## AIP <br> The Journal of <br> Chemical Physics

New Type of Molecular Perturbation Treatment
Joseph O. Hirschfelder and Robert Silbey

Citation: J. Chem. Phys. 45, 2188 (1966); doi: 10.1063/1.1727907
View online: http://dx.doi.org/10.1063/1.1727907
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v45/i6
Published by the American Institute of Physics.

## Additional information on J. Chem. Phys.

Journal Homepage: http://jcp.aip.org/
Journal Information: http://jcp.aip.org/about/about_the_journal
Top downloads: http://jcp.aip.org/features/most_downloaded
Information for Authors: http://jcp.aip.org/authors

## ADVERTISEMENT


may be more important. ${ }^{13}$ The present theory applies to both of these cases, provided the quantity $a / 2 l_{\sigma}$ 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 $e \psi / k T \gg 1$, 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 $\psi$ dropping off very fast in a short distance. Since $a / 2 l_{\sigma}$ is proportional to the net charge

[^0]per unit length within a cylinder of radius $a$, there will be a certain distance $a^{\prime}$ where the net charge per unit length within the cylinder of radius $a^{\prime}$ is such that $a^{\prime} / 2 l_{\sigma^{\prime}}=1$. Here $l_{\sigma^{\prime}}$ 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 $\psi$ 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.

## ACKNOWLEDGMENT

The numerical integrations were performed on the IBM 7044 of the University Computing Center of the State University of New York at Buffalo.

# New Type of Molecular Perturbation Treatment* 

Joseph O. Hirschfelder and Robert Silbey $\dagger$<br>Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin, and<br>Quantum Theory Project, University of Florida, Gainesville, Florida

(Received 8 April 1966)


#### Abstract

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 $\mathrm{H}_{2}{ }^{+}$where the 1 s atomic orbital leads to both a symmetric and antisymmetric molecular state, our basic equation is $$
H a=\frac{1}{2}\left(E_{\varepsilon}+E_{a}\right) a+\frac{1}{2}\left(E_{s}-E_{a}\right) b
$$ 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 perturba-

[^1]tion schemes ${ }^{1}$ 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

[^2]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 $R_{i}$ :
\[

$$
\begin{equation*}
R_{i} H=B R_{i} . \tag{1}
\end{equation*}
$$

\]

Usually $G$ is the direct product of the group of electron permutations and the symmetry group of the nuclear framework. Let $D^{(\alpha)}\left(R_{i}\right)_{k j}$ be the $k j$ th matrix element of the $\alpha$ th irreducible unitary representation of the transformation $R_{i}$. The dimensionality of the $\alpha$ th irreducible representation is $h_{\alpha}$.

We choose a zeroth-order unsymmetrized wavefunction $F_{1}{ }^{(0)}$ (which might be, for example, a product of atomic or molecular orbitals, $F_{1}{ }^{(0)}=a_{1}{ }^{(0)} b_{2}{ }^{(0)} c_{3}{ }^{(0)} \ldots$ ). Corresponding to $F_{1}{ }^{(0)}$ there is a set of zeroth-order wavefunctions $\psi_{k j}{ }^{(0)}(\alpha)$ which are the projections of $F_{1}{ }^{(0)}$ for every type of symmetry,

$$
\begin{equation*}
\psi_{k j}^{(0)}(\alpha)=\left(h_{\alpha} / g\right) \sum_{i} D^{(\alpha)}\left(R_{i}\right)_{j k} * R_{i} F_{1}^{(0)} . \tag{2a}
\end{equation*}
$$

According to the completeness theorem for the projection operators, ${ }^{2}$

$$
\begin{equation*}
F_{1}^{(0)}=\sum_{\alpha, k} \psi_{k k}^{(0)}(\alpha) . \tag{3a}
\end{equation*}
$$

The application of the transformations $R_{i}$ to the $\psi_{k j}{ }^{(0)}(\alpha)$ produces a linear combination of the $h_{\alpha}$ functions $\psi_{k 1}{ }^{(0)}(\alpha), \psi_{k 2}{ }^{(0)}(\alpha), \cdots$.

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

$$
\begin{equation*}
\Phi_{k}{ }^{(0)}(\alpha ; \mathbf{r}, \mathbf{s})=\sum_{j} \psi_{k j}{ }^{(0)}(\alpha ; \mathbf{r}) \chi_{j}(\mathbf{s}) \tag{4}
\end{equation*}
$$

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 $\psi_{k j}{ }^{(0)}(\alpha)$ go adiabatically into the exact wavefunctions $\Phi_{k}(\alpha)$ and $\psi_{k j}(\alpha)$,

$$
H \Phi_{k}(\alpha)=E_{k}(\alpha) \Phi_{k}(\alpha)
$$

and

$$
\begin{equation*}
H \psi_{k j}(\alpha)=E_{k}(\alpha) \psi_{k j}(\alpha) . \tag{5}
\end{equation*}
$$

[^3]Correspondingly, under the influence of the perturbations, the $F_{1}{ }^{(0)}$ goes adiabatically into a new function $F_{1}$. Thus

$$
\begin{equation*}
\psi_{k k}(\alpha)=\left(h_{\alpha} / g\right) \sum_{i} D^{(\alpha)}\left(R_{i}\right)_{k k} * R_{i} F_{1} \tag{2b}
\end{equation*}
$$

and

$$
\begin{equation*}
F_{1}=\sum_{\alpha, k} \psi_{k k}(\alpha) \tag{3b}
\end{equation*}
$$

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

$$
\begin{equation*}
H F_{1}=\sum_{\alpha, k} E_{k}(\alpha) \psi_{k k}(\alpha) . \tag{6}
\end{equation*}
$$

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 $F_{1}, F_{2}=R_{2} F_{1}, \cdots, F_{k}=R_{k} F_{1}, \cdots$, $F_{g}=R_{g} F_{1}$ forms a basis to a reducible representation of the symmetry group $G$. The functions $\psi_{k j}(\alpha)$ form the corresponding basis to the irreducible representations of the symmetry group. As is well known, the function set $F_{1}, F_{2}, \cdots, F_{g}$ is therefore expressible in terms of the $\psi_{k j}(\alpha)$ by means of a nonsingular transformation matrix; or, conversely, the $\psi_{k j}(\alpha)$ may be expressed in terms of the $F_{1}, F_{2}, \cdots, F_{g}$ by means of a nonsingular transformation matrix [for example, Eq. (2)].

Applying the operator $R_{j}$ on Eq. (6) and making use of Eqs. (1) and (2b),

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

Now letting $R_{m}=R_{j} R_{t}$,

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

Equation (8) has the form

$$
\begin{equation*}
H F_{j}=\sum_{m} A_{j m} F_{m}, \tag{9}
\end{equation*}
$$

where

$$
\begin{equation*}
A_{j m}=\sum_{\alpha, k} E_{k}(\alpha)\left(h_{\alpha} / g\right) D^{(\alpha)}\left(R_{j}^{-1} R_{m}\right)_{k k}{ }^{*} \tag{10}
\end{equation*}
$$

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 $A_{j j}$ is given by

$$
A_{j j}=\sum_{\alpha, k} E_{k}(\alpha)\left(h_{\alpha} / g\right) .
$$

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-
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:

$$
\begin{equation*}
F_{j}=\sum_{n=0} F_{j}^{(n)} ; \quad E_{k}(\alpha)=\sum_{n=0} \epsilon_{k}(\alpha)^{(n)} . \tag{11}
\end{equation*}
$$

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

$$
\begin{equation*}
A_{j m}=\sum_{n=0} A_{j m}{ }^{(n)} \tag{12}
\end{equation*}
$$

where

$$
\begin{equation*}
A_{j m}^{(n)}=\sum_{\alpha, k} \epsilon_{k}(\alpha)^{(n)}\left(h_{\alpha} / g\right) D^{(\alpha)}\left(R_{j}^{-1} R_{m}\right)_{k k} * \tag{13}
\end{equation*}
$$

We also define

$$
\begin{equation*}
H_{j} F_{j}{ }^{(0)}=\epsilon^{(0)} F_{j}{ }^{(0)} \tag{14}
\end{equation*}
$$

and

$$
\begin{equation*}
H=H_{j}+V_{j} . \tag{15}
\end{equation*}
$$

From Eq. (13) we see that $A_{j 1}{ }^{(0)}=\epsilon^{(0)} \delta_{j 10}$. We, then, may resolve the fundamental equation (9) into per-
turbation equations

$$
\begin{array}{r}
{\left[H_{j}-\epsilon^{(0)}\right] F_{j}^{(1)}+V_{j} F_{j}^{(0)}=\sum_{m} A_{j m}{ }^{(1)} F_{m}{ }^{(0)},} \\
{\left[H_{j}-\epsilon^{(0)}\right] F_{j}^{(n)}+V_{j} F_{j}^{(n-1)}=\sum_{m} \sum_{k=1}^{n} A_{j m}{ }^{(k)} F_{m}^{(n-k)} .} \tag{17}
\end{array}
$$

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 $\widetilde{F}_{j}^{(1)}$, where

$$
\begin{array}{r}
J=\left\langle\widetilde{F}_{j}^{(1)}\right| H_{j}-\epsilon^{(0)}\left|\widetilde{F}_{j}^{(1)}\right\rangle+2\left\langle\widetilde{F}_{j}^{(1)}\right| V_{j}\left|F_{j}^{(0)}\right\rangle \\
-2 \sum_{m} A_{j m}^{(1)}\left\langle\widetilde{F}_{j}^{(1)} \mid F_{m}^{(0)}\right\rangle . \tag{18}
\end{array}
$$

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

$$
\begin{equation*}
\psi_{k k}(\alpha)=\sum_{n=0} \psi_{k k}(\alpha)^{(n)}, \tag{19}
\end{equation*}
$$

where according to Eq. (2b)

$$
\begin{equation*}
\psi_{k k}(\alpha)^{(n)}=\left(h_{\alpha} / g\right) \sum_{m} D^{(\alpha)}\left(R_{m}\right)_{k k} F_{m}^{(n)} \tag{20}
\end{equation*}
$$

or

$$
\begin{equation*}
\psi_{k k}(\alpha)^{(n)}=\left(h_{\alpha} / g\right) \sum_{t} D^{(\alpha)}\left(R_{t}^{-1}\right)_{k k} F_{t}^{(n)}, \tag{21}
\end{equation*}
$$

so that

$$
\begin{align*}
\left\langle\psi_{k k}(\alpha)^{(n)}\right| H\left|\psi_{k k}(\alpha)^{\left(n^{\prime}\right)}\right\rangle & =\left(h_{\alpha} / g\right)^{2} \sum_{t, t} D^{(\alpha)}\left(R_{i}^{-1}\right)_{k k^{\prime}}^{*} D^{(\alpha)}\left(R_{t^{\prime}}\right)_{k k}\left\langle R_{t} F_{1}^{(n)}\right| H\left|R_{t^{\prime}} F_{1}^{\left(n^{\prime}\right)}\right\rangle \\
& =\left(h_{\alpha} / g\right) \sum_{m} D^{(\alpha)}\left(R_{m}\right)_{k k}\left\langle R_{m} F_{1}^{(n)}\right| H\left|F_{1}^{\left(n^{\prime}\right)}\right\rangle . \tag{22}
\end{align*}
$$

But from Eq. (5),

$$
\begin{equation*}
E_{k}(\alpha)=\left\langle\psi_{k k}(\alpha)\right| H\left|\psi_{k k}(\alpha)\right\rangle /\left\langle\psi_{k k}(\alpha) \mid \psi_{k k}(\alpha)\right\rangle . \tag{23}
\end{equation*}
$$

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

$$
\begin{equation*}
E_{k}(\alpha)=\left[\sum_{n, n^{\prime}} \sum_{m} D^{(\alpha)}\left(R_{m}\right)_{k k}\left\langle F_{m}^{(n)}\right| H\left|F_{1}^{\left(n^{\prime}\right)}\right\rangle\right] /\left[\sum_{n, n^{\prime}} \sum_{m} D^{(\alpha)}\left(R_{m}\right)_{k k}\left\langle F_{m}^{(n)} \mid F_{1}^{\left(n^{\prime}\right)}\right\rangle\right] . \tag{24}
\end{equation*}
$$

Here $H F_{1}^{\left(n^{\prime}\right)}=H_{1} F_{1}^{\left(n^{\prime}\right)}+V_{1} F_{1}{ }^{\left(n^{\prime}\right)}$. 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 $A_{i 1}{ }^{(n)}$. 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 ( $2 n+1$ )th order.
We obtained the following explicit formulas:

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

and

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

Also

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

## EXAMPLE: $\mathrm{H}_{\mathbf{2}}{ }^{+}$

Consider the hydrogen molecule ion. For this case

$$
\begin{equation*}
H=K-r_{a}^{-1}-r_{b}^{-1}, \tag{28}
\end{equation*}
$$

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 ${ }^{2} \Sigma_{g}{ }^{+}$and the antisymmetric ${ }^{2} \Sigma_{u}{ }^{+}$). We write

$$
\begin{align*}
& \psi_{s}\left(\Sigma_{g}^{+}\right)=\left(1 / N_{s}\right)\left(\phi_{a}+\phi_{b}\right), \\
& \psi_{a}\left(\Sigma_{u}^{+}\right)=\left(1 / N_{a}\right)\left(\phi_{a}-\phi_{b}\right) \tag{29}
\end{align*}
$$

where $\phi_{a}$ is a function centered on Center $a$ and $\phi_{b}$ 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 $\sigma_{v}$ is the reflection in the vertical plane).

Using Eq. (9) we find

$$
\begin{align*}
& H F_{1}=\frac{1}{2}\left[E_{z}\left(\Sigma_{\theta}^{+}\right)+\right. \\
& \left.E_{a}\left(\Sigma_{u}^{+}\right)\right] F_{1}  \tag{30}\\
& \\
& \quad+\frac{1}{2}\left[E_{s}\left(\Sigma_{g}^{+}\right)-E_{a}\left(\Sigma_{u}^{+}\right)\right] F_{2}
\end{align*}
$$

We can, of course, derive an exactly analogous equation for $F_{2}$, by replacing $F_{1}$ by $F_{2}$ in Eq. (30). Now, write $H=H_{1}+V_{1}\left(=H_{2}+V_{2}\right)$, where

$$
\begin{align*}
H_{1} & =K-r_{a}^{-1}, \\
V_{1} & =-r_{b}^{-1}, \tag{31}
\end{align*}
$$

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)

$$
\begin{align*}
F_{1} & =\sum_{n=0}^{\infty} F_{1}^{(n)}, \\
E_{s}\left(\Sigma_{g}^{+}\right) & =\sum_{n=0}^{\infty} \epsilon_{s}^{(n)}, \\
E_{a}\left(\Sigma_{u}^{+}\right) & =\sum_{n=0}^{\infty} \epsilon_{a}^{(n)} . \tag{32}
\end{align*}
$$

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

$$
\begin{align*}
&\left(H_{1}-\epsilon^{(0)}\right) F_{1}{ }^{(0)}=0,  \tag{33a}\\
&\left(H_{1}-\epsilon^{(0)}\right) F_{1}^{(1)}+\left(V_{1}-\epsilon_{a}^{(1)}\right) F_{1}^{(0)} \\
&=\frac{1}{2}\left(\epsilon_{a}^{(1)}-\epsilon_{a}^{(1)}\right)\left(F_{2}^{(0)}-F_{1}^{(0)}\right)  \tag{33b}\\
&\left(H_{1}-\epsilon^{(0)}\right) F_{1}^{(n)}+\left(V_{1}-\epsilon_{t}^{(1)}\right) F_{1}^{(n-1)} \\
&=\frac{1}{2}\left(\epsilon_{a}^{(1)}-\epsilon_{a}^{(1)}\right)\left(F_{2}^{(n-1)}-F_{1}^{(n-1)}\right) \\
&+\frac{1}{2} \sum_{m=2}^{n}\left[\left(\epsilon_{a}^{(m)}+\epsilon_{a}^{(m)}\right) F_{1}^{(n-m)}+\left(\epsilon_{s}^{(m)}-\epsilon_{a}^{(m)}\right) F_{2}^{(n-m)}\right] . \tag{33c}
\end{align*}
$$

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

$$
\begin{equation*}
\left\langle F_{2}^{(0)}\right| H_{1}-\epsilon^{(0)}\left|F_{1}^{(1)}\right\rangle=0 \tag{34}
\end{equation*}
$$

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

$$
\begin{gather*}
\left\langle F_{2}^{(0)}\right| H_{1}-\epsilon^{(0)}\left|F_{1}^{(2)}\right\rangle=0,  \tag{35}\\
\left\langle F_{2}^{(0)}\right| H_{1}-\epsilon^{(0)}\left|F_{1}^{(3)}\right\rangle+\left\langle F_{2}^{(1)}\right| H_{1}-H_{2}\left|F_{1}^{(2)}\right\rangle=0 . \tag{36}
\end{gather*}
$$

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

$$
\begin{equation*}
\sum_{m=0}^{j_{n}}\left\langle F_{2}^{(m)}\right| H_{1}-H_{2}\left|F_{1}^{(n-m)}\right\rangle=0 . \tag{37}
\end{equation*}
$$

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

$$
\begin{equation*}
\delta J=0 \tag{38}
\end{equation*}
$$

where

$$
\begin{gather*}
J=\left\langle\tilde{F}_{1}^{(1)}\right| H_{1}-\epsilon^{(0)}\left|\widetilde{F}_{1}^{(1)}\right\rangle+\left\langle\tilde{F}_{1}^{(1)}\right| V_{1}-\epsilon_{a}^{(1)}\left|F_{1}^{(0)}\right\rangle \\
+\left\langle F_{1}^{(0)}\right| V_{1}-\epsilon_{s}^{(1)}\left|\tilde{F}_{1}^{(1)}\right\rangle \\
-\frac{1}{2}\left(\epsilon_{s}^{(1)}-\epsilon_{a}^{(1)}\right)\left\langle\widetilde{F}_{1}^{(1)} \mid\left(F_{2}^{(0)}-F_{1}^{(0)}\right)\right\rangle \\
-\frac{1}{2}\left(\epsilon_{s}^{(1)}-\epsilon_{a}^{(1)}\right)\left\langle\left(F_{2}^{(0)}-F_{1}^{(0)}\right) \mid \widetilde{F}_{1}^{(1)}\right\rangle . \tag{39}
\end{gather*}
$$

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).

[^4]
## EXAMPLE: $\mathrm{H}_{3}$

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 by ${ }^{6}$

$$
\begin{align*}
& \Phi_{1}{ }^{(0)}=\frac{1}{3} \mathbb{Q}\left[a_{1} b_{2} c_{3}\left[2 \alpha_{1} \beta_{2} \alpha_{3}-\alpha_{1} \alpha_{2} \beta_{3}-\beta_{1} \alpha_{2} \alpha_{3}\right)\right], \\
& \Phi_{2}{ }^{(0)}=\frac{1}{3} \mathbb{Q}\left[a_{1} b_{2} c_{3}\left(\alpha_{1} \alpha_{2} \beta_{3}-\beta_{1} \alpha_{2} \alpha_{3}\right)\right], \\
& \Phi_{3}{ }^{(0)}=(\sqrt{2} / 6) Q\left[a_{1} b_{2} c_{3}\left(\alpha_{1} \alpha_{2} \beta_{3}+\beta_{1} \alpha_{2} \alpha_{3}+\alpha_{1} \beta_{2} \alpha_{3}\right)\right], \tag{40}
\end{align*}
$$

with $a_{1} b_{2} c_{3}$ meaning that Electron 1 is on Center $a$, Electron 2 on Center $b$, and Electron 3 on Center $c ; \alpha$ and $\beta$ are the usual one-electron spin functions for $s_{z}=\frac{1}{2}$ and $-\frac{1}{2}$. Here $\mathbb{Q}$ is the usual antisymmetrizer,

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

These may be written as

$$
\begin{align*}
& \Phi_{1}{ }^{(0)}=\psi_{22}{ }^{(0)}(E) \chi_{1}(E)+\psi_{21}{ }^{(0)}(E) \chi_{2}(E), \\
& \Phi_{2}{ }^{(0)}=\psi_{11}{ }^{(0)}(E) \chi_{2}(E)+\psi_{12}{ }^{(0)}(E) \chi_{1}(E), \\
& \Phi_{3}{ }^{(0)}=\psi^{(0)}\left(A_{2}\right) \chi\left(A_{1}\right), \tag{41}
\end{align*}
$$

with

$$
\begin{align*}
& \psi_{11}^{(0)}(E)=\frac{1}{3}\left(a_{1} b_{2} c_{3}+a_{3} b_{2} c_{1}-\frac{1}{2} a_{2} b_{1} c_{3}-\frac{1}{2} a_{1} b_{3} c_{2}-\frac{1}{2} a_{2} b_{3} c_{1}-\frac{1}{2} a_{3} b_{1} c_{2}\right), \\
& \psi_{21}\left({ }^{(0)}(E)\right.=(\sqrt{3} / 6)\left(a_{2} b_{1} c_{3}-a_{1} b_{3} c_{2}+a_{2} b_{3} c_{1}-a_{3} b_{1} c_{2}\right), \\
& \psi_{12}^{(0)}(E)=(\sqrt{3} / 6)\left(a_{2} b_{1} c_{3}-a_{1} b_{3} c_{2}-a_{2} b_{3} c_{1}+a_{3} b_{1} c_{2}\right), \\
& \psi_{22}^{(0)}(E)=\frac{1}{3}\left(a_{1} b_{2} c_{3}-a_{3} b_{2} c_{1}+\frac{1}{2} a_{2} b_{1} c_{3}+\frac{1}{2} a_{1} b_{3} c_{2}-\frac{1}{2} a_{2} b_{3} c_{1}-\frac{1}{2} a_{3} b_{1} c_{2}\right), \\
& \psi^{(0)}\left(A_{2}\right)=\frac{1}{6}\left(a_{1} b_{2} c_{3}-a_{2} b_{1} c_{3}-a_{3} b_{2} c_{1}-a_{1} b_{3} c_{2}+a_{2} b_{3} c_{1}+a_{3} b_{1} c_{2}\right), \\
& \chi_{1}(E)=\left[1 /(6)^{\frac{1}{2}}\right]\left(2 \alpha_{1} \beta_{2} \alpha_{3}-\alpha_{1} \alpha_{2} \beta_{3}-\beta_{1} \alpha_{2} \alpha_{3}\right), \\
& \chi_{2}(E)=(1 / \sqrt{2})\left(\alpha_{1} \alpha_{2} \beta_{3}-\beta_{1} \alpha_{2} \alpha_{3}\right), \\
& \chi\left(A_{1}\right)=(1 / \sqrt{3})\left(\alpha_{1} \alpha_{2} \beta_{3}+\beta_{1} \alpha_{2} \alpha_{3}+\alpha_{1} \beta_{2} \alpha_{3}\right), \tag{42}
\end{align*}
$$

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 $A_{2}$ ),

$$
\begin{equation*}
\psi^{(0)}\left(A_{1}\right)=\frac{1}{6}\left(a_{1} b_{2} c_{3}+a_{2} b_{3} c_{1}+a_{3} b_{2} c_{1}+a_{1} b_{3} c_{2}+a_{2} b_{3} c_{1}+a_{3} b_{1} c_{2}\right) . \tag{43}
\end{equation*}
$$

Thus,

$$
\begin{align*}
F_{1} 1^{(0)} & =\psi_{11^{(0)}}(E)+\psi_{22^{(0)}}^{(0)}(E)+\psi^{(0)}\left(A_{1}\right)+\psi^{(0)}\left(A_{2}\right)  \tag{44}\\
& =a_{1} b_{2} c_{3},
\end{align*}
$$

and, operating on $F_{1}{ }^{(0)}$ with a transformation $R_{j}$ of the group,

$$
\begin{equation*}
F_{j}^{(0)}=R_{j} F_{1}^{(0)} . \tag{45}
\end{equation*}
$$

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 $\psi_{j k^{(0)}}{ }^{(0)}(\alpha)$ go into the $\psi_{j k}(\alpha)$. 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

[^5]$F_{j}{ }^{(0)}$ 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.

## ACKNOWLEDGMENTS

The authors wish to thank Professor Saul T. Epstein, Professor W. Byers Brown, and Professor Per-Olov Löwdin for many helpful discussions.


[^0]:    ${ }^{13}$ E. J. Verwey and J. Th. G. Overbeek, Theory of the Stability of Lyophobic Colloids (Elsevier Publ. Co., New York, 1948), p. 53.

[^1]:    * This research was supported by National Aeronautics and Space Administration Grant NsG-275-62 at the University of Wisconsin Theoretical Chemistry Institute and by the University of Florida Quantum Theory Project, Gainesville, Fla.
    $\dagger$ National Academy of Sciences-National Research Council Postdoctoral Fellow (supported by the U.S. Air Force Office of Scientific Research) 1965-1966. Present address: Chemistry Department, MIT.

[^2]:    ${ }^{1}$ J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Advances in Quantum Chemistry (Academic Press Inc., New York, 1964), Vol. 1, 255.

[^3]:    ${ }^{2}$ See for example, E. P. Wigner, and J. J. Griffin, Group Theory (Academic Press Inc., New York, 1959).

[^4]:    ${ }^{5}$ W. D. Lyon, R. L. Matcha, W. A. Sanders, W. J. Meath, and J. O. Hirshfelder, J. Chem. Phys. 43, 1095 (1965).
    ${ }^{4}$ 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).
    ${ }^{5}$ D. K. Harriss and A. A. Frost, Theoret. Chim Acta 3, 174 (1965).

[^5]:    ${ }^{6}$ J. O. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. 4, 121 (1936).

