However, it is emphasized that the additional terms of g in Eq. (5) behave for $\theta=0°$ like

$$\frac{Z^6}{U^3q^2_{\theta=0°}}\simeq\frac{4}{Z^2}\left(\frac{k_0}{Z}\right)^{-4}\left(\frac{1}{n_0}-\frac{1}{n}\right)^{-2}\left(\frac{1}{n_0}+\frac{1}{n}\right)^{-2}. \tag{9}$$

It is the behavior of $Z^6/(U^3q^2)$ which is responsible for the peaking of the differential cross sections in the near forward direction. In fact, such an asymptotic behavior was predicted for excitation processes in 1966 by one of us (I. J. K.).[8] It was then conjectured that the excitation exchange amplitude for processes with $(n_0-n)/n_0\ll1$ might even be dominant over the direct scattering amplitude in the forward direction, a prediction which may be tested experimentally in the future.

Finally, it is desirable to have more experimental results for the process, inasmuch as the data on total cross sections vary somewhat among the authors.[11] It is also conceded that there is room for improvement toward better quantitiative agreement between theory and experiment in regard to the magnitude and fine structure of the differential cross section.

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[11] See, for example, Table IV in Ref. 1.

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Perturbation Theory for Exchange Interactions between Atoms and Molecules. I

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A perturbation theory has been developed for interatomic or intermolecular forces with exchange. The method requires the use of label-free operators in a representation of nonorthogonal, antisymmetrized states. The introduction of this representation shows that the explicit construction of a complete orthogonalized set is unnecessary. The antisymmetry of the exact wave function is preserved to all orders, and hence exchange is treated exactly.

INTRODUCTION

RECENTLY, a number of papers[1–4] have appeared on the perturbation theory of interatomic or intermolecular forces at distances close enough so that exchange effects become important. Treatment of exchange entails the antisymmetrization of the zeroth-order representation of simple-product states for the particles at infinite separation, and this process destroys the orthogonality of the set and H_0 as a diagonal operator. Jansen[1] has given a brief history of the problem and has recast the Rayleigh-Schrödinger (RS) series to handle it. The main idea of his paper is the *orthogonalization* of the antisymmetrized set and the introduction of label-free operators H_0' and V', such that H_0' remains diagonal in the old antisymmetrized, *nonorthogonal* set. The extra terms which arise in the RS series are the matrix elements of H_0', which is *not* diagonal in the orthogonalized set. The main difficulty in this treatment is the labor required to obtain a complete orthogonalized set.

Murrell and Shaw[2] have briefly criticized several other papers and have formulated a Brillouin-Wigner-type expansion for the exchange problem. The main idea is the definition of a projection operator,

$$O=|a\rangle(a|/(a|a\rangle \tag{1}$$

($|\rangle$ means antisymmetrized and $|)$ means a simple-product-type function), which, since any function is projected along $|a\rangle$, insures the antisymmetry of the exact wave function. Formally,[5,6]

$$\Psi=|a\rangle+\frac{(I-O)}{E-H}H|a\rangle, \tag{2}$$

where I is the identity. The argument[2] is that in the equation

$$(I-O)(E-H)TH|a\rangle=(I-O)H|a\rangle \tag{3}$$

$H|a\rangle$ is antisymmetric (since H is symmetric in the electrons). O projects out an antisymmetric function; therefore $(E-H)TH|a\rangle$ is antisymmetric, and since $(E-H)$ is symmetric, $TH|a\rangle$ is antisymmetric. Hence (2) is also antisymmetric. This antisymmetry is lost

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[1] Laurens Jansen, Phys. Rev. **162**, 63 (1967), and references therein.

[2] J. N. Murrell and G. Shaw, J. Chem. Phys. **46**, 1768 (1967), and references therein.

[3] J. I. Musher and A. T. Amos, Phys. Rev. **164**, 31 (1967).

[4] Ad van der Avoird, J. Chem. Phys. **47**, 3649 (1967).

[5] R. Yaris, J. Chem. Phys. **44**, 3894 (1966).

[6] P. O. Lowdin, J. Math. Phys. **6**, 1341 (1965)

once $(E-H)^{-1}$ is expanded $(E-H_0)^{-1}+$etc., since H_0 is not symmetric in electron exchange. For the identity the authors take

$$I=\sum_b |b)(b| \tag{4}$$

over the complete set of simple-product states. Hence a mixed representation is used; H_0 is diagonal in bra space and is chosen such that $(a|a\rangle$ cancels all overlap integrals which result when H_0 operates. Because of this fact and the condition

$$(b|H|a\rangle=\langle b|H|a) \tag{5}$$

resulting from the symmetry of H, all terms in H_0 are cancelled. The divergent term at $E=E_a$ is cancelled, but because of the presence of $|a\rangle$ an extra term of the form

$$\sum_{b\neq a}\frac{|b)(b|a\rangle}{(E-E_b)(a/a\rangle}(a|V|a\rangle \tag{6}$$

is introduced. The main defect of this theory is the use of a mixed representation in $|a\rangle$ and $\{|b)\}$. While the ground state is antisymmetrized, the excited states are not. Since Ψ is no longer antisymmetric upon expanding $(E-H)^{-1}$, this use is not justified. Exchange cannot be fully accounted for in this way, since all matrix elements are evaluated in a representation for which some exchange terms involving the excited states and the ground state and all exchange terms involving the excited states only cannot be present.

It is the purpose of this paper to present a perturbation series in which the antisymmetry of Ψ is not lost in the expansion of $(E-H)^{-1}$ so that the treatment of electron exchange is exact. The identity will be defined such that the set of antisymmetrized, nonorthogonal states can be introduced into the series, showing explicitly that the construction of a complete orthogonalized set (Jansen's treatment) is not necessary.

PERTURBATION THEORY

Following Jansen we will define "label-free" operators H_0' and V' because of the convenience that H_0' is diagonal in the nonorthogonal set of antisymmetrized functions $\{|b\rangle\}$. The special case of two interacting hydrogen atoms will be considered, since the many-electron atom or molecule problem will involve only a nonessential generalization of what follows.

We relate the orthonormal product states to the nonorthogonal, antisymmetrized states through the relations

$$\begin{aligned}\mathcal{A}|a)&=|a\rangle,\\ \mathcal{A}&=f(1+(-1)^S P_{12}),\\ \mathcal{A}^\dagger&=\mathcal{A},\quad (\mathcal{A}^{-1})^\dagger=\mathcal{A}^{-1},\end{aligned} \tag{7}$$

where P permutes the functions on the coordinates,

$$P_{12}i(1)j(2)=j(1)i(2). \tag{8}$$

Define

$$\Lambda|a)=(\Lambda_{12}+\Lambda_{21})|a\rangle=|a\rangle \tag{9}$$

so that

$$\begin{aligned}\Lambda&=I,\\ \Lambda_{12}|a\rangle&=f_a|a),\\ \Lambda_{21}|a\rangle&=f_a(-1)^S P_{12}|a),\end{aligned} \tag{10}$$

where f_a is the normalization of $|a\rangle$. Hence we can define

$$\begin{aligned}H_0'&=H_0(1,2)\Lambda_{12}+H_0(2,1)\Lambda_{21},\\ V'&=V(1,2)\Lambda_{12}+V(2,1)\Lambda_{21},\\ H&=H_0'+V'.\end{aligned} \tag{11}$$

H_0' and V' are seen to be symmetric in the electrons (Jansen[1] has proved this permutation invariance). This definition has the effect of permitting H_0 to project its eigenfunction out of the antisymmetrized function, so that

$$H_0'|a\rangle=E_a|a\rangle, \tag{12}$$

and V its direct and exchange terms. Note that these operators are non-Hermitian and operate only in the ket space of the set $\{|b\rangle\}$.

We now insist that we carry out the perturbation expansion in the set of nonorthogonal eigenfunctions of H_0', $\{|b\rangle\}$. We define the density operator

$$\rho=\sum_b |b\rangle\langle b|. \tag{13}$$

From

$$\begin{aligned}(a|b)&=\delta_{ab},\\ I&=\sum_b |b)(b|.\end{aligned} \tag{14}$$

Now

$$\begin{aligned}I&=\sum_b \mathcal{A}^{-1}|b\rangle\langle b|\mathcal{A}^{-1}\\ &=\sum_b |b\rangle\langle b|\mathcal{A}^{-2}=\rho\mathcal{A}^{-2},\end{aligned} \tag{15}$$

since

$$[\rho,\mathcal{A}^{-1}]=0. \tag{16}$$

Using

$$\mathcal{A}^{-2}=\frac{1}{N!f}\mathcal{A}^{-1} \tag{17}$$

(15) becomes,

$$I=\tfrac{1}{2}\sum_b \frac{1}{f_b}|b\rangle\langle b|. \tag{18}$$

Thus the introduction of the nonorthogonal set requires only that each function be normalized. All operations of H_0' and V' will be carried out on $\{|b\rangle\}$, so that all exchange terms will be generated.

Consider the formal solution to the Schrödinger equation,

$$\Psi=|a\rangle+\frac{(I-O)}{E-H}H|a\rangle. \tag{19}$$

As with Murrell and Shaw, define

$$O=|a\rangle(a|/(a|a\rangle. \qquad (20)$$

Substitution of (18) and (20) into (19), and expansion of $(E-H)^{-1}$ in powers of V' gives to first order

$$\Psi=|a\rangle+\tfrac{1}{2}\sum_{b\neq a}\frac{1}{f_b}\frac{|b\rangle(b|V'|a\rangle}{E-E_b}. \qquad (21)$$

The projection O is sufficient to insure the antisymmetry of (19) and as pointed out earlier H_0' is symmetric so that *the antisymmetry of (19) is preserved on expanding*. Terms in H_0' have cancelled, owing to the result

$$\sum_b \frac{|b\rangle}{E-E_b}(b|\mathfrak{A}^{-2}H_0'|a\rangle=\sum_b\frac{|b\rangle E_a}{E-E_b}\delta_{ba}, \qquad (22)$$

which at $b=a$ is cancelled by the term arising from (20). The divergent term of V' at $E=E_a$ has also been cancelled by the term arising from (20). Permitting V' to operate, (21) becomes

$$\Psi=|a\rangle+\tfrac{1}{2}\sum_{b\neq a}\frac{1}{f_b}\frac{|b\rangle}{E-E_b}$$
$$\times\{(b|V(1,2)|a)f_a+(b|V(2,1)\Lambda_{21}|a\rangle\}. \qquad (23)$$

For the energy, multiplication from the left by $(a|$ yields

$$(a|\Psi\rangle E=(a|a\rangle E_a+(a|V'|a\rangle$$
$$+\tfrac{1}{2}\sum_{b\neq a}\frac{1}{f_b}\frac{1}{E-E_b}\{(a|V(1,2)|b)f_b[(b|V(1,2)|a)f_a+(b|V(2,1)\Lambda_{21}|a\rangle]$$
$$+(a|V(2,1)\Lambda_{21}|b\rangle[(b|V(1,2)|a)f_a+(b|V(2,1)\Lambda_{21}|a\rangle]\}. \qquad (24)$$

The integrals $(a|\Psi\rangle$ and $(a|a\rangle$ are equal to unity in an orthogonal basis. The second term on the right is of the form of the first-order energy. The third term is of the form of the second-order energy and deserves further comment. Within the normalization factors, the first product is the second-order energy without exchange; the second contains nonexchange in the excited states and exchange in the ground state; the third exchange in the excited states and nonexchange in the ground state; and the fourth exchange in both the excited and the ground states. Hence all possible unique exchange terms appear, which within the normalization is just the result that would have been obtained had the orthogonality of the set not been destroyed on antisymmetrization and conventional perturbation theory used (in a problem involving antisymmetrization of a set on a *single* center, for example). Products three and four are absent in the treatment of Murrell and Shaw. The terms involving overlap which occur in Murrell and Shaw arise from their definition of O for an H_0 not diagonal in $\{|b\rangle\}$ and are absent altogether in this treatment. Note that the normalization constants for the excited states cancel in the energy.

Note that the above formulation does not require the orthogonalization of the antisymmetrized set, as does Jansen's. The definitions of H_0' diagonal in the nonorthogonal set, of the identity (18), and of the projection (20) were sufficient to derive an expansion in which Ψ is antisymmetric to all orders and hence exchange is treated exactly.

Equations (23) and (24) are in the general form of the Brillouin-Wigner expansion. Using the expansion[6] of $(E-H)^{-1}$ in powers of $(V-E+E_a)$, the Rayleigh-Schrödinger series can be generated.