (1958).
 ⁶ D. K. Harriss and A. A. Frost, Theoret. Chim Acta 3, 174 (1965)

^{(1965).}

EXAMPLE: H₃

Consider a system of three hydrogen atoms in their ground states. The Heitler-London functions (our zeroorder functions) for $S_z = \frac{1}{2}$ are given by⁶

$$\Phi_{1}^{(0)} = \frac{1}{3} \Omega \Big[a_{1} b_{2} c_{3} \Big[2\alpha_{1} \beta_{2} \alpha_{3} - \alpha_{1} \alpha_{2} \beta_{3} - \beta_{1} \alpha_{2} \alpha_{3} \Big],$$

$$\Phi_{2}^{(0)} = \frac{1}{3} \Omega \Big[a_{1} b_{2} c_{3} (\alpha_{1} \alpha_{2} \beta_{3} - \beta_{1} \alpha_{2} \alpha_{3}) \Big],$$

$$\Phi_{3}^{(0)} = (\sqrt{2}/6) \Omega \Big[a_{1} b_{2} c_{3} (\alpha_{1} \alpha_{2} \beta_{3} + \beta_{1} \alpha_{2} \alpha_{3} + \alpha_{1} \beta_{2} \alpha_{3}) \Big],$$
(40)

with $a_1b_2c_3$ meaning that Electron 1 is on Center *a*, Electron 2 on Center *b*, and Electron 3 on Center *c*; α and β are the usual one-electron spin functions for $s_z = \frac{1}{2}$ and $-\frac{1}{2}$. Here α is the usual antisymmetrizer,

$$\alpha = 6^{-\frac{1}{2}} \sum_{P} (-1)^{p} \mathcal{O}.$$

These may be written as

$$\Phi_{1}^{(0)} = \psi_{22}^{(0)}(E)\chi_{1}(E) + \psi_{21}^{(0)}(E)\chi_{2}(E),$$

$$\Phi_{2}^{(0)} = \psi_{11}^{(0)}(E)\chi_{2}(E) + \psi_{12}^{(0)}(E)\chi_{1}(E),$$

$$\Phi_{3}^{(0)} = \psi^{(0)}(A_{2})\chi(A_{1}),$$
(41)

with

$$\begin{split} \psi_{11}^{(0)}(E) &= \frac{1}{3} \left(a_1 b_2 c_3 + a_3 b_2 c_1 - \frac{1}{2} a_2 b_1 c_3 - \frac{1}{2} a_1 b_3 c_2 - \frac{1}{2} a_2 b_3 c_1 - \frac{1}{2} a_3 b_1 c_2 \right), \\ \psi_{21}^{(0)}(E) &= \left(\sqrt{3}/6\right) \left(a_2 b_1 c_3 - a_1 b_3 c_2 + a_2 b_3 c_1 - a_3 b_1 c_2 \right), \\ \psi_{12}^{(0)}(E) &= \left(\sqrt{3}/6\right) \left(a_2 b_1 c_3 - a_1 b_3 c_2 - a_2 b_3 c_1 + a_3 b_1 c_2 \right), \\ \psi_{22}^{(0)}(E) &= \frac{1}{3} \left(a_1 b_2 c_3 - a_3 b_2 c_1 + \frac{1}{2} a_2 b_1 c_3 + \frac{1}{2} a_1 b_3 c_2 - \frac{1}{2} a_2 b_3 c_1 - \frac{1}{2} a_3 b_1 c_2 \right), \\ \psi^{(0)}(A_2) &= \frac{1}{6} \left(a_1 b_2 c_3 - a_2 b_1 c_3 - a_3 b_2 c_1 - a_1 b_3 c_2 + a_2 b_3 c_1 + a_3 b_1 c_2 \right), \\ \chi_1(E) &= \left[1/(6)^{\frac{1}{2}} \right] \left(2 \alpha_1 \beta_2 \alpha_3 - \alpha_1 \alpha_2 \beta_3 - \beta_1 \alpha_2 \alpha_3 \right), \\ \chi_2(E) &= \left(1/\sqrt{2} \right) \left(\alpha_1 \alpha_2 \beta_3 - \beta_1 \alpha_2 \alpha_3 \right), \\ \chi(A_1) &= \left(1/\sqrt{3} \right) \left(\alpha_1 \alpha_2 \beta_3 + \beta_1 \alpha_2 \alpha_3 + \alpha_1 \beta_2 \alpha_3 \right). \end{split}$$

$$(42)$$

In the above, the wavefunctions are labeled by their transformation properties under the permutation group S_3 of the electrons. We also consider the spatial wavefunction transforming like the A_1 (completely symmetric) irreducible representation of S_3 (this state cannot give rise to a physical state obeying the Pauli principle, since there is no spin state which transforms like A_2),

 $\psi^{(0)}(A_1) = \frac{1}{6} (a_1 b_2 c_3 + a_2 b_3 c_1 + a_3 b_2 c_1 + a_1 b_3 c_2 + a_2 b_3 c_1 + a_3 b_1 c_2).$ (43)

Thus,

$$F_{1}^{(0)} = \psi_{11}^{(0)}(E) + \psi_{22}^{(0)}(E) + \psi^{(0)}(A_{1}) + \psi^{(0)}(A_{2})$$

$$= a_{1}b_{2}c_{3},$$
(44)

and, operating on $F_1^{(0)}$ with a transformation R_j of the group,

$$F_j^{(0)} = R_j F_1^{(0)}. \tag{45}$$

Following the discussion given in the first part of this paper, the $F_{j}^{(0)}$ go into the exact F_{j} as the perturbation is adiabatically turned on. Similarly, the $\psi_{jk}^{(0)}(\alpha)$ go into the $\psi_{jk}(\alpha)$. The problem is now completely specified and we may use Eqs. (16), (17), and (18), in conjunction with the representation matrices of S_3 and the

⁶ J. O. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. 4, 121 (1936). $F_{j}^{(0)}$ as given above, in order to solve the problem of three hydrogen atoms interacting with one another.

We have presented a new perturbation scheme in this paper which we hope will provide a fast convergence in both the energy and wavefunction expansions. Calculations are now under way in this laboratory on applications of this procedure to simple problems.

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