At photon energies greater than 3.5 eV, the present results are in better agreement with experiment than previous theoretical calculations.[12,25,26] However the experimental results are not reliable in this energy region, as calibration of the apparatus is difficult due to photoelectric effects from the walls of the apparatus.[34]

In the above analysis, the exchange terms have been treated exactly, and the corrections for atomic distortion have arisen naturally in the formalism, rather than through the use of semiempirical parameters. These are the chief advantages of the polarized orbital method over previous theoretical treatments.

PHYSICAL REVIEW VOLUME 162, NUMBER 1 5 OCTOBER 1967

Schrödinger Perturbation Formalism for Exchange Interactions between Atoms or Molecules

Laurens Jansen
Battelle Institute, Advanced Studies Center, Geneva, Switzerland

(Received 28 December 1966; revised manuscript received 10 May 1967)

A Schrödinger perturbation expansion is developed for exchange interactions between atoms or molecules, starting from a complete, orthonormal set of symmetrized basis functions. The unperturbed Hamiltonian H_0 and the perturbation H' are defined in such a way that they are separately permutation-invariant. First- and second-order results are compared with those obtained by Eisenschitz and London for nonorthonormal basis functions, and with those derived from a Brillouin expansion.

INTRODUCTION

In applying the Schrödinger perturbation formalism to the evaluation of intermolecular forces at large distances (large on the scale of atomic dimensions), it is possible to neglect symmetrization of the basis functions with respect to permutation of electrons and to start from a complete, orthonormal set of product-type unperturbed wave functions. Usually, these basis functions are eigenfunctions of the unperturbed Hamiltonian H_0 for the system; the unperturbed system is that of an assembly of isolated atoms (or molecules), i.e., at infinite distances from each other.

When the interatomic distances decrease, exchange becomes important, i.e., the basis functions must be chosen so that they satisfy the Pauli principle. When, however, the product-type basis vectors are symmetrized (we call any vector or function, whose space part is either symmetric or antisymmetric under exchange of two electrons, a *symmetrized* vector or function), then the new vectors do not form an orthonormal set, and they "overspan" the space of symmetrized vectors, i.e., they become linearly dependent. As early as 1930, Eisenschitz and London[1] developed an elegant method for overcoming these difficulties by a judicious choice of a particular type of basis set in symmetrized space. They derived expressions for first- and second-order perturbation energies; the first-order result is of the same form as in the case without exchange, whereas the second-order expression contains correction terms due to nonorthogonality of the basis vectors. A reformulation and an extension of the Eisenschitz-London method has recently been undertaken by van der Avoird.[2]

Since the early work of Eisenschitz and London, and especially during the past ten years or so, a considerable number of different types of perturbation expansion for exchange interactions has appeared in the literature. Generally, the authors refer at most only superficially to the Eisenschitz-London paper, although several later analyses can be regarded as various approximations to the early method, or as modifications along much the same lines. This later work can be roughly divided in two categories: (a) Evaluation of exchange forces based on a Brillouin-Wigner type expansion.[3,4] To this category belong, e.g., the analysis by Dalgarno and Lynn[5] and that by Lynn,[6] to which we will return later on. Convergence properties of the Brillouin series are determined by the smallness of the quantity $H_{mn}/(E-H_{mm})$, where H is the *total* Hamiltonian of the system, and where $H_{mn}(m\neq n)$ and H_{mm} are matrix elements of the total Hamiltonian with respect to a given set of basis functions. The energy E is computed by iteration. (b) Evaluation of exchange interactions on the basis of a Schrödinger type of perturbation expansion. Here, the total Hamiltonian H is split into an "unperturbed" part H_0 and a "perturbation" H'. This type of procedure immediately poses a complication, since, because of

---

[1] R. Eisenschitz and F. London, Z. Physik **60**, 491 (1930).

[2] A. van der Avoird, Chem. Phys. Letters (Amsterdam) **1**, 24 (1967).

[3] L. Brillouin, J. Phys. Radium **3**, 373 (1932); E. Wigner, Math. Naturw. Anz. Ungar. Akad. Wiss. **53**, 427 (1935).

[4] P. O. Löwdin, J. Chem. Phys. **19**, 1396 (1951).

[5] A. Dalgarno and N. Lynn, Proc. Phys. Soc. (London) **A69**, 821 (1956).

[6] N. Lynn, Proc. Phys. Soc. (London) **A72**, 201 (1958).

electron exchange, the explicit expressions for H_0 and H' for the case of product wave functions (no exchange) cannot be taken over for the case of symmetrized vectors. Usually, H_0 and H' are defined in such a way that they are attached to a *specific* simple-product component of the symmetrized wave functions. To this category of methods, including the Eisenschitz-London procedure, belong the formal analysis by Carr[7] of exchange forces in terms of an explicit "exchange Hamiltonian," and the procedures proposed by Murrell, Randič, and Williams,[8] Musher and Salem,[9] Murrell and Shaw,[10] and Salem.[11] Hirschfelder and Silbey[12] solve the perturbation equations directly, without using linear expansions. Finally, Amos and Musher[13] have recently shown that the Eisenschitz-London results can also be obtained by expanding the perturbed symmetrized wave function in terms of the complete set of atomic product-type vectors.

A critical discussion of perturbation methods with exchange has recently been given by Herring.[14] An important problem in this context concerns the type of basis set employed for the expansion of the perturbed symmetrized wave functions of the system. Usually, the members of this basis set are the symmetrized excited-state wave functions for the individual atoms (or molecules) which form the system considered. This total set, as we remarked before, is highly overcomplete, and consequently its members can not all be orthogonal to one another. In certain approximations the basis functions are nevertheless supposed to be orthogonal[11]; in others the perturbed wave function is no longer symmetric or antisymmetric.[10] Since on the whole, numerical calculations are not carried through on the basis of the different approximations, it is impossible to judge their range of validity. It seems that among the perturbation methods proposed for evaluating exchange interactions, the Eisenschitz-London procedure is still the most direct, comparable to a Brillouin-type expansion as applied by Dalgarno and Lynn.[5]

Among the perturbation expansions with exchange, a direct Schrödinger formalism in symmetrized space is still lacking. It is the main purpose of the present paper to show how such a development can be given, with appropriate definitions of the unperturbed Hamiltonian H_0 and the perturbation H'. The idea behind this development is that in symmetrized space H_0 and H' should "follow" the wave functions on which they operate, i.e., that the explicit forms of these operators depend on the particular association of electrons with nuclei represented by the different components of a symmetrized wave function. This procedure was implicitly adopted by the present author and Lombardi in the analysis of crystal stability for rare-gas and ionic crystals[15,16]; it was also followed by Salem.[11] We may call H_0 and H' "label-free" operators in symmetrized space. In the next section it will be shown how these label-free H_0 and H' can be defined in a mathematically consistent manner. We mention similar efforts by Corinaldesi,[17,18] who attempted to incorporate in the Schrödinger equation the symmetry properties of H_0 and H' separately, leading to the interpretation of any symmetrized wave function as a many-component column vector (one component for each permutation). The proposed formalism offers many complications, but no further insight into the problem of exchange forces between atoms or molecules.

FORMALISM

We consider the simplest system of interest, i.e., that of two (hydrogen) atoms a and b, each with one electron; the two electrons are denoted by 1 and 2. If exchange is not taken into account, then the unperturbed system (two isolated atoms) is described by the basis set $\{\phi_k(1,2)\}$, $k=0, 1, 2, \cdots$, of simple product eigenfunctions of the unperturbed Hamiltonian $H_0(1,2)$; here (1,2) signifies that electron 1 is located on atom a, electron 2 on atom b. Equivalently, if we localize electron 1 on atom b, electron 2 on atom a, then the set of unperturbed basis functions is composed of the eigenfunctions $\phi_k(2,1)$ of the unperturbed Hamiltonian $H_0(2,1)$. When the two atoms interact, then these interactions are described by the operator $H'(1,2)$ in the first configuration and by $H'(2,1)$ with the electron labels reversed. The ground-state unperturbed wave functions are denoted by $\phi_0(1,2)$ and by $\phi_0(2,1)$, respectively.

Next, we introduce the effect of electron exchange, i.e., we pass from a simple-product basis to a basis of symmetrized vectors. A complete, orthonormal basis in symmetrized space can be constructed as follows. As the first basis vector $\psi_0^\pm$, we choose $\phi_0(1,2)\pm\phi_0(2,1)$, except for a normalization constant. For the second basis vector we select $\phi_1(1,2)\pm\phi_1(2,1)$ and orthogonalize this vector to $\psi_0^\pm$. The third basis vector is then $\phi_2(1,2)\pm\phi_2(2,1)$, orthogonalized to both $\psi_1^\pm$ and $\psi_0^\pm$, etc.; this process is formally continued until the basis of symmetrized vectors is complete. Denote this basis by $\{\psi_k^\pm\}$; each basis vector can be written, except for

---

[7] W. J. Carr, Jr., Phys. Rev. **131**, 1947 (1963).

[8] J. N. Murrell, N. Radič, and D. R. Williams, Proc. Roy. Soc. (London) **A284**, 566 (1965).

[9] J. I. Musher and L. Salem, J. Chem. Phys. **44**, 2943 (1966); see also J. I. Musher, Rev. Mod. Phys. **39**, 203 (1967).

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

[11] L. Salem, Discussions Faraday Soc. **40**, 150 (1965).

[12] J. O. Hirschfelder and R. T. Silbey, J. Chem. Phys. **41**, 2588 (1966).

[13] A. T. Amos and J. I. Musher, Chem. Phys. Letters (Amsterdam) **1**, 149 (1967).

[14] C. Herring, in *Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IIB, pp. 1–183.

[15] L. Jansen, Phys. Rev. **125**, 1798 (1961); **135**, A1292 (1964).

[16] E. Lombardi and L. Jansen, Phys. Rev. **136**, A1011 (1964); **148**, A275 (1965); **151**, 694 (1966).

[17] E. Corinaldesi, Nuovo Cimento **25**, 1190 (1963); **30**, 105 (1963).

[18] E. Corinaldesi and H. E. Lin, Nuovo Cimento **28**, 654 (1963).

a normalization constant, as

$$\psi_k^\pm=[\phi_k(1,2)\pm\phi_k(2,1)]+\sum_{l<k} a_l^\pm[\phi_l(1,2)\pm\phi_l(2,1)], \quad (1)$$

where the coefficients $a_l^\pm$ are determined by the orthogonalization procedure. The vectors $\psi_k^\pm$ are neither eigenfunctions of $H_0(1,2)$, nor of $H_0(2,1)$.

Since the basis $\{\psi_k^\pm\}$ is complete, any symmetrized vector ψ can (uniquely) be written as

$$\psi=\sum_k (\psi_k^\pm,\psi)\psi_k^\pm. \quad (2)$$

In its turn, each vector $\psi_k^\pm$ can, from Eq. (1), be decomposed as

$$\psi_k^\pm=\psi_k^\pm(1,2)+\psi_k^\pm(2,1),$$

where

$$\psi_k^\pm(1,2)=\phi_k(1,2)+\sum_{l<k} a_l^\pm\phi_l(1,2),$$

and

$$\psi_k^\pm(2,1)=\pm P\psi_k^\pm(1,2); \quad (3)$$

the operator P permutes the labels of electrons 1 and 2.

We now turn to the definition of the "label-free" Hamiltonians H_0 and H'.[19] Since H_0 and H' are to "follow" the wave function on which they operate, we define two linear operators, $\Lambda_{12}^\pm$ and $\Lambda_{21}^\pm$, which project from the symmetrized to the simple-product vectors, as follows:

$$\begin{aligned}\Lambda_{12}^\pm\psi_k^\pm&=\psi_k^\pm(1,2),\\ \Lambda_{21}^\pm\psi_k^\pm&=\psi_k^\pm(2,1)=\pm P\psi_k^\pm(1,2).\end{aligned} \quad (4)$$

Note that the sum of the two Λ operators equals the identity operator. Then the desired H_0 and H' are defined by

$$\begin{aligned}H_0&=H_0(1,2)\Lambda_{12}^\pm+H_0(2,1)\Lambda_{21}^\pm,\\ H'&=H'(1,2)\Lambda_{12}^\pm+H'(2,1)\Lambda_{21}^\pm.\end{aligned} \quad (5)$$

It follows at once that, with the definitions (5), H_0 and H' are *no longer Hermitian operators.* To verify that the sum of H_0 and H' equals H, the total Hamiltonian, we only have to remember that H can be written as $H=H_0(1,2)+H'(1,2)=H_0(2,1)+H'(2,1)$ and that the sum of $\Lambda_{12}^\pm$ and $\Lambda_{21}^\pm$ equals the identity operator. Then $H_0+H'=H$ follows directly from (5). Further, we note that the symmetrized, but not orthogonal functions $\phi_k(1,2)\pm\phi_k(2,1)$ are *eigenfunctions* of H_0 with the unperturbed eigenvalues E_k. The symmetrized basis vectors $\psi_k^\pm$ have one further interesting property: Although they are not eigenfunctions of H_0, it is still true that $(\psi_k^\pm,H_0\psi_k)=E_k$, the unperturbed energy value associated with the eigenfunction $\phi_k(1,2)\pm\phi_k(2,1)$ of H_0. This can easily be verified by writing down the orthogonalization coefficients $a_l^\pm$ explicitly and by normalizing the $\psi_k^\pm$.

For the Λ operators, we find that

$$\begin{aligned}P\Lambda_{12}^\pm\psi&=P\sum_k(\psi_k^\pm,\psi)\Lambda_{12}^\pm\psi_k^\pm\\ &=\sum_k(\psi_k^\pm,\psi)P\psi_k^\pm(1,2)=\pm\Lambda_{21}^\pm\psi\end{aligned}$$

for any symmetrized vector ψ. Further, since $P\psi=\pm\psi$, we obtain

$$P\Lambda_{12}^\pm=\pm\Lambda_{21}^\pm \text{ and } \Lambda_{12}^\pm P=\pm\Lambda_{12}^\pm, \quad (6)$$

with similar equalities for $\Lambda_{21}^\pm$ on the left of the equations. It then follows at once, from Eqs. (5) and (6), that

$$\begin{aligned}PH_0P\psi&=H_0(2,1)(P\Lambda_{12}^\pm)P\psi+H_0(1,2)(P\Lambda_{21}^\pm)P\psi\\ &=H_0(2,1)\Lambda_{21}^\pm\psi+H_0(1,2)\Lambda_{12}^\pm\psi=H_0\psi,\end{aligned}$$

and similarly with H', so that we may write

$$PH_0P=H_0;\quad PH'P=H', \quad (7)$$

implying that H_0 and H', defined by Eq. (5), *are separately permutation-invariant* as is required of label-free operators. Because of this property, any linear combination $H_0+\lambda H'$ is invariant under permutation of the electrons, enabling us to carry through the usual Schrödinger expansion for the perturbed energy and wave function of the system as a series of powers of a perturbation parameter λ:

$$\begin{aligned}&H(\lambda)=H_0+\lambda H';\quad \psi(\lambda)=\psi_0+\lambda\psi'+\lambda^2\psi''+\cdots;\\ &E(\lambda)=E_0+\lambda E_1+\lambda^2E_2+\cdots.\end{aligned}$$

These expansions, when substituted into the Schrödinger equation $H\psi=E\psi$, lead in the usual way to the different-order expressions for E and ψ, by putting the coefficient of each power of λ equal to zero and then substituting $\lambda=1$. To simplify the notation, we will henceforth omit the superscript $\pm$ on the symmetrized basis functions, i.e., we will simply write ψ_k instead of $\psi_k^\pm$.

FIRST-ORDER ENERGY

The first-order energy E_1 satisfies the usual relation

$$E_1\psi_0=H'\psi_0+(H_0-E_0)\psi'; \quad (8)$$

we expand ψ' as $\sum_{k\neq0}a_k\psi_k$, a linear combination of the complete set $\{\psi_k\}$ of unperturbed, orthonormal, symmetrized functions. Multiplication of Eq. (8) by ψ_0 on the left, and integration, yields

$$E_1=(\psi_0,H'\psi_0)+\sum_{k\neq0}a_k(\psi_0,H_0\psi_k); \quad (9)$$

the first term on the right is of the same form as in perturbation theory without exchange. The second term is in general not zero since ψ_k is not an eigenfunction of H_0, or, equivalently, since H_0 is not Hermitian. To determine the coefficient a_k, we multiply both sides of

---

[19] I am greatly indebted to Dr. C. Herring for suggesting the following explicit expressions.

Eq. (8) by ψ_k on the left and integrate. The result is

$$a_k = \frac{(\psi_k, H'\psi_0) + \sum_{l\neq 0, \neq k} a_l(\psi_k, H_0\psi_l)}{E_0 - E_k}. \tag{10}$$

In first instance we neglect the sum in Eq. (10) and obtain

$$a_k \cong (\psi_k, H'\psi_0)/(E_0 - E_k);$$

this result is the same as in perturbation theory without exchange. Higher-order corrections to a_k can be obtained by iteration. The expression for the first-order energy E_1 now becomes

$$E_1 = (\psi_0, H'\psi_0) = \sum_{k\neq 0} \frac{(\psi_0, H_0\psi_k)(\psi_k, H'\psi_0)}{E_0 - E_k}. \tag{11}$$

We can obtain an alternative expression for the correction term in Eq. (11) by using the Unsöld averaging procedure (average energy ϵ), leading to

$$\epsilon^{-1} \sum_{k\neq 0} (\psi_0, H_0\psi_k)(\psi_k, H'\psi_0) = \epsilon^{-1}[(\psi_0, H_0 H'\psi_0) - E_0(\psi_0, H'\psi_0)] = \epsilon^{-1}(\psi_0, [H_0, H']\psi_0), \tag{12}$$

where $[H_0, H'] \equiv H_0 H' - H' H_0$, the commutator of H_0 and H'. The final result for the first-order energy then becomes

$$E_1 = (\psi_0, H'\psi_0) + \epsilon^{-1}(\psi_0, [H_0, H']\psi_0). \tag{13}$$

By writing out the commutator expression in Eq. (13) in terms of electron labels, it is easily established that

$$(\psi_0, [H_0, H']\psi_0) = -2(\psi_0(1,2), [H_0(2,1), H'(2,1)]\psi_0(2,1)),$$

showing that the correction is of exchange type. The explicit evaluation of this term should, in principle, be based on Eq. (11) rather than on Eq. (13), since, in passing from Eq. (11) to Eq. (13), we have made use of the fact that ψ_0 is an *exact* eigenfunction of H_0. This correction term will, in principle, be small in view of the occurrence of the matrix element of the perturbation H' between an excited state and the ground state.

It should be noted, from Eq. (13), that $E_0 + E_1$ is no longer equal to the expectation value of H for the unperturbed ground state. This implies that $E_0 + E_1$ is not an upper bound to the energy of the system and, therefore, that the sum of perturbation energies higher than first order is not necessarily negative definite.

SECOND-ORDER ENERGY

The second-order perturbation energy E_2 satisfies the usual equation

$$E_2\psi_0 = (H_0 - E_0)\psi'' + (H' - E_1)\psi'. \tag{14}$$

We expand ψ'' as $\sum_{s\neq 0} b_s\psi_s$, substitute the expansion for ψ' of the previous section, multiply both sides of Eq. (14) on the left by ψ_0, and integrate; the result is

$$E_2 = \sum_{k\neq 0} \frac{(\psi_0, H'\psi_k)(\psi_k, H'\psi_0)}{E_0 - E_k} + \sum_{s\neq 0} b_s(\psi_0, H_0\psi_s). \tag{15}$$

If we assume that the ψ_s are still very nearly eigenfunctions of H_0, or, equivalently, that H_0 is still nearly Hermitian, then the second sum in Eq. (15) may be neglected; the first sum is of the same form as that occurring in perturbation theory without exchange. To investigate the correction term, we multiply Eq. (14) by $\psi_l (l\neq 0)$ on the left, substitute the expansions for ψ' and ψ'' and integrate to obtain

$$b_l = \sum_{s\neq 0,} b_s(\psi_l, H_0\psi_s)/(E_0 - E_l) + \sum_{k\neq 0} \frac{(\psi_l, H'\psi_k)(\psi_k, H'\psi_0)}{(E_0 - E_k)(E_0 - E_l)} - E_1(\psi_l, H'\psi_0)/(E_0 - E_l)^2. \tag{16}$$

We now apply a similar approximation as in first order, namely, we neglect on the right of Eq. (16) the terms with b_s, $s\neq 0, l$. The second-order energy Eq. (15) then becomes

$$E_2 = \sum_{k\neq 0} \frac{(\psi_0, H'\psi_k)(\psi_k, H'\psi_0)}{(E_0 - E_k)} + \sum_{l\neq 0} \frac{(\psi_0, H_0\psi_l)}{E_0 - E_l} \times \left\{ \sum_{k\neq 0} \frac{(\psi_l, H'\psi_k)(\psi_k, H'\psi_0)}{E_0 - E_k} - \frac{(\psi_l, H'\psi_0)}{E_0 - E_l} E_1 \right\}. \tag{17}$$

Higher approximations can be obtained by iteration. The first sum on the right of Eq. (17) is of the same form as in the Schrödinger formalism without exchange. By using the Unsöld averaging procedure in the remaining terms and summing over excited states, we obtain

$$\sum_{k,l\neq 0} \frac{(\psi_0, H_0\psi_l)}{E_0 - E_l} \frac{(\psi_l, H'\psi_k)(\psi_k, H'\psi_0)}{E_0 - E_k} = (\epsilon'\epsilon'')^{-1} \times [(\psi_0, [H_0, H'^2]\psi_0) - (\psi_0, [H_0, H']\psi_0)(\psi_0, H'\psi_0)],$$

whereas

$$\sum_{l\neq 0} \frac{(\psi_0, H_0\psi_l)(\psi_l, H'\psi_0)}{(E_0 - E_l)^2} = (\epsilon''')^{-2}(\psi_0, [H_0, H']\psi_0);$$

ϵ', ϵ'', and ϵ''' are Unsöld average energies. Explicit evaluation of these corrections should, in principle, be based on Eq. (17) rather than on the commutators, for the same reason as mentioned earlier. All commutators in first and second orders vanish if the ψ_k were eigenfunctions of H_0; equivalently, they vanish if H_0 were Hermitian.

The commutator term involving $[H_0, H'^2]$ can be written out in terms of the electron labels, with the result that

$$(\psi_0, [H_0, H'^2]\psi_0) = -2(\psi_0(1,2), \times [H_0(2,1), H'^2(2,1)]\psi_0(2,1)),$$ i.e.,

this term is of exchange type, just as that containing the commutator $[H_0,H']$.

The correction terms in first and second orders are quite similar. We make the assumption that they can be neglected, for not too small interatomic distances, *relative to the leading term in their respective orders*. With this assumption, the first- and second-order results are of the same form as those occurring in a perturbation treatment without exchange, the second-order energy reducing to

$$E_2 \cong \sum_{k\neq 0} \frac{(\psi_0,H'\psi_k)(\psi_k,H'\psi_0)}{E_0-E_k} = \epsilon^{-1}[(\psi_0,H'^2\psi_0)-(\psi_0,H'\psi_0)^2]. \quad (18)$$

In this expression

$$H'^2\psi_0 = H'H'\psi_0 = H'\psi_0' = H'(1,2)\psi_0'(1,2) \pm H'(2,1) \times\psi_0'(2,1) = H'^2(1,2)\psi_0(1,2) \pm H'^2(2,1)\psi_0(2,1).$$

It was noted earlier that E_0+E_1 is no longer equal to the expectation value of H for the ground state. This implies that the sum of second- and higher-order energies is not necessarily negative and, in fact, Eq. (18) is not negative definite. The upperbound property is restored when we transfer the first-order commutator in Eq. (13) to the expression for E_2, Eq. (18). Assuming that the Unsöld average energies may be taken as equal, the result is, from Eq. (18) and (13),

$$\begin{aligned}\epsilon^{-1}[(\psi_0,H'^2\psi_0)-(\psi_0,H'\psi_0)^2+(\psi_0,[H_0,H']\psi_0)] &= \epsilon^{-1}[(\psi_0,HH'\psi_0)-(\psi_0,H'\psi_0)^2-(\psi_0,H'H_0\psi_0)] \\ &= \epsilon^{-1}[(H'\psi_0,H'\psi_0)-(\psi_0,H'\psi_0)^2] \\ &= \epsilon^{-1}\sum_{k\neq 0} |(\psi_k,H'\psi_0)|^2, \quad (19)\end{aligned}$$

where we have used the property that the total Hamiltonian H is Hermitian. Since $\epsilon<0$, we obtain a *negative definite* "second-order" energy. The modified first-order energy is simply $(\psi_0,H'\psi_0)$, and the sum of E_0 and the modified E_1 is an upper bound to the energy of the system. Note, however, that in the present formalism the commutator in E_1 results from a first-order equation.

It is easy to show that the sum of E_1 [Eq. (13)] and the approximate expression (18) for E_2 is the same as that obtained directly from the first two terms of a Brillouin expansion.[5,6] Remembering that the basis functions are orthonormal and that, except for ψ_0, they are not eigenfunctions of H_0, the Brillouin expansion takes the form

$$E=(\psi_0,H\psi_0)+\sum_{k\neq 0}\frac{(\psi_0,H\psi_k)(\psi_k,H\psi_0)}{E-(\psi_k,H\psi_k)}+\cdots. \quad (20)$$

To establish the correspondence with the first two orders of the Schrödinger formalism, it is permitted to replace, on the right of Eq. (20), $E-(\psi_k,H\psi_k)$ by $E_0-(\psi_k,H_0\psi_k)$. We now write $H=H_0+H'$ and obtain

$$E-E_0=(\psi_0,H'\psi_0)+\sum_{k\neq 0}\frac{(\psi_0,H_0\psi_k)(\psi_k,H'\psi_0)}{E_0-E_k} +\sum_{k\neq 0}\frac{(\psi_0,H'\psi_k)(\psi_k,H'\psi_0)}{E_0-E_k}.$$

The first two terms on the right are just the first-order energy (11), whereas the last term is the approximate second-order energy (18). Alternatively, we can in Eq. (20) make use of the Hermiticity of H and write

$$(\psi_0,H\psi_k)(\psi_k,H\psi_0)=(H\psi_0,\psi_k)(\psi_k,H\psi_0) =(H'\psi_0,\psi_k)(\psi_k,H'\psi_0);$$

substitution into the second term of Eq. (20) then yields directly the same expression as Eq. (19).

The results of Eisenschitz and London agree in first order with Eq. (13) without the commutator expression, whereas their second-order energy expression can be transformed into Eq. (19) under the assumption that ψ_0 is an exact eigenfunction of $H_0{}^2$.

DISCUSSION OF RESULTS

We have shown how a Schrödinger perturbation formalism can be developed directly in the space of symmetrized vectors for interactions between atoms or molecules including exchange effects. The analysis, formulated for the particular case of two interacting one-electron atoms, can be readily extended to many-electron systems by nonessential generalizations of the formalism. The unperturbed Hamiltonian H_0 and the perturbation H' have been redefined so that they are "label-free" operators, like the total Hamiltonian H (i.e., they are invariant under permutation of the electron labels). The first- and second-order expressions obtained are related in a simple manner to those derived from a Brillouin expansion and to those obtained on the basis of the Eisenschitz-London procedure.

In practice, however, the different methods will generally lead to different results. This is true, first of all, for the separate orders, since these are defined in a different manner in the different formalisms. Moreover, the simple relations between these formalisms are valid only if *exact* unperturbed wave functions are used, a condition which is rarely fulfilled in actual calculations.

The evaluation of second-order perturbation interactions poses a particular problem, since the expression for the energy involves all the excited-state wave functions. The Unsöld averaging procedure does not provide a solution, since the "average energy" cannot be calculated. Only for the interactions of longest range (the van der Waals induced-dipole forces) is the Unsöld average energy independent of the interatomic distances. Generally, however, it is a distance-dependent function which can only be determined in a semi-empirical manner.[5,6] This dependence on distance should be such that second-order exchange interactions are relatively unimportant at small interatomic separations, otherwise the validity of a Heitler-London type of calculation for the binding energy of the hydrogen molecule remains unexplained. We note that, on the basis of the definitions H_0 and H' [Eq. (5)], the Heitler-London analysis corresponds precisely to a first-order perturbation treatment for the energy of interaction between two hydrogen atoms.

In certain problems the fact that the Unsöld average energies are not known plays only a minor role. In particular, this is the case when we are essentially interested in *relative* perturbation energies, e.g., in simultaneous interactions between three atoms *relative* to the sum of pair interactions between the atoms, as occurs in the problem of crystal stability for molecular and ionic solids.[15,16] We have carried out a quantitative comparison between results obtained by different perturbation methods, as applied to this problem of many-atom interactions and crystal stability. These results will be reported separately.

The analysis presented here adds nothing to a solution of the difficult problem concerning convergence properties of perturbation series; for more details we refer to the review article by Herring.[14] The principal assumption inherent in these perturbation procedures is that terms of higher order constitute at most a modification of the van der Waals interactions between the atoms or molecules.

ACKNOWLEDGMENTS

I am indebted to my collaborators Dr. A. van der Avoird, Dr. E. Lombardi, and Dr. M. H. Boon for many stimulating discussions. I also wish to express my gratitude to Professor Henry Margenau for his interest in these problems and to Dr. C. Herring for important observations.

PHYSICAL REVIEW VOLUME 162, NUMBER 1 5 OCTOBER 1967

Transition Matrix Elements for Large Momentum or Energy Transfer*

A. R. P. Rau and U. Fano
Department of Physics, University of Chicago, Chicago, Illinois

(Received 17 April 1967)

The radial matrix element $M=\int_0^\infty R_{kl'}(r)j_L(qr)R_{nl}(r)r^2dr$, which appears in collision theory and photon absorption ($L=1$, $q\sim 0$), has been studied in the past for hydrogenic wave functions. Its behavior for large q or large k is now shown to depend only on the expansion of the wave functions near the nucleus and on an application of selection rules. For large q, the trend is $M\propto q^{-(l+l'+4)}$ and for large k and normalization per unit energy, $M\propto k^{-(l+L+7/2)}q^L$. The asymptotic trend of Altshuler's equivalent forms of the matrix elements is discussed.

THE Born approximation to the theory of inelastic collisions of charged particles with atoms involves the generalized form factor $\int\Psi_f^*\sum_j \exp(i\mathbf{q}\cdot\mathbf{r}_j)\Psi_i d\tau$, where $\hbar\mathbf{q}$ is the momentum transfer, $\mathbf{r}_j$ is the position of the jth electron, Ψ_i and Ψ_f are the initial and final wave functions of the atom, respectively, and $\int d\tau$ covers all coordinates. The dipole integral which determines photon absorption is the low-q limit of this matrix element. Expansion of $\exp(i\mathbf{q}\cdot\mathbf{r}_j)$ into spherical waves and assumption of a determinant form for the many-electron wave functions reduce the nontrivial portion of the form factor to the single-electron radial integral

$$M=\int_0^\infty R_{kl'}(r)j_L(qr)R_{nl}(r)r^2\,dr\,, \tag{1}$$

where the spherical Bessel function is defined as

$$j_L(qr)=[\pi/2qr]^{1/2}J_{L+1/2}(qr)\,, \tag{2}$$

and where the final state kl' of the electron may belong to the discrete or to the continuous spectrum, whereas nl is bound. [The simplifying assumption of determinant wave functions is actually unnecessary. One could replace the product $R_{kl'}R_{nl}$ by a coefficient of the spherical wave expansion of the one-particle reduced density matrix $\int\Psi_f^*\Psi_i\prod_{j>1}d\mathbf{r}_j$ and proceed along the same lines as in this paper.] In the expansion of the form factor, the radial integral M is multiplied by an angular integral of the form

$$\int Y_{l'm'}^*(\theta,\varphi)P_L(\cos\theta)Y_{lm}(\theta,\varphi)\,d\Omega.$$

The parity selection rule and the triangular condition that are implied in this integral will be of importance in determining the asymptotic behavior of M.

The integral (1) and especially its particular case $L=1$, $q\sim 0$ have been calculated analytically for

---

* Work supported in part by the U. S. Atomic Energy Commission under Contract No. COO-1674-1.