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PERTURBATION THEORY OF MANY ELECTRON

ATOMS AND MOLECULES

Oktay Sinanoglu

July 1960

Perturbation Theory of Many Electron Atoms and Molecules

Oktaç Sinanoğlu

ABSTRACT

Perturbation theory with operator techniques is applied to a non-degenerate many electron system taking the electron repulsions,  $\sum_{i < j}^N r_{ij}^{-1}$ , as the perturbation. The first order wave function (W.F.),  $\chi_1$ , is obtained rigorously in terms of the first order W.F.'s of independent two electron systems. The pair functions containing nuclear parameters can be solved for 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  $\chi_1$  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.

Perturbation Theory of Many Electron Atoms and Molecules

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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, 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.

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The shell structure of atoms, the independent behaviour 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  $\text{Li}^+$  ion and the core of Li atom?

Recently<sup>1</sup> we treated a many electron system by second order perturbation theory starting from the Hartree-Fock energy. We used the ordinary Rayleigh-Schrödinger (R.S.) method and classified all the virtual transitions

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<sup>1</sup>Oktay Sinanoglu, J. Chem. Phys., Oct. 1960 (in press).

represented by the unperturbed determinantal eigenfunctions<sup>†</sup>. Thus the energy was obtained as a sum of pair energies and "exclusion effects,"

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<sup>†</sup>This is equivalent to the second quantized or hole-particle formalism.

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<sup>2</sup>

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<sup>2</sup>See e.g.

K. A. Brueckner, in "The Many Body Problem," Grenoble Université (Wiley, New York, 1959).

This theory is also based on pair correlations, but for finite systems (See R. J. Eden, in Nuclear Reactions, I (North-Holland Publ. Co., Amsterdam 1958) it requires as yet formidable self-consistency procedures.

all the electrons of the N-electron system (the "medium") affect a correlating pair i) by their average (SCF) 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 non-degenerate N-electron system taking the entire interelectronic repulsion,  $\sum_{i>j=1}^N 1/r_{ij}$  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 determined mainly for He-like systems.<sup>3</sup> These can be used for

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<sup>3</sup>E. A. Hylleraas, Z. Physik 65, 209 (1930).

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 Section IV. The formalism will also be applied separately<sup>4</sup> to the correlation energy of

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<sup>4</sup>Oktay Sinanoğlu, Proc. Roy. Soc. (London), (to be published).

a many electron system starting from its Hartree-Fock solution and obtaining the results of Reference 1 in closed and rigorous form.

## II. The Perturbation Method

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

$$\begin{aligned} (H_0 + H_1)\psi &= E\psi \\ H_0 \phi_0 &= E_0 \phi_0 ; \quad \langle \phi_0, \phi_0 \rangle = 1. \end{aligned} \quad (1)$$

If we write:

$$\psi = \phi_0 + \chi$$

such that

$$\langle \phi_0, \psi \rangle = 1, \quad \langle \phi_0, \chi \rangle = 0 \quad (2)$$

we get exactly

$$E = \langle \phi_0, H\psi \rangle = E_0 + \langle \phi_0, H_1 \chi \rangle \quad (3)$$

Perturbation solution is obtained by:

$$\begin{aligned} \chi &= \chi_1 + \chi_2 + \dots \\ \text{and } E - E_0 &= E_1 + E_2 + E_3 + \dots \end{aligned} \quad (4)$$

$\chi_1$  is a solution of:

$$(H_0 - E_0) \chi_1 = (E_1 - H_1) \phi_0 = -Q H_1 \phi_0, \quad (5)$$

where

$$E_1 = \langle \phi_0, H_1 \phi_0 \rangle$$

and

$$Q = 1 - \phi_0 \langle \phi_0, \quad \text{is an operator that projects out } \phi_0.$$

The  $x_1$  determines the energy to third order:<sup>5</sup>

<sup>5</sup>Bethe and Salpeter, *Encyclopedia of Physics*, Vol. 35, (Springer-Verlag, Berlin 1957).

$$E_2 = \langle \phi_0, H_1 x_1 \rangle - E_1 \langle \phi_0, x_1 \rangle \quad (6)$$

$$E_3 = \langle x_1, H_1 x_1 \rangle - E_1 \langle x_1, x_1 \rangle - 2E_2 \langle \phi_0, x_1 \rangle \quad (7)$$

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.<sup>6</sup> Energies to even orders, however, do not have this

<sup>6</sup>To see the relation between the energy calculated to third order and the exact  $E$ , substitute  $(\phi_0 + x_1)$  with  $\langle \phi_0, x_1 \rangle = 0$  in  $(\langle \psi, H \psi \rangle / \langle \psi, \psi \rangle) \geq E$  and use Eqs. (6), (7) and the relation:  $\langle x_1, H_0 x_1 \rangle = E_0 \langle x_1, x_1 \rangle - \langle x_1, H_1 \phi_0 \rangle$  which follows from Eq. (5). Then we have

$$E < E_0 + E_1 + \frac{E_2 + E_3}{1 + \langle x_1, x_1 \rangle} < E_0 + E_1 + E_2 + E_3$$

since  $\langle x_1, x_1 \rangle = |x_1|^2 > 0$ . The normalization correction is of the fourth higher orders.

and/ See also: Morse and Feshbach, Methods of Theoretical Physics, Vol. II

(McGraw Hill Book Co., New York 1953); pp. 1119-20.

relation to  $\underline{E}$ .

Equation (5) is a non-homogeneous partial differential equation. It has solutions only if the solutions of the corresponding homogeneous equation are orthogonal to the non-homogeneity,<sup>7</sup>  $QH_1\phi_0$ .

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<sup>7</sup>B. Friedman, Principles and Techniques of Applied Mathematics, (J. Wiley and Sons, Inc., New York 1957).

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This means that in cases of degeneracy, the degenerate zero order eigenfunctions,  $\phi_0^k$ , must be chosen so as to satisfy

$$\langle \phi_0^i, QH_1\phi_0^k \rangle = 0 \quad (8)$$

Then a different equation like Eq. (5) can be written down for every  $\phi_0^k$  with a solution  $x_1^k$ .

Equation (5) is equivalent to the extremum condition:

$$\delta \left\{ 2 \langle x_1, (H_1 - E_1) \phi_0 \rangle + \langle x_1, (H_0 - E_0) x_1 \rangle \right\} = 0 \quad (9a)$$

In particular, the  $x_1$  for the lowest  $\frac{\text{state of a given symmetry}}{\text{state of a given symmetry}}$  can be found approximately by minimizing

$$E_2 \leq \left\{ 2 \langle x_1^{\text{tr}}, (H_1 - E_1) \phi_0 \rangle + \langle x_1^{\text{tr}}, (H_0 - E_0) x_1^{\text{tr}} \rangle \right\} \quad (9b)$$

with suitable trial functions,  $x_1^{\text{tr}}$ . Hylleraas has used Eq. (9) to obtain the  $\underline{E}_2$  and  $x_1$  for the ground state of the He atom<sup>3</sup>.

The  $\chi_1$  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<sup>8</sup> and shown that for an excited state,  $\chi_1^{tr}$  must be chosen subject to some restrictions which require a knowledge of only the unperturbed W. F.'s of the lower states.

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<sup>8</sup>O. Sinanoğlu, Phys. Rev. (To be published).

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The particular solution,  $x_1^P$ , of Eq. (5) is given by:

$$x_1^P = L_0^{-1} (E_1 - H_1) \phi_0 \quad (10)$$

where  $L_0^{-1} = (H_0 - E_0)^{-1}$  is the Green's function operator. But the general solution,  $x_1$ , is:

$$x_1 = x_1^P + C \phi_0; \quad (11a)$$

$C$  is an arbitrary constant which can be chosen such that

$$\langle \phi_0, x_1 \rangle = 0 \quad (11b)$$

Let the non-degenerate ground state of an  $N$  electron system be :

$$\begin{aligned} \phi_0(x_1, x_2, \dots, x_N) &= \frac{1}{\sqrt{N!}} \det \left\{ 1(x_1) \ 2(x_2) \ \dots \ N(x_N) \right\} \\ &= \mathcal{A} \left\{ 1(x_1) \ 2(x_2) \ \dots \ N(x_N) \right\} = \mathcal{A}(123\dots N) \end{aligned}$$

$\mathcal{A}$  is the anti-symmetrizing operator:

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P = \frac{1}{\sqrt{N!}} \det \quad (13)$$

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

$$H_0 = \sum_{i=1}^N h_i^0; \quad h_i^0 = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{R_{\alpha i}}$$

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

$$H_1 = \sum_{i>j=1}^N \epsilon_{ij}; \quad \epsilon_{ij} = \frac{1}{r_{ij}} \quad (14)$$

in atomic units (1 a.u. = 27.2 ev. ).  $R_{\alpha i}$  is the distance of electron  $i$  to nucleus  $\alpha$ .  $1(x_1), 2(x_2), \dots, k(x_k)$  in Eq. (12) are the spin-orbitals satisfying

$$h_i^0 k(x_i) = \epsilon_k^0 k(x_i) \quad (15)$$

$x_i$  designates both the space ( $r_i$ ) and the spin ( $s_i$ ) coordinates of the electron  $i$ . In atoms, the complete one electron basis set  $\{k\}$  is the hydrogen-like orbitals multiplied by spin  $\alpha$  or  $\beta$ . Thus  $1 = 1s_\alpha, 2 = 1s_\beta, \dots$  so that all odd integers stand for spin-orbitals with  $\alpha$  spin, and all even ones for those with  $\beta$ .

From Eqs. (12) and (14):

$$E_1 = \langle \phi_0, H_1 \phi_0 \rangle = \sum_{i>j=1}^N (J_{ij} - K_{ij}^{11}) \quad (16)$$

$J_{ij}$  and  $K_{ij}^{11}$  are the coulomb and exchange integrals between the orbitals  $i$  and  $j$ :

$$J_{ij} = \langle 1(x_1) j(x_2), \epsilon_{12} 1(x_1) j(x_2) \rangle = \langle ij, \epsilon_{12} ij \rangle \quad (17)$$

$$K_{ij}^{11} = \langle 1(x_1) j(x_2), \epsilon_{12} j(x_1) i(x_2) \rangle = \langle ij, \epsilon_{12} ji \rangle$$

$K_{ij}^{11}$  is non-zero only for  $i$  and  $j$  of like spin.

Notice that in Eq. (12), before  $\epsilon_{ij}$  is applied, a spin-orbital and the electron occupying it are designated by the same numeral, e.g.  $1(x_1), 2(x_2)$ , etc.

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

$$L_0^{-1} = \sum_{\substack{k=1 \\ \vdots \\ n=1}}^N \frac{k(x_1) \delta(x_2) \dots n(x_N) \rangle \langle k(x_1) \delta(x_2) \dots n(x_N)}{(\epsilon_k^0 + \epsilon_l^0 + \dots + \epsilon_n^0) - (\epsilon_1^0 + \epsilon_2^0 + \dots + \epsilon_N^0)} \quad (18)$$

for the space of distinguishable electrons, and by

$$L_0^{-1} = \sum_{\substack{kl \dots n \\ \Rightarrow k > 1}} \frac{\mathcal{A}(kl \dots n) \rangle \langle \mathcal{A}(kl \dots n)}{(\epsilon_k^0 + \epsilon_l^0 + \epsilon_n^0) - (\epsilon_1^0 + \epsilon_2^0 + \epsilon_N^0)} \quad (19)$$

for the anti-symmetric space of N fermions. In Eq. (18), *k*, *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  $\frac{N!}{N!} = 1$  Slater determinants, i.e. "ordered configurations" <sup>1</sup> that can be formed from  $\{k\}$ . For use in the next section we also define:

$$e_1 = h_1^0 - \epsilon_1^0 + (\text{spin part})_1 \quad (20a)$$

and write

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

III. Separation into Pairs

We now write  $\chi_1$ , 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 <sup>e.g.</sup> of the He atom.<sup>3</sup>

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:

$$\chi_1 = L_0^{-1} (E_1 - H_1) \phi_0 = L_0^{-1} \left\{ \sum_{1>j=1}^N (J_{1j} - K_{1j}^{11}) - \sum_{1>j=1}^N g_{1j} \right\} \Delta (123\dots N) \quad (21)$$

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

$$\chi_1 = L_0^{-1} \Delta \left\{ \sum_{1>j=1}^N (J_{1j} - K_{1j}^{11} - g_{1j}) \right\} (123\dots N) \quad (22)$$

where

$$(123\dots N) = (1(x_{\tilde{1}}) 2(x_{\tilde{2}}) 3(x_{\tilde{3}}) \dots N(x_{\tilde{N}})) .$$

In  $g_{1j}$ ,  $\tilde{1}$  and  $\tilde{j}$  refer to the electrons ( $r_{\tilde{1}}$  and  $r_{\tilde{j}}$ ), whereas in  $(J_{1j} - K_{1j}^{11})$  they refer to the orbitals  $\underline{1}$  and  $\underline{j}$ . Since there is a one-to-one correspondence between  $\underline{1}$  and  $\tilde{1}$  before operating by  $\Delta$ , we associate a  $(J_{1j} - K_{1j}^{11})$  with each  $g_{1j}$  and write

$$m_{1j} = J_{1j} - K_{1j}^{11} - g_{1j} \quad ; \quad (23)$$

then in Eq. (22):

$$\mathcal{A} \left\{ \sum_{i>j=1}^N (J_{ij} - K_{ij}^{11} - \epsilon_{ij}) (123\dots N) \right\} = \sum_{i>j} \mathcal{A} \left\{ m_{ij}(123\dots N) \right\} \quad (24)$$

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

$$\chi_1 = L_0^{-1} \sum_{i>j} \mathcal{A} \left\{ m_{ij}(123\dots N) \right\} = \mathcal{A} L_0^{-1} \sum_{i>j=1}^N m_{ij}(123\dots N) \quad (25)$$

If now  $L_0^{-1} = (e_1 + e_2 + \dots + e_N)^{-1}$  were applied to each  $m_{ij}(123\dots N)$  term in Eq. (25) separately, it would have singularities in each such term, corresponding to degeneracies of the type  $1(x_1) 2(x_2)$  with  $1(x_2) 2(x_1)$ , etc. (See e.g. Eq. (18)). Of course these singularities cancel in the sum after applying  $\mathcal{A}$  in Eq. (25), so that  $\chi_1$  is finite.

To get  $\chi_1$  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  $B_{ij}$  in front of each  $m_{ij}$ .  $B_{ij}$  is the anti-symmetrizer that operates only on  $x_i$  and  $x_j$ ; i.e.

$$B_{ij} = \frac{1}{\sqrt{2!}} (1 - P_{ij}) = \frac{1}{\sqrt{2!}} \det \quad (26)$$

$P_{ij}$  interchanges only  $x_i$  and  $x_j$  and leaves the other electrons the same. Since  $P_{ij}$  is an element of the permutation group of  $N$  electrons, the following relation holds:

$$\frac{1}{\sqrt{2}} \mathcal{A} B_{ij} = \mathcal{A} \quad (27)$$

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

$$\begin{aligned} \sum_{i>j=1}^N \mathcal{A} \{m_{ij} (123\dots N)\} &= \sum_{i>j=1}^N \frac{\mathcal{A}}{\sqrt{2}} B_{ij} \{m_{ij} (123\dots N)\} \\ &= \frac{\mathcal{A}}{\sqrt{2}} \sum_{i>j=1}^N m_{ij} B_{ij} (123\dots N) \end{aligned} \quad (28)$$

and 
$$\chi_1 = \frac{1}{\sqrt{2}} \mathcal{A} \sum_{i>j=1}^N \frac{1}{e_1 + e_2 + \dots + e_N} m_{ij} B_{ij} (123\dots N) \quad (29)$$

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

$$e_1 i(\chi_1) = 0, \quad (30a)$$

thus<sup>7</sup> for any analytic function,  $f$  of  $e_1$ :

$$f(e_1) i = f(0) i \quad (30b)$$

Therefore:

$$\begin{aligned} \frac{1}{e_1 + e_2 + \dots + e_N} m_{ij} B_{ij} (12\dots ij\dots N) &= (12\dots (i-1)(j+1)\dots N) \\ &\times \frac{1}{e_1 + e_j} m_{ij} B_{ij} (ij) \end{aligned} \quad (31)$$

and

$$\begin{aligned} \chi_1 &= \frac{1}{\sqrt{2}} \mathcal{A} \left\{ \sum_{i>j=1}^N (12\dots (i-1)(j+1)\dots N) \right. \\ &\times \left. \frac{1}{e_1 + e_j} m_{ij} B_{ij} (ij) \right\} \end{aligned} \quad (32)$$

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

Some of the (1j) terms in Eq. (32) are already in the desired non-singular forms, others are not. To examine each term in detail concretely we now continue the derivation with a specific case: The Li atom.

Then  $\phi_0(x_1, x_2, x_3) = \mathcal{A}(123)$  and

$$(123) = \left( 1s_\alpha(x_1) 1s_\beta(x_2) 2s_\alpha(x_3) \right) \quad (33)$$

$\chi_1$  becomes:

$$\chi_1 = \frac{1}{\sqrt{2}} \mathcal{A} \left\{ 1(x_1) u_{23}(x_2, x_3) + 2(x_2) u_{13}(x_1, x_3) + 3(x_3) u_{12}(x_1, x_2) \right\} \quad (34a)$$

where

$$u_{ij} \equiv \frac{1}{e_i + e_j} m_{ij} B(1j) \quad (34b)$$

Our aim is to write each  $u_{ij}$  as the solution of a non-homogeneous 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

$$(e_i + e_j) u_{ij} = m_{ij} B(1j) \quad (35)$$

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

$$\langle \phi_{ij}^k, m_{ij} B(1j) \rangle = 0 \quad (36)$$

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

$$(e_1 + e_j) \phi_{ij}^k = 0 \quad (37)$$

degenerate with it. If Eq. (36) holds, then  $u_{ij}$  can be obtained from Eq. (35) by any method (including variational,<sup>8</sup> 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:  $u_{12}(x_1, x_2)$  is the first order wave function of free  $\text{Li}^+$  ion in its ground state and satisfies

$$(e_1 + e_2) u_{12} = (J_{12} - \mathcal{E}_{12}) \mathcal{B}(1s_\alpha 1s_\beta) \quad (38)$$

Also,  $u_{13}$  is given by:

$$(e_1 + e_3) u_{13} = (J_{13} - K_{13} - \mathcal{E}_{13}) \mathcal{B}(1s_\alpha 2s_\alpha) \quad (39)$$

and is the same as the  $(1s2s) {}^3S$  state of  $\text{Li}^+$ . It is not possible to write directly such an equation for  $u_{23}$ . This case violates Eq. (36), because  $\mathcal{B}_{23}(23) = \frac{1}{\sqrt{2!}} \det(1s_\beta 2s_\alpha)$  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:

$$\frac{1}{e_1 + e_2 + e_3} \frac{\mathcal{A}}{\sqrt{2}} (J_{23} - \mathcal{E}_{23}) \left\{ 1(x_1) \mathcal{B}(23) \right\} \quad (40)$$

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

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

(+) sign refers to the triplet state and  $B(14) = \frac{1}{\sqrt{2!}} \det(1s_{\alpha} 2s_{\beta})$ .

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

$$L_0^{-1} \frac{1}{2} \frac{\mathcal{A}}{\sqrt{2}} \left\{ (J_{23} - K_{23} - \epsilon_{23}) (1B(23)) + (J_{23} + K_{23} - \epsilon_{23}) (1B(23)) \right\} \quad (42)$$

If  $(J_{23} - \epsilon_{23}) [1(x_1)B(1(x_2)4(x_3))]$  is added and subtracted and then

$K_{23} [1(x_1)B(1(x_2)4(x_3))]$  is added to each one of its terms, Eq. (42)

remains unchanged, since

$$\mathcal{A} \left\{ 1(x_1)B(1(x_2)4(x_3)) \right\} = 0 \quad (43)$$

Then using Eq. (41), we get:

$$L_0^{-1} \frac{\mathcal{A}}{\sqrt{2}} (J_{23} - \epsilon_{23}) \left\{ 1B(23) \right\} = L_0^{-1} \frac{1}{2} \frac{\mathcal{A}}{\sqrt{2}} \left\{ 1(x_1) \left[ (J_{23} - K_{23} - \epsilon_{23}) \right. \right. \\ \left. \left. 3\phi_{23}(x_2, x_3) + (J_{23} + K_{23} - \epsilon_{23}) 1\phi_{23}(x_2, x_3) \right] \right\} \quad (44)$$

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):

$$u_{23}(x_2, x_3) = \frac{1}{\sqrt{2}} \left( {}^3u_{23}(x_2, x_3) + {}^1u_{23}(x_2, x_3) \right) \quad (45a)$$

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

$$\left. \begin{aligned} (e_2 + e_3) {}^3u_{23} &= (J_{23} - K_{23} - g_{23}) {}^3\phi_{23} \\ (e_2 + e_3) {}^1u_{23} &= (J_{23} + K_{23} - g_{23}) {}^1\phi_{23} \end{aligned} \right\} \quad (45b)$$

${}^3u_{23}$  and  ${}^1u_{23}$  must be made orthogonal to  ${}^3\phi_{23}$  and  ${}^1\phi_{23}$  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  $\chi_1$  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 no.  $Z$  as Hylleraas<sup>3</sup> 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! In general the number of independent pair states needed will be less than the total no. of pairs, because of the multiplicity of some of the pair states.

For the  $N$ -electron system with a single determinant  $\phi_0$ , we now have (cf Eq. (32)):

$$\chi_1 = \frac{1}{\sqrt{2}} \mathcal{A} \left\{ \sum_{i>j=1}^N (12\dots(i-1)(j+1)\dots N) u_{ij} \right\} \quad (46)$$

Wherever  $B(ij)$  belongs to a row of an irreducible representation of the symmetry group of the two electron Hamiltonian,  $(h_1^0 + h_j^0 + g_{ij})$ , the corresponding  $u_{ij}$  is the solution of:

$$(e_i + e_j) u_{ij} = m_{ij} B(ij) \quad (47)$$

such that,  $\langle u_{ij}, B(ij) \rangle = 0$ . 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<sup>5</sup>, and the variational extension to any excited state has been discussed by the author<sup>3</sup> method, Eq. (9), and its/ All the two electron degeneracies, e.g. arising from angular momentum, etc., can first be removed in the same way as shown for the  $1s\ 2s_{\beta\alpha}$  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.,  $\chi_1$ . Since each  $u_{ij}$  in Eq. (46) is orthogonal to its  $B(ij)$  or  $\phi_{ij}$ , we have  $\langle \phi_0, \chi_1 \rangle = 0$ ; then

$$E_2 = \langle \phi_0, H_1 \chi_1 \rangle = \langle \mathcal{A}(123\dots N), \left( \sum_{i>j=1}^N g_{ij} \right) \frac{\mathcal{A}}{\sqrt{2}} \left\{ \sum_{i>j} (12\dots(i-1)(j+1)\dots N) u_{ij} \right\} \rangle$$

$$= \sqrt{N!}/2 \langle \mathcal{A}(123\dots N), (g_{12} + g_{13} + \dots) \left[ (34\dots N) u_{12} + (1256\dots N) u_{34} + \dots \right] \rangle$$

The last step follows because  $\mathcal{A}$  is self-adjoint and  $\mathcal{A}^2 = \sqrt{N!} \mathcal{A}$ .

In  $(34\dots N) u_{12}$ , etc. orbital and electron indices are the same ( $3(x_3)$ , etc.).

For Li atom, Eq. (48) gives:

$$\begin{aligned}
E_2 = & \langle \mathcal{B}(12), \varepsilon_{12} u_{12} \rangle + \langle \mathcal{B}(13), \varepsilon_{13} u_{13} \rangle + \langle \mathcal{B}(23), \varepsilon_{23} u_{23} \rangle \\
& + \sqrt{3! 2!} \left\{ \langle \mathcal{A}(123), \varepsilon_{13} {}^3(x_3) u_{12}(x_1, x_2) \rangle \right. \\
& + \langle \mathcal{A}(123), \varepsilon_{13} {}^1(x_1) u_{23}(x_2, x_3) \rangle \\
& \left. + \langle \mathcal{A}(123), \varepsilon_{12} {}^2(x_2) u_{13}(x_1, x_3) \rangle \right\} \quad (49)
\end{aligned}$$

The first term is simply the ground state  $E_2$  of  $(Li^+)$ ; from Eq. (45a), the sum of <sup>the</sup> 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.  $\langle \mathcal{B}(12), \varepsilon_{12} u_{12} \rangle$  is the entire  $E_2$  of  $Li^+$  ion. It includes both the dispersion and the "orbital average polarization" terms<sup>1</sup> 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-pairwise 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:

$$\begin{aligned}
\sqrt{3! 2!} \langle \mathcal{A}(123), \varepsilon_{13} {}^3(x_3) u_{12}(x_1, x_2) \rangle = & 2 \left\{ \langle {}_2 \mathcal{B}(1_1 3_3), \varepsilon_{13} {}^3 u_{12} \rangle \right. \\
& \left. - \langle {}_1 \mathcal{B}(2_1 3_3), \varepsilon_{13} {}^3 u_{12} \rangle - \langle {}_3 \mathcal{B}(1_1 2_3), \varepsilon_{13} {}^3 u_{12} \rangle \right\} \quad (50)
\end{aligned}$$

where we have used subscripts for electron coordinates, e.g.  $1_2 = 1(x_2)$ , etc., and  $u_{12} = u_{12}(x_1, x_2)$ . The last term is the "exclusion effect"<sup>1</sup> of the occupied orbital 3 on the correlating pair of electrons<sup>#</sup> in  $u_{12}$ . As

# 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  $u'_{12}(x_1, x_2) = u_{12}(x_1, x_2)$

Continuation of Footnote #.

$$-\sqrt{2} B_{12} \left\{ \langle u_{12}(x_1, x_2), 3(x_2) \rangle_{x_2} 3(x_2) \right\} \text{ for } u_{12} \text{ in } \langle B(12), g_{12} u_{12} \rangle.$$

The  $\langle \rangle_{x_2}$  means integration over  $x_2$  only. We have  $\langle u_{12}^y(x_1, x_2), 3(x_2) \rangle_{x_2} = 0$ .

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<sup>4</sup>. These arise because double excitations to a pair of orbitals occupied by two other electrons in  $\Phi_0$  are excluded by the Pauli Principle<sup>1, 4</sup>. 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 4).

discussed in reference 1, this is a three body Fermi correlation. In the theory of nuclear matter<sup>9</sup>, 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 last 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"<sup>1</sup> terms like  $\langle \Phi(123), (\sum_{i,j} g_{ij}) \Phi(12K) \rangle$ . Such "cross polarization" terms come up, as shown in the Appendix, ~~up~~ 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. ~~as it is shown in this appendix.~~

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  $\Phi_0$  and  $\Delta_1$  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<sup>6</sup> in Section 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  $E$ .

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<sup>9</sup>H. A. Bethe, Phys. Rev., ~~99~~ 1353 (1956).

## V. Conclusion

We have shown that the first order wave function,  $\chi_1$ , 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 non-homogeneous differential equation, e.g. by a variational method<sup>8</sup>. Then both the individual pair energies and the non-pairwise additive effects in  $E_2$  and  $E_3$  follow from this  $\chi_1$ . These results should be immediately applicable to atoms, since  $u_{1j}$  can be obtained with explicit  $Z$  dependence<sup>3</sup>, 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<sup>1, 5, 10</sup>. In many molecular problems it is also possible to calculate  $\chi_1$ ,  $E_2$  and  $E_3$  starting from a Hartree-Fock  $\Phi_0$ . There are now many Hartree-Fock molecular orbital (M.O.S.C.F.) calculations available, and we have separately developed<sup>5</sup> methods similar to those given here to obtain correlation energies starting from Hartree-Fock solutions.

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<sup>10</sup>Oktay Sinanoğlu and E. M. Mortensen, J. Chem. Phys. (To be published).

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APPENDIX

Non-pairwise 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:

$$\chi_1 = \frac{1}{e_a + e_b + e_c} \left\{ (J_{ab} - V_{AB}) + (J_{ac} - V_{AC}) + (J_{bc} - V_{BC}) \right\} (abc) \quad (A1)$$

where e.g.  $J_{ab} = \langle ab, V_{AB} ab \rangle$ .

Using Eq. (30):

$$\chi_1 = a u_{bc} + b u_{ac} + c u_{ab} \quad (A2)$$

$$u_{ab} = \frac{1}{e_a + e_b} (J_{ab} - V_{AB}) (ab), \text{ etc.}$$

Then

$$E_2 = \langle (abc), (V_{AB} + V_{BC} + V_{AC}) \chi_1 \rangle \quad (A3)$$

or:

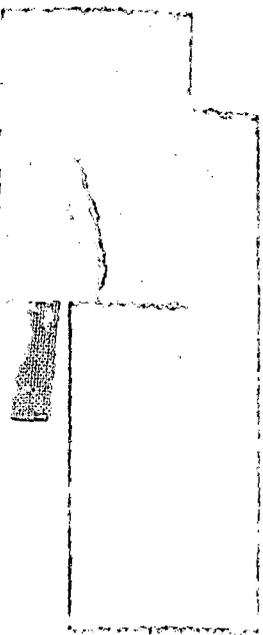
$$E_2 = \langle ab, V_{AB} u_{ab} \rangle + \langle ac, V_{AC} u_{ac} \rangle + \langle bc, V_{BC} u_{bc} \rangle + 2 \left[ \langle abc, V_{AC} a u_{ab} \rangle \right. \\ \left. + \langle abc, V_{AC} a u_{bc} \rangle + \langle abc, V_{AB} b u_{ac} \rangle \right] \quad (A4)$$

The first three terms of Eq. (A4) are the pair interactions. Notice that they include the mutual electrostatic polarization within a pair in addition to the usual dispersion forces.<sup>10</sup> The last three terms are the 3-body "cross-polarization" terms mentioned in the text (cf. 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<sup>11, 12</sup>.

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<sup>10</sup> F. London, Z. Physik. Chem. B11, 222 (1930).

<sup>12</sup> H. Margenau, Revs. Mod. Phys. 11, 1 (1939).



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