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Perturbation Theory of Many-Electron Atoms and Molecules*

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Perturbation theory with operator techniques is applied to a nondegenerate many-electron system taking the entire electron-electron repulsions, $\Sigma_{i>j} r_{ij}^{-1}$, as the perturbation. The first order wave function χ_1, is obtained rigorously in terms of the first order wave functions of independent two-electron systems. The wave functions of these electron pairs contain nuclear parameters and can be obtained individually by variational or other methods, then used in various atoms or molecules. For example Li atom is built up completely from the $(1s)^2\,{}^1S$, $(1s2s)\,{}^1S$ and ${}^3S$ states of Li^+. The χ_1 gives the energy to third order and as an upper limit to the exact E. The E_2 is equal to the sum of complete pair interactions plus many-body terms of two types: (a) "cross polarization," which exists even in no-exchange intermolecular forces, and (b) Fermi correlations.

I. INTRODUCTION

THE single-particle theories of atoms and molecules do not take into account the correlations in the motions of electrons. Large errors result in the calculation of energy differences of chemical and spectroscopic interest. To introduce electron correlation, the variation method has been used extensively. In the most common form of this method, a finite number of Slater determinants formed from a set of one-electron spin-orbitals are linearly combined into a trial function. This method suffers from very slow convergence. Also, it does not allow one to draw general conclusions which can be extended to larger systems since each atom or molecule is treated as a new numerical problem.

How can a large atom or molecule be built up from smaller groups of electrons each containing some correlation? A treatment directed at answering this question would reduce a many-electron problem to several fewer-electron problems, but perhaps more importantly, would extend the qualitative concepts of quantum chemistry so as to include correlation.

The shell structure of atoms and the independent behavior of certain regions of molecules are undoubtedly valid beyond the usual orbital approximations. For atoms and molecules as they exist in nature, we wish to ask questions such as: What is the difference between the free Li^+ ion and the core of Li atom?

Recently[1] we treated a many-electron system by second-order perturbation theory starting from the Hartree-Fock energy. We used the ordinary form of the Rayleigh-Schrödinger (R.S.) method and classified all the virtual transitions represented by the unperturbed determinantal eigenfunctions.[2] Thus the energy was obtained as a sum of pair energies and "exclusion effects," i.e., three- and four-particle Fermi correlations, although, to obtain each term in closed form and not as an infinite series, the approximation of replacing the energy denominators by pair "mean excitation energies" was made.

In this theory as well as in Brueckner's theory of nuclear matter[3] all the electrons of the N-electron system (the "medium") affect a correlating pair (i) by their average (self-consistent field) potential, and (ii) by their "exclusion effects" mentioned above. On the other hand, for the purpose of building up an atom or molecule from some groups of electrons which can be transferred from one atom or molecule to another, each group must be independent of the other electrons of the system and any extra "medium" effects should be added on rather than being implicit.

To do this, we apply here formal perturbation theory to a nondegenerate N-electron system taking the entire interelectronic repulsions, $\sum^{N}_{i>j=1} 1/r_{ij}$, as the perturbation. We consider only the first order wave function (W.F.) and show how it can be built up from independent two-electron solutions. The formalism avoids the infinite sums of R.S. method over complete sets of eigenfunctions with very large continuum contributions. Instead each pair function is obtainable from a two-electron differential equation or an equivalent variational principle. So far, first order W.F.'s have been determinated mainly for He-like systems.[4] These can be used for instance to build up larger atoms. The first order W.F. determines the energy to third order. The energy comes out as a sum of independent pair energies and some added "medium" effects. The latter are examined in Sec. IV. The formalism of this Article will also be applied separately[5] to the correlation energy of a many-electron system starting from its Hartree-Fock solution and obtaining the results of reference 1 in closed and rigorous form.

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[1] Oktay Sinanoğlu, J. Chem. Phys. **33**, 1212 (1960).

[2] This is equivalent to the second quantized or hole-particle formalism.

[3] See, e.g., K. A. Brueckner, in *The Many-Body Problem*, (John Wiley & Sons, New York, 1959). This theory is also based on pair correlations, but for finite systems [See R. J. Eden, in *Nuclear Reactions* (North-Holland Publishing Company, Amsterdam, 1958), Vol. 1] it requires as yet formidable self-consistency procedures.

[4] E. A. Hylleraas, Z. Physik **65**, 209 (1930).

[5] Oktay Sinanoğlu, Proc. Roy. Soc. (London) (to be published).

II. THE PERTURBATION METHOD

Let H_0 be the unperturbed Hamiltonian and H_1 the perturbation; then

$$(H_0+H_1)\Psi=E\Psi,$$

$$H_0\Phi_0=E_0\Phi_0;\quad \langle\Phi_0,\Phi_0\rangle=1. \tag{1}$$

If we write:

$$\Psi\equiv\Phi_0+\mathrm{X},$$

such that

$$\langle\Phi_0,\Psi\rangle=1,\quad \langle\Phi_0,\mathrm{X}\rangle=0, \tag{2}$$

we get exactly

$$E=\langle\Phi_0,H\Psi\rangle=E_0+\langle\Phi_0,H_1\Psi\rangle. \tag{3}$$

The perturbation solution is obtained by

$$\mathrm{X}=\mathrm{X}_1+\mathrm{X}_2+\cdots,$$

$$E-E_0=E_1+E_2+E_3+\cdots. \tag{4}$$

X_1 is a solution of

$$(H_0-E_0)\mathrm{X}_1=(E_1-H_1)\Phi_0=-QH_1\Phi_0, \tag{5}$$

where $E_1=\langle\Phi_0,H_1\Phi_0\rangle$, and $Q=1-\Phi_0\rangle\langle\Phi_0$ is an operator that projects out Φ_0.

The X_1 determines the energy to third order[6]:

$$E_2=\langle\Phi_0,H_1\mathrm{X}_1\rangle-E_1\langle\Phi_0,\mathrm{X}_1\rangle, \tag{6}$$

$$E_3=\langle\mathrm{X}_1,H_1\mathrm{X}_1\rangle-E_1\langle\mathrm{X}_1,\mathrm{X}_1\rangle-2E_2\langle\Phi_0,\mathrm{X}_1\rangle. \tag{7}$$

This is closely related to the fact that energies to odd orders are higher limits to the exact energy, E, and thus also follow from the standard variational method.[7] Energies to even orders, however, do not have this relation to E.

Equation (5) is a nonhomogeneous partial differential equation. It has solutions only if the solutions of the corresponding homogeneous equation are orthogonal to the nonhomogeneity,[8] $QH_1\Phi_0$. This means that in cases of degeneracy, the degenerate zero order eigenfunctions, $\Phi_0{}^k$, must be chosen so as to satisfy

$$\langle\Phi_0{}^i,QH_1\Phi_0{}^k\rangle=0. \tag{8}$$

Then a different equation like Eq. (5) can be written down for every $\Phi_0{}^k$ with a solution $\mathrm{X}_1{}^k$.

Equation (5) is equivalent to the extremum condition:

$$\delta\{2\langle\mathrm{X}_1,\,(H_1-E_1)\Phi_0\rangle+\langle\mathrm{X}_1,\,(H_0-E_0)\mathrm{X}_1\rangle\}=0. \tag{9a}$$

In particular, the X_1 for the lowest state of a given symmetry can be found approximately by minimizing

$$E_2\leq\{2\langle\mathrm{X}_1{}^{tr},\,(H_1-E_1)\Phi_0\rangle+\langle\mathrm{X}_1{}^{tr},\,(H_0-E_0)\mathrm{X}_1{}^{tr}\rangle\}, \tag{9b}$$

with suitable trial functions, $\mathrm{X}_1{}^{tr}$. Hylleraas has used Eq. (9) to obtain the E_2 and X_1 for the ground state of the He atom.[4] The X_1 of an arbitrary excited state which may be of the same symmetry as some of the lower states may also be found by a minimization procedure. We have developed such a procedure[9] and shown that for an excited state, $\mathrm{X}_1{}^{tr}$ must be chosen subject to some restrictions which require a knowledge of only unperturbed W.F.'s of the lower states.

The particular solution, $\mathrm{X}_1{}^P$, of Eq. (5) is given by:

$$\mathrm{X}_1{}^P=L_0{}^{-1}(E_1-H_1)\Phi_0, \tag{10}$$

where $L_0{}^{-1}\equiv(H_0-E_0)^{-1}$ is the Green's function operator. But the general solution, X_1, is

$$\mathrm{X}_1=\mathrm{X}_1{}^P+C\Phi_0; \tag{11a}$$

C is an arbitrary constant which can be chosen such that

$$\langle\Phi_0,\mathrm{X}_1\rangle=0. \tag{11b}$$

Let the nondegenerate ground state of an N electron system be

$$\begin{aligned}\Phi_0(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N)&=\frac{1}{\sqrt{(N!)}}\det\{1(\mathbf{x}_1)2(\mathbf{x}_2)\cdots N(\mathbf{x}_N)\}\\&=\mathcal{A}\{1(\mathbf{x}_1)2(\mathbf{x}_2)\cdots N(\mathbf{x}_N)\}\\&\equiv\mathcal{A}(123\cdots N),\end{aligned} \tag{12}$$

$\mathcal{A}$ is the antisymmetrizing operator:

$$\mathcal{A}=\frac{1}{\sqrt{(N!)}}\sum_P(-1)^PP=\frac{1}{\sqrt{(N!)}}\det. \tag{13}$$

We shall take for the unperturbed system the bare nuclei Hamiltonian:

$$H_0=\sum_{i=1}^N h_i{}^0;\quad h_i{}^0\equiv-\tfrac{1}{2}\nabla_i{}^2-\sum_\alpha(Z_\alpha/R_{\alpha i}),$$

so that

$$E_0=\sum_{i=1}^N\epsilon_i{}^0,$$

and

$$H_1=\sum_{i>j=1}^N g_{ij};\quad g_{ij}\equiv\frac{1}{r_{ij}}. \tag{14}$$

in atomic units (1 a.u. = 27.2 ev). $R_{\alpha i}$ is the distance of electron i to nucleus α. The $1(\mathbf{x}_1)$, $2(\mathbf{x}_2)$, $\cdots k(\mathbf{x}_i)$ in Eq. (12) are the spin-orbitals satisfying

$$h_i{}^0k(\mathbf{x}_i)=\epsilon_k{}^0k(\mathbf{x}_i); \tag{15}$$

$\mathbf{x}_i$ designates both the space $(\mathbf{r}_i)$ and the spin (ξ_i)

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[6] H. A. Bethe and E. E. Salpeter, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35.

[7] To see the relation between the energy calculated to third order and the exact E, substitute $(\Phi_0+\mathrm{X}_1)$ with $\langle\Phi_0,\mathrm{X}_1\rangle=0$ in $(\langle\Psi,H\Psi\rangle/\langle\Psi,\Psi\rangle)\geq E$ and use Eqs. (6), (7) and the relation: $\langle\mathrm{X}_1,H_0\mathrm{X}_1\rangle=E_0\langle\mathrm{X}_1,\mathrm{X}_1\rangle-\langle\mathrm{X}_1,H_1\Phi_0\rangle$ which follows from Eq. (5). Then we have

$$E\langle E_0+E_1+\frac{E_2+E_3}{1+\langle\mathrm{X}_1,\mathrm{X}_1\rangle}\langle E_0+E_1+E_2+E_3,$$

since $\langle\mathrm{X}_1,\mathrm{X}_1\rangle=|\mathrm{X}_1|^2\rangle 0$. The normalization correction is of the fourth and higher orders. See also: P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, New York, 1953), Vol. 2, pp. 1119–20.

[8] B. Friedman, *Principles and Techniques of Applied Mathematics* (John Wiley & Sons, Inc., New York, 1957).

[9] O. Sinanoğlu, this issue [Phys. Rev. **122**, 491 (1961)].

coordinates of the electron i. In atoms, the complete one-electron basis set $\{k\}$ is the hydrogen-like orbitals multiplied by spin α or β. Thus $1\equiv 1s_\alpha$, $2\equiv 1s_\beta$, $\cdots$ so that all odd integers stand for spin-orbitals with α spin, and all even ones for those with β.

From Eqs. (12) and (14),

$$E_1=\langle\Phi_0,H_1\Phi_0\rangle=\sum_{i>j=1}^{N}(J_{ij}-K_{ij}^{\|}). \qquad (16)$$

J_{ij} and $K_{ij}^{\|}$ are the Coulomb and exchange integrals between the orbitals i and j:

$$\begin{aligned} J_{ij}&=\langle i(\mathbf{x}_1)j(\mathbf{x}_2),g_{12}i(\mathbf{x}_1)j(\mathbf{x}_2)\rangle=\langle ij,g_{12}ij\rangle,\\ K_{ij}^{\|}&\equiv\langle i(\mathbf{x}_1)j(\mathbf{x}_2),g_{12}j(\mathbf{x}_1)i(\mathbf{x}_2)\rangle=\langle ij,g_{12}ji\rangle, \end{aligned} \qquad (17)$$

$K_{ij}^{\|}$ is nonzero only for i and j of like spin.

Notice that in Eq. (12), before $\mathcal{A}$ is applied, a spin-orbital and the electron occupying it are designated by the same numeral, e.g., $1(\mathbf{x}_1)$, $2(\mathbf{x}_2)$, etc.

In the spectral representation of H_0, the Green's function, L_0^{-1}, in Eq. (10) is given by

$$L_0^{-1}=\sum_{k\geq 1,\, l\geq 1(\cdots)n\geq 1}^{\infty} \times\frac{k(\mathbf{x}_1)l(\mathbf{x}_2)\cdots n(\mathbf{x}_N)\rangle\langle k(\mathbf{x}_1)l(\mathbf{x}_2)\cdots n(\mathbf{x}_N)}{(\epsilon_k{}^0+\epsilon_l{}^0+\cdots\epsilon_n{}^0)-(\epsilon_1{}^0+\epsilon_2{}^0+\cdots\epsilon_N{}^0)} \qquad (18)$$

for the space of distinguishable electrons, and by

$$L_0^{-1}=\sum_{n>\cdots>l>k\geq 1}\frac{\mathcal{A}(kl\cdots n)\rangle\langle\mathcal{A}(kl\cdots n)}{(\epsilon_k{}^0+\epsilon_l{}^0+\epsilon_n{}^0)-(\epsilon_1{}^0+\epsilon_2{}^0+\epsilon_N{}^0)} \qquad (19)$$

for the antisymmetric space of N fermions. In Eq. (18), $\boldsymbol{k}$, $\boldsymbol{l}$, etc., each runs over the complete one electron basis set of spin-orbitals. The sum in Eq. (19), on the other hand, is over all the unique N by N Slater determinants, i.e., "ordered configurations"[1] that can be formed from $\{k\}$. For use in the next section we also define

$$e_i\equiv h_i{}^0-\epsilon_i{}^0+(\text{spin part})_i, \qquad (20a)$$

and write

$$L_0^{-1}=\frac{1}{H_0-E_0}=\frac{1}{e_1+e_2+e_3+\cdots e_n}. \qquad (20b)$$

III. SEPARATION INTO PAIRS

We now write X_1, of Eq. (5), in terms of the first order wave functions of *independent two-electron systems* each one of which can be obtained from an Eq. (5) or Eq. (9) in exactly the same way as solving for the ground or an excited state[9] of, e.g., the He atom.[4]

Consider an N-electron state whose zero-order W.F. can be written as a single Slater determinant (closed shell or closed shell plus one electron system). From Eqs. (5), (10) to (17), and (20) we have

$$\mathrm{X}_1=L_0^{-1}(E_1-H_1)\Phi_0=L_0^{-1}\Big\{\sum_{i>j=1}^{N}(J_{ij}-K_{ij}^{\|}) -\sum_{i>j=1}^{N}g_{ij}\Big\}\mathcal{A}(123\cdots N) \qquad (21)$$

(E_1-H_1) commutes with $\mathcal{A}$, since it is unchanged after any permutation of the electron indices. Thus

$$\mathrm{X}_1=L_0^{-1}\mathcal{A}\Big\{\sum_{i>j=1}^{N}(J_{ij}-K_{ij}^{\|}-g_{ij})\Big\}(123\cdots N), \qquad (22)$$

where

$$(123\cdots N)=[1(\mathbf{x}_1)2(\mathbf{x}_2)3(\mathbf{x}_2)\cdots N(\mathbf{x}_N)].$$

In g_{ij}, i and j refer to the electrons ($\mathbf{r}_i$ and $\mathbf{r}_j$), whereas in $(J_{ij}-K_{ij}^{\|})$ they refer to the orbitals i and j. Since there is a one-to-one correspondence between i and $\mathbf{x}_i$ before operating by $\mathcal{A}$, we associate a $(J_{ij}-K_{ij})$ with each g_{ij} and write

$$m_{ij}\equiv J_{ij}-K_{ij}-g_{ij}; \qquad (23)$$

then in Eq. (22),

$$\mathcal{A}\Big\{\sum_{i>j=1}^{N}(J_{ij}-K_{ij}^{\|}-g_{ij})(123\cdots N)\Big\} =\sum_{i>j}\mathcal{A}\{m_{ij}(123\cdots N)\}, \qquad (24)$$

$\mathcal{A}$ commutes with H_0 and hence also with L_0^{-1}, so that

$$\begin{aligned}\mathrm{X}_1&=L_0^{-1}\sum_{i>j}\mathcal{A}\{m_{ij}(123\cdots N)\}\\ &=\mathcal{A}L_0^{-1}\sum_{i>j=1}^{N}m_{ij}(123\cdots N).\end{aligned} \qquad (25)$$

If now $L_0^{-1}=(e_1+e_2+\cdots e_N)^{-1}$ were applied to each $m_{ij}(123\cdots N)$ term in Eq. (25) separately, it would have singularities in each such term, corresponding to degeneracies of the type $1(\mathbf{x}_1)2(\mathbf{x}_2)$ with $1(\mathbf{x}_2)2(\mathbf{x}_1)$, etc. [see, e.g., Eq. (18)]. Of course these singularities cancel in the sum after applying $\mathcal{A}$ in Eq. (25), so that X_1 is finite.

To get X_1 *as a sum of terms, each term containing an independent two-electron solution, Eq.* (25) *must be so rearranged that each term will have no singularities before operating on it by* $\mathcal{A}$.

To achieve this we go back to Eq. (24) and introduce first the operator $\mathcal{B}_{ij}$ in front of each m_{ij}. The $\mathcal{B}_{ij}$ is the antisymmetrizer that operates only on $\mathbf{x}_i$ and $\mathbf{x}_j$; i.e.,

$$\mathcal{B}_{ij}\equiv\frac{1}{\sqrt{2}}(1-P_{ij})=\frac{1}{\sqrt{2}}\det, \qquad (26)$$

P_{ij} interchanges only $\mathbf{x}_i$ and $\mathbf{x}_j$ and leaves the other electrons the same. Since P_{ij} is an element of the permutation group of N electrons, the following relation holds:

$$\frac{1}{\sqrt{2}}\mathcal{A}\mathcal{B}_{ij}=\mathcal{A}, \tag{27}$$

$\mathcal{A}$ was defined in Eq. (13). From Eqs. (24) and (27) and considering that g_{ij} is symmetric with respect to P_{ij}, we get

$$\begin{aligned}\sum_{i>j=1}^{N}\mathcal{A}\{m_{ij}(123\cdots N)\}&=\sum_{i>j=1}^{N}\frac{\mathcal{A}}{\sqrt{2}}\mathcal{B}_{ij}\{m_{ij}(123\cdots N)\}\\&=\frac{\mathcal{A}}{\sqrt{2}}\sum_{i>j=1}^{N}m_{ij}\mathcal{B}_{ij}(123\cdots N),\end{aligned} \tag{28}$$

and

$$\mathrm{X}_1=\frac{1}{\sqrt{2}}\mathcal{A}\sum_{i>j=1}^{N}\frac{1}{e_1+e_2+\cdots e_N}m_{ij}\mathcal{B}_{ij}(123\cdots N). \tag{29}$$

From Eqs. (15) and (20a),

$$e_i i(\mathbf{x}_i)=0; \tag{30a}$$

thus[8] for any analytic function, f of e_i,

$$f(e_i)i=f(0)i. \tag{30b}$$

Therefore:

$$\begin{aligned}&\frac{1}{e_1+e_2+\cdots e_N}m_{ij}\mathcal{B}_{ij}(12\cdots ij\cdots N)\\&\qquad=(12\cdots(i-1)(j+1)\cdots N)\frac{1}{e_i+e_j}m_{ij}\mathcal{B}_{ij}(ij),\end{aligned} \tag{31}$$

and

$$\mathrm{X}_1=\frac{1}{\sqrt{2}}\mathcal{A}\left\{\sum_{i>j=1}^{N}(12\cdots(i-1)(j+1)\cdots N)\times\frac{1}{e_i+e_j}m_{ij}\mathcal{B}_{ij}(ij)\right\}. \tag{32}$$

Equation (31) can be verified also from Eq. (18).

Some of the (ij) terms in Eq. (32) are already in the desired nonsingular forms, others are not. To examine each term in detail concretely, we now continue the derivation with a specific case: the Li atom. Then $\Phi_0(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)=\mathcal{A}(123)$ and

$$(123)=(1s_\alpha(\mathbf{x}_1)1s_\beta(\mathbf{x}_2)2s_\alpha(\mathbf{x}_3)), \tag{33}$$

X_1 becomes

$$\mathrm{X}_1=\frac{1}{\sqrt{2}}\mathcal{A}\{1(\mathbf{x}_1)u_{23}(\mathbf{x}_2,\mathbf{x}_3)+2(\mathbf{x}_2)u_{13}(\mathbf{x}_1,\mathbf{x}_3)+3(\mathbf{x}_3)u_{12}(\mathbf{x}_1,\mathbf{x}_2)\}, \tag{34a}$$

where

$$u_{ij}\equiv\frac{1}{e_i+e_j}m_{ij}\mathcal{B}(ij). \tag{34b}$$

Our aim is to write each u_{ij} as the solution of a nonhomogeneous 2-electron equation in the form of Eqs. (5) and (9). The condition that u_{ij} in Eq. (34b) not be infinite is equivalent to the condition that

$$(e_i+e_j)u_{ij}=m_{ij}\mathcal{B}(ij) \tag{35}$$

has a solution. As given by Eq. (2), this condition is

$$\langle\varphi_{ij}{}^k,m_{ij}\mathcal{B}(ij)\rangle=0, \tag{36}$$

$\varphi_{ij}{}^k$ denotes either $\mathcal{B}(ij)$ or one of the other solutions of

$$(e_i+e_j)\varphi_{ij}{}^k=0 \tag{37}$$

degenerate with it. If Eq. (36) holds, then u_{ij} can be obtained from Eq. (35) by any method [including variational,[9] Eq. (9)]. But Eqs. (34a), (10), and (11) show that it must be made orthogonal to $\mathcal{B}(ij)$ before it is inserted into Eq. (34a).

In Eq. (34), two of the u_{ij}'s already correspond to physically existing two-electron systems: $u_{12}(\mathbf{x}_1,\mathbf{x}_2)$ is the first order wave function of a free Li$^+$ ion in its ground state and satisfies

$$(e_1+e_2)u_{12}=(J_{12}-g_{12})\mathcal{B}(1s_\alpha 1s_\beta). \tag{38}$$

Also, u_{13} is given by

$$(e_1+e_3)u_{13}=(J_{13}-K_{13}-g_{13})\mathcal{B}(1s_\alpha 2s_\alpha), \tag{39}$$

and is the same as the $(1s2s)\ {}^3S$ state of Li$^+$. It is not possible to write directly such an equation for u_{23}. This case violates Eq. (36), because

$$\mathcal{B}_{23}(23)=(1/\sqrt{2})\det(1s_\beta 2s_\alpha)$$

is degenerate with $\mathcal{B}(1s_\alpha 2s_\beta)$ and is not a pure spin state. To solve this difficulty we recall that in the over-all Li atom this degeneracy is finally removed after the application of $\mathcal{A}$ in Eq. (34a). Thus, again we go back to Eq. (28), where $L_0{}^{-1}$ had not been applied yet, and remove the degeneracy in the following way:

From Eqs. (29) and (34), the (23) term is

$$\frac{1}{e_1+e_2+e_3}\frac{\mathcal{A}}{\sqrt{2}}(J_{23}-g_{23})\{1(\mathbf{x}_1)\mathcal{B}(23)\}. \tag{40}$$

$\mathcal{B}(1s_\beta 2s_\alpha)$ is a mixture of a singlet and a triplet state, so that

$$\left.\begin{matrix}{}^3\varphi_{23}\\{}^1\varphi_{23}\end{matrix}\right\}=\frac{1}{\sqrt{2}}[\mathcal{B}(23)\pm\mathcal{B}(14)]. \tag{41}$$

The $(+)$ sign refers to the triplet state

$$\mathcal{B}(14)\equiv(1/\sqrt{2})\det(1s_\alpha 2s_\beta).$$

To split Eq. (40) into two parts such that both will satisfy Eq. (8), we multiply it by 2/2, then add and subtract $K_{23}[1\mathcal{B}_{23}(23)]$, obtaining

$$\tfrac{1}{2}L_0{}^{-1}\frac{\mathcal{A}}{\sqrt{2}}\{(J_{23}-K_{23}-g_{23})[1\mathcal{B}(23)]+(J_{23}+K_{23}-g_{23})[1\mathcal{B}(23)]\}. \tag{42}$$

If $(J_{23}-g_{23})[1(\mathbf{x}_1)\mathcal{B}(1(\mathbf{x}_2)4(\mathbf{x}_3))]$ is added and subtracted and then $K_{23}[1(\mathbf{x}_1)\mathcal{B}(1(\mathbf{x}_2)4(\mathbf{x}_3))]$ is added to each one of its terms, Eq. (42) remains unchanged, since

$$\mathcal{A}\{1(\mathbf{x}_1)\mathcal{B}(1(\mathbf{x}_2)4(\mathbf{x}_3))\}=0. \tag{43}$$

Then using Eq. (41), we get

$$\begin{aligned}L_0^{-1}\frac{\mathcal{A}}{\sqrt{2}}(J_{23}-g_{23})\{1\mathcal{B}(23)\}\\ =\tfrac{1}{2}L_0^{-1}\mathcal{A}\{1(\mathbf{x}_1)[(J_{23}-K_{23}-g_{23})^3\varphi_{23}(\mathbf{x}_2,\mathbf{x}_3)\\ +(J_{23}+K_{23}-g_{23})^1\varphi_{23}(\mathbf{x}_2,\mathbf{x}_3)]\}.\end{aligned} \tag{44}$$

Finally we commute L_0^{-1} and $\mathcal{A}$ and use Eq. (30b). The result is that u_{23} in Eq. (34a) is now given by two terms, instead of by Eq. (34b):

$$u_{23}(\mathbf{x}_2,\mathbf{x}_3)=\frac{1}{\sqrt{2}}[{}^3u_{23}(\mathbf{x}_2,\mathbf{x}_3)+{}^1u_{23}(\mathbf{x}_2,\mathbf{x}_3)]. \tag{45a}$$

The triplet and singlet components of u_{23} are the solutions of

$$\begin{aligned}(e_2+e_3)\,{}^3u_{23}&=(J_{23}-K_{23}-g_{23})^3\varphi_{23},\\ (e_2+e_3)\,{}^1u_{23}&=(J_{23}+K_{23}-g_{23})^1\varphi_{23},\end{aligned} \tag{45b}$$

${}^3u_{23}$ and ${}^1u_{23}$ must be made orthogonal to ${}^3\varphi_{23}$ and ${}^1\varphi_{23}$ before they are inserted in Eq. (34a).

The first of Eqs. (45b) and the spatial part of ${}^3u_{23}$ are the same as Eq. (39) and the spatial part of u_{13}, respectively. The ${}^3u_{23}$ and u_{13} differ only in their spin factors, one being the $M_s=0$, $(\alpha\beta+\beta\alpha)$, and the other $M_s=+1$, $(\alpha\alpha)$, component of the triplet. Thus the entire X_1 for the ground state of the Li atom is obtained by combining in Eq. (34a) the first order W.F.'s of the $(1s)^2\,{}^1S$, $(1s2s)\,{}^3S$ and $(1s2s)\,{}^1S$ states of the free (Li^+) ion. The advantage of this approach is that the two electron solutions u_{ij} can be obtained independently and when they are obtained as a function of the atomic number, Z, as Hylleraas[4] has done for H^-, He, Li^+, etc., they can be used to build up larger atoms. In going from Li to Be, *only one more* pair function, the one for the $(2s)^2\,{}^1S$ state, is needed. (For this state the $(2s)^2$, $(2p)^2$ degeneracy would be removed first.) In general the number of independent pair states needed will be less than the total number of pairs, because of the multiplicity of some of the pair states.

For the N-electron system with a single determinant Φ_0, we now have [see Eq. (32)]:

$$X_1=\frac{1}{\sqrt{2}}\mathcal{A}\{\sum_{i>j=1}^{N}(12\cdots(i-1)(j+1)\cdots N)u_{ij}\}. \tag{46}$$

Wherever $\mathcal{B}(ij)$ belongs to a row of an irreducible representation of the symmetry group of the two-electron Hamiltonian, $(h_i^0+h_j^0+g_{ij})$, the corresponding u_{ij} is the solution of

$$(e_i+e_j)u_{ij}=m_{ij}\mathcal{B}(ij), \tag{47}$$

such that $\langle u_{ij},\mathcal{B}(ij)\rangle=0$. In other cases, u_{ij} must be decomposed into symmetry eigenfunctions as in Eq. (45a), and each part determined from equations such as Eq. (45b). A survey of the approximate methods for solving such two-electron equations are given by Bethe and Salpeter,[6] and the variational method, Eq. (9), and its extension to any excited state has been discussed by the author.[9] All the two-electron degeneracies, e.g., arising from angular momentum, etc., can first be removed in the same way as shown for the $1s_\beta 2s_\alpha$ pair of Li.

IV. THE ENERGY

We now turn to the examination of the energy of an N-electron system obtained from the first order W.F., X_1. Since each u_{ij} in Eq. (46) is orthogonal to its $\mathcal{B}(ij)$ or φ_{ij}, we have $\langle\Phi_0,X_1\rangle=0$; then

$$\begin{aligned}E_2=\langle\Phi_0,H_1X_1\rangle=\Big\langle\mathcal{A}(123\cdots N),\Big(\sum_{i>j=1}^{N}g_{ij}\Big)\frac{\mathcal{A}}{\sqrt{2}}\\ \times\{\sum_{i>j}(12\cdots(i-1)(j+1)\cdots N)u_{ij}\}\Big\rangle\\ =(N!/2)^{\frac{1}{2}}\langle\mathcal{A}(123\cdots N),(g_{12}+g_{13}+\cdots)\\ \times[(34\cdots N)u_{12}+(1256\cdots N)u_{34}+\cdots]\rangle.\end{aligned} \tag{48}$$

The last step follows because $\mathcal{A}$ is self-adjoint and $\mathcal{A}^2=(N!)^{\frac{1}{2}}\mathcal{A}$. In $(34\cdots N)u_{12}$, etc., orbital and electron indices are the same [$3(\mathbf{x}_3)$, etc.].

For the Li atom, Eq. (48) gives

$$\begin{aligned}E_2=\langle\mathcal{B}(12),g_{12}u_{12}\rangle+\langle\mathcal{B}(13),g_{13}u_{13}\rangle+\langle\mathcal{B}(23),g_{23}u_{23}\rangle\\ +(3!2)^{\frac{1}{2}}\{\langle\mathcal{A}(123),g_{13}3(\mathbf{x}_3)u_{12}(\mathbf{x}_1,\mathbf{x}_2)\rangle\\ +\langle\mathcal{A}(123),g_{13}1(\mathbf{x}_1)u_{23}(\mathbf{x}_2,\mathbf{x}_3)\rangle\\ +\langle\mathcal{A}(123),g_{12}2(\mathbf{x}_2)u_{13}(\mathbf{x}_1,\mathbf{x}_3)\rangle\}\end{aligned} \tag{49}$$

The first term is simply the ground state E_2 of (Li^+); from Eq. (45a), the sum of the second and third terms are the sum of the E_2's of $(1s2s)\,{}^3S$ and ${}^1S$ states of Li^+. Notice that this result is more than the usual pairwise-additivity of dispersion forces: e.g., $\langle\mathcal{B}(12),g_{12}u_{12}\rangle$ is the *entire* E_2 of Li^+ ion. It includes both the dispersion and the "orbital average polarization" terms[1] which arise from double and single virtual transitions, respectively, in the Rayleigh-Schrödinger expression for E_2 [i.e., using Eq. (19)].

The remaining terms of Eq. (49) are the non-pair-wise-additive interactions in second order. Their meaning is made clear by expanding $\mathcal{A}(123)$ in its minors, in each of the last three terms of Eq. (49). For instance, the first of these terms becomes

$$\begin{aligned}(3!2)^{\frac{1}{2}}\langle\mathcal{A}(123),g_{13}3(\mathbf{x}_3)u_{12}(\mathbf{x}_1,\mathbf{x}_2)\rangle\\ =2\{\langle 2_2\mathcal{B}(1_13_3),g_{13}3_3u_{12}\rangle-\langle 1_2\mathcal{B}(2_13_3),g_{13}3_3u_{12}\rangle\\ -\langle 3_2\mathcal{B}(1_13_3),g_{13}3_3u_{12}\rangle\},\end{aligned} \tag{50}$$

where we have used subscripts for electron coordinates, e.g., $1_2=1(\mathbf{x}_2)$, etc., and $u_{12}=u_{12}(\mathbf{x}_1,\mathbf{x}_2)$. The last term is the "exclusion effect"[1] of the occupied orbital 3 on the correlating pair of electrons[10] in u_{12}. As discussed in reference 1, this is a three-body Fermi correlation. In the theory of nuclear matter,[11] these exclusion effects turn out to be partly responsible for the smallness of the three-body Coulombic correlations which appear first in E_3. Whether the same thing is true in atoms and molecules or not is a point that requires future investigation.

The first two terms of Eq. (50) are of a different nature. They arise in Rayleigh-Schrödinger E_2 [using Eq. (19)], as the cross terms upon squaring the single excitation, i.e., "orbital average polarization"[1] terms like $\langle \mathcal{A}(123),(\sum g_{ij})\mathcal{A}(12k)\rangle$. Such "cross-polarization" terms come up, as shown in the Appendix, even in the second order Van der Waals attraction of three separate atoms even when they are so far apart that all exchange effects can be neglected.

Thus, for the energy of an N electron system to second order, we have from Eqs. (14), (16), and (48):

$$E_0+E_1+E_2=\sum_{i>j=1}^{N} \text{(pair energies)}$$
$$+\sum \text{(cross-polarization and exclusion effects)}. \quad (51)$$

All of these terms and also E_3 in Eq. (7) are obtained from Φ_0 and X_1 given by Eq. (46). The components of E_3 can be similarly separated and contribute to the energies of the independent pairs and three-electron terms. As mentioned[7] in Sec. II, it is important to carry out the energy calculations to E_3 rather than E_2 so as to get an upper limit to the exact E.

V. CONCLUSION

We have shown that the first order wave function, X_1, of an N-electron system can be obtained from the first order functions of the ground and excited states of a two-electron system with the same nuclear framework. Each pair function can be obtained from a 2-electron nonhomogeneous differential equation, e.g., by a variational method.[9] Then both the individual pair energies and the nonpairwise additive effects in E_2 and E_3 follow from this X_1. These results should be immediately applicable to atoms, since u_{ij} can be obtained with explicit Z dependence,[4] and Li, Be, etc., can be calculated from mostly existing calculations on the ground and excited states of He-like ions. Similar calculations may be made on molecules, where, e.g., inner shell pairs can be taken over from atomic calculations, and core-valence electron interactions obtained using core polarization potentials.[1,5,12] In many molecular problems it is also possible to calculate X_1, E_2, and E_3 starting from a Hartree-Fock Φ_0. There are now many Hartree-Fock molecular orbital (M.O.S.C.F.) calculations available, and we have separately developed[6] methods similar to those given here to obtain correlation energies starting from Hartree-Fock solutions.

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APPENDIX. NONPAIRWISE FORCES IN THE SECOND ORDER INTERACTION OF THREE SEPARATE ATOMS

Consider three identical atoms A, B, C sufficiently far apart so that all exchange effects can be neglected. Let a, b, and c be their ground states and V_{AB}, etc., denote the instantaneous electrostatic potential between A and B, etc. Using definitions similar to those in the text, we have

$$X_1=\frac{1}{e_a+e_b+e_c}\{(J_{ab}-V_{AB})+(J_{ac}-V_{AC})+(J_{bc}-V_{BC})\}(abc), \quad \text{(A1)}$$

where, e.g., $J_{ab}=\langle ab,V_{AB}ab\rangle$. Using Eq. (30), we obtain

$$X_1=au_{bc}+bu_{ac}+cu_{ab},$$
$$u_{ab}=\frac{1}{e_a+e_b}(J_{ab}-V_{AB})(ab), \quad \text{etc.} \quad \text{(A2)}$$

Then

$$E_2=\langle(abc),\ (V_{AB}+V_{BC}+V_{AC})X_1\rangle, \quad \text{(A3)}$$

or

$$E_2=\langle ab,V_{AB}\,u_{ab}\rangle+\langle ac,V_{AC}\,u_{ac}\rangle+\langle bc,V_{BC}\,u_{bc}\rangle +2[\langle abc,V_{AC}\,cu_{ab}\rangle+\langle abc,V_{AC}\,au_{bc}\rangle +\langle abc,V_{AB}\,bu_{ac}\rangle]. \quad \text{(A4)}$$

The first three terms of Eq. (A4) are the pair inter-

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[10] The "exclusion effects" can be formally incorporated into the pair energies by making each u_{ij} orthogonal to the remaining occupied orbitals $k\neq i,\ j$; e.g., in Li, we substitute

$$u_{12}'(\mathbf{x}_1,\mathbf{x}_2)=u_{12}(\mathbf{x}_1,\mathbf{x}_2)-\sqrt{2}\mathcal{B}_{12}\{\langle u_{12}(\mathbf{x}_1,\mathbf{x}_2),3(\mathbf{x}_2)\rangle_{\mathbf{x}_2}3(\mathbf{x}_2)\}$$

for u_{12} in $\langle\mathcal{B}(12),g_{12}u_{12}\rangle$. The $\langle\quad\rangle_{\mathbf{x}_2}$ means integration over $\mathbf{x}_2$ only. We have $\langle u_{12}'(\mathbf{x}_1,\mathbf{x}_2),3(\mathbf{x}_2)\rangle_{\mathbf{x}_2}=0$. The u_{12}'s in the other two terms of Eq. (50) are left unchanged. In an atom or molecule with more than three electrons, there will also be four-electron exclusion effects.[5] These arise because double excitations to a pair of orbitals occupied by two other electrons in Φ_0 are excluded by the Pauli principle.[1,5] The four-body exclusion effect will be much less than a three-body exclusion effect; because in the latter, not just one, but a whole set of double excitations are involved. These are the missing transitions of an electron to a complete set orbitals while another is prevented from going into an orbital already occupied by a third electron (see reference 5).

[11] H. A. Bethe, Phys. Rev. **103**, 1353 (1956).

[12] Oktay Sinanoğlu and E. M. Mortensen, J. Chem. Phys. (to be published).

actions. Notice that they include the mutual *electrostatic polarization within a pair in addition to the usual dispersion forces*. The last three terms are the 3-body "cross-polarization" terms mentioned in the text [see Eq. (50)]. If the atoms A, B, and C are neutral and spherical and if V_{AB} is expanded in a multipole series keeping only the dipole-dipole term, the pair polarization and the cross terms vanish. Then E_2 reduces simply to the sum of the usual London dispersion energies.[13,14]

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[13] F. London, Z. Physik Chem. **B11**, 222 (1930).

[14] H. Margenau, Revs. Modern Phys. **11**, 1 (1939).

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Proton-Hydrogen Scattering System*

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The impact parameter treatment of the scattering of protons by hydrogen is derived and is shown to be valid for energies greater than a few electron volts. A novel treatment of the resultant equations is given which significantly modifies previously obtained results for inelastic scattering and charge-exchange scattering.

I. INTRODUCTION

It has long been realized that the system of two protons and an electron is one of the simpler three-body problems in quantum mechanics because of the large disparity in the electron and proton masses. Born and Oppenheimer[1] used this fact to treat the bound states of H_2^+. They made the approximation that the protons moved very slowly compared with the electrons. The resultant problem, the motion of the electron in the field of two fixed protons, could then be solved exactly.[2] Similar approximations were made for the scattering problem,[3] resulting in good agreement with experiment for low energies. The high-energy problem has been treated by Born approximation,[4] but the discussion of capture collisions has been somewhat clouded by the lack of orthogonality of the initial and final states and the consequent ambiguity in the contribution of the proton-proton potential to these rearrangement processes.[5] The high-energy scattering has also been treated by an "impact parameter method," where it has been shown that a "Born approximation" in this method is equivalent to the usual Born approximation in the limit of the electron-to-proton mass ratio vanishing.[6]

It is the object of this paper to present a systematic derivation of the "impact parameter method" (Sec. II). It will develop that it is suitable for the description of collisions for proton energies of the order of a few hundred electron volts and greater. In Sec. III an expansion is made which is suitable for direct (not rearrangement) collisions. This is used to develop an "improved Born approximation" which is used to calculate the cross section for the transition

$$p+\mathrm{H}(1s) \rightarrow p+\mathrm{H}(2s)$$

as an example. In Sec. IV an expansion is made which is suitable for the description of rearrangement collisions. A similar "improved Born approximation" is developed here with the result that the initial and final states are automatically orthogonalized, thus eliminating the difficulties mentioned above in connection with this calculation. The method is applied to the calculation of the cross section for the process

$$p+\mathrm{H}(1s) \rightarrow \mathrm{H}(1s)+p$$

as an example.

In Sec. V the problem of handling the low-energy and intermediate-energy ranges is briefly discussed.

II. THE IMPACT PARAMETER METHOD

A Born approximation calculation for the total scattering of a proton by atomic hydrogen yields the fact that the mean angle of scattering is of the order $(m|W_0|/ME)^{\frac{1}{2}}$, where $|W_0|=13.6$ ev is the binding energy of hydrogen and E is the incident proton energy.[5] For incident proton energies above an electron volt or so this is an extremely small angle, indicating that the proton travels in essentially a straight line. This means that the protons are distinguishable and that the Pauli

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[1] M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

[2] E. Teller, Z. Physik **61**, 458 (1930).

[3] N. F. Mott, Proc. Cambridge Phil. Soc. **27**, 553 (1931); D. R. Bates, H. S. W. Massey, and A. L. Stewart, Proc. Roy. Soc. (London) **A216**, 437 (1953); D. R. Bates and R. McCarroll, Proc. Roy. Soc. (London) **A245**, 175 (1958); A. Dalgarno and H. N. Yadav, Proc. Phys. Soc. (London) **A66**, 173 (1953).

[4] H. C. Brinkmann and H. A. Kramers, Proc. Acad. Sci. Amsterdam **33**, 973 (1930); referred to hereafter as B-K.

[5] J. D. Jackson and H. Schiff, Phys. Rev. **89**, 359 (1953); D. R. Bates and G. Griffing, Proc. Phys. Soc. (London) **A66**, 961 (1953).

[6] J. W. Frame, Proc. Cambridge Phil. Soc. **27**, 511 (1931).