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IN ATOMS AND MOLECULES

Oktay Sinanoğlu

July 1960

Theory of Electron Correlation in Atoms and Molecules

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ABSTRACT

Corrections to the Hartree-Fock (H.F.) wave function, Φ_0 , and energy of a many electron system are given. By the use of operator techniques in perturbation theory, the first order W.F., X'_1 , is obtained in terms of pair functions. These satisfy equations just like those of an actual two electron system except that now each electron moves in the H.F. field of the entire N-electron "medium" added to the field of nuclei. Every pair function must be orthogonalized to each of the two H.F. orbitals associated with it to get the complete X'_1 . This X'_1 determines both E_2 and E_3 . The second order energy, E_2 , comes out as the sum of pair interactions and three and four body correlations due to the exclusion principle. The latter may be incorporated into the pair energies if each pair function is orthogonalized also to the remaining H.F. orbitals of Φ_0 . The approach allows the valence and inner shells, etc. to be discussed separately and extends some of the concepts of quantum chemistry based on orbital approximations so as to include correlation.

Theory of Electron Correlation in Atoms and Molecules

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INTRODUCTION

The best solution of an N-electron system in the form of a determinant of N spin-orbitals is given by the Hartree-Fock method. This is a very good starting point, but not good enough to yield the small energy differences of chemistry and spectroscopy. The energy difference between the Hartree-Fock (H.F.) and the exact non-relativistic solution is called the "correlation energy" and amounts to about 23 kcal/mole per doubly filled orbital.

The next best thing to the orbital approximation is to try to build up a many electron system from groups of electrons each containing some correlation. A natural building block to choose for this would be an electron pair, since the only satisfactory energy calculations so far have been on He and H₂.

As we showed recently (Sinanoğlu 1960a) perturbation theory allows one to talk of groups of electrons in a non-arbitrary way, i.e. by taking the indistinguishability of the electrons fully into account. We started from the occupied H.F. orbitals and classified the complete set of Slater

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determinants as to the virtual transitions they represent. In this way, the second order energy, E_2 , was separated into the energies of antisymmetrized pairs and three and four-body Fermi correlations ("exclusion effects"). The use of ordinary Schrödinger-type perturbation theory leads to infinite sums, e.g. in E_2 , which are very difficult to evaluate. The largest contributions to such sums come from the continuum part of the orbital basis set used (Lowdin 1959). Hence we suggested semi-empirical means of getting the pair energies. The exclusion effects were separated and obtained in closed form but approximately by replacing the energy denominators with "mean excitation energies".

In this article we develop a rigorous theory to obtain the corrections to the H.F. wave function (W.F.) and energy of a many electron system in terms of those of electron pairs and added exclusion effects. Formal perturbation theory with operator technique_g is used and the infinite sums of the usual form of the Schrödinger method are avoided. We take the single determinant H.F. solution of an atom or molecule as its non-degenerate zero order W.F., Φ_0 , and then give its first order W.F., X_1 , rigorously in terms of pair functions. Each pair function satisfies an independent equation which can be solved separately (e.g. by variational principles) just like the ground or an excited state of any two electron system. The only difference is that the electrons of the pair in the N-electron "medium", move in a Hartree-Fock potential rather than in the field of

bare nuclei. The techniques used for He and H_2 (e.g. W.F. with r_{12} in it) can now be applied to such "immersed" pairs. The "immersed pair" functions as such do not determine X_1^I completely. It will be shown below that the exact X_1^I is obtained after orthogonalizing each "immersed pair" function to its pair of the H.F. orbitals. X_1^I yields E_2 as the sum of pair energies and exclusion effects. The latter can be formally incorporated into the pair energies by orthogonalizing the new pair functions to the remaining H.F. orbitals of Φ_0 .

The same X_1^I yields the third order energy, E_3 , as well. Then having started from an H.F. solution, this should give the correlation energy to sufficient accuracy. The approach presented here also provides basis for many chemical concepts (Sinanoglu 1960a). It allows the core and valence electrons, sigma and pi electrons, etc. to be treated in a separate, yet non-arbitrary fashion.

We have applied the same formalism before to an N-electron system starting with the bare nuclei Hamiltonian instead of the Hartree-Fock solution and taking the entire interelectronic repulsion ($H_1 = \sum_{i>j=1}^N r_{ij}^{-1}$) as the perturbation (Sinanoglu 1960b). The pair functions in this case are totally independent of the "medium" and correspond to the first order W.F.'s of the actual states of a real two electron system. For example, Li atom is built up from the $(1s)^2 {}^1S$, $(1s2s) {}^3S$ and 1S states of Li^+ . With $H_1 = \sum_{i>j} r_{ij}^{-1}$ the entire X_1 is given by the independent pair functions. The effects of the "medium" show

up in E_2 only as "cross polarization" terms (Sinanoglu 1960b) which are simply added on. This advantage is lost upon starting with an H.F. Φ_0 where the effects of medium become implicit in each pair. On the other hand, the H.F. Φ_0 treatment has the advantage of greater accuracy.

There have been other attempts at obtaining solutions for many electron systems in terms of pairs (Hurley, et. al. 1953) or larger groups (Lykos~~and~~ Parr 1956; McWeeny 1960). These use arbitrary orthogonalization conditions which divide a complete set of one electron orbitals into mutually exclusive subsets. Thus they violate the exclusion principle and are valid only for widely separated groups (Sinanoglu 1960a) (e.g. the far ends of a long molecule).

Pair correlations have been used also in the theory of nuclear matter (Brueckner 1959) and other infinite Fermi gases. But the present form of these theories for finite systems (Eden 1958) require ^{formidable} self-consistency procedures many times more involved than those in the Hartree-Fock method.

THE PERTURBATION METHOD STARTING FROM A HARTREE-FOCK SOLUTION

Perturbation method will be used in the following form:
Let $H = H_0 + H_1$ with H_0 the unperturbed Hamiltonian, H_1 some perturbation and

$$\begin{aligned} (H_0 + H_1)\Psi &= E\Psi \\ H_0\Phi_0 &= E_0\Phi_0; \langle \Phi_0, \Phi_0 \rangle = 1 \end{aligned} \tag{1}$$

ϕ_0 is the zero order W.F., E , Ψ the exact energy and eigenfunction. If we write

$$\Psi = \phi_0 + X \quad (2)$$

such that $\langle \phi_0, \Psi \rangle = 1$, $\langle \phi_0, X \rangle = 0$

we get exactly

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

Upon expanding X and E in terms of a parameter λ and then setting $\lambda = 1$, the perturbation series

$$\begin{aligned} X &= X_1 + X_2 + \dots \\ E &= E_0 + E_1 + E_2 + E_3 + \dots \end{aligned} \quad (4)$$

is obtained. The first order W.F., X_1 is the solution of

$$(H_0 - E_0)X_1 = (E_1 - H_1)\phi_0$$

where

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

and it determines the energy to third order (see e.g. Bethe and Salpeter 1957).

$$E_2 = \langle \phi_0, (H_1 - E_1)X_1 \rangle \quad (6)$$

$$E_3 = \langle X_1, (H_1 - E_1)X_1 \rangle \quad (7)$$

This is general; each order of W.F. (except ϕ_0) determines the energy to two higher orders. Moreover if calculations are carried out to odd orders of energy, e.g. both E_2 and E_3 are obtained from X_1 , the resulting energy will be an upper limit to the exact E (Morse and Feshbach 1953). The same is not true to even orders only.

In cases of degeneracy, the degenerate zero order W.F.'s, ϕ_0^k , corresponding to E_0 , must be so chosen that each $(E_1^k - H_1)\phi_0^k$, where $E_1^k = \langle \phi_0^k, H_1 \phi_0^k \rangle$, will be orthogonal to all ϕ_0^l

$$\langle \phi_0^l, (E_1^k - H_1)\phi_0^k \rangle = 0 \quad (8)$$

(Sinanoglu 1960b). Then there will be a different equation, equation (5), for each ϕ_0^k , and equation (8) will ensure that solutions to these equations exist.

To solve equation (5) for X_1 , one is not restricted to the Schrödinger method of expanding X_1 in terms of the eigenfunctions of H_0 . Other direct means of solving non-homogeneous differential equations may be used. Approximations to X_1 can also be found by minimizing the expression (See e.g. Bethe and Salpeter 1957):

$$E_2 < E_2(X_1^{\text{trial}}) = 2 \langle \phi_0, (H_1 - E_1)X_1^{\text{trial}} \rangle + \langle X_1^{\text{trial}}, (H_0 - E_0)X_1^{\text{trial}} \rangle \quad (9)$$

with respect to trial functions, X_1^{trial} . Equation (9) applies directly if ϕ_0 is a ground state or the lowest state of a given symmetry. For a general excited state a modified minimization procedure has been developed (Sinanoglu 1960c).

The approach to be followed here is to analyze X_1 into components exactly using the inverse operator $L_0^{-1} = (H_0 - E_0)^{-1}$. The components turn out to be pair functions which satisfy 2 electron equations similar to equation (5) and to which the variational principle, equation (9), or its modification (Sinanoglu 1960c) can be applied individually. We start with the zero order W.F., the Hartree-Fock solution.

Consider an N-electron atom or molecule with a Hamiltonian

$$H = \sum_{i=1}^N h_i^0 + \sum_{1>j=1}^N g_{1j} \quad (10)$$

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

$Z_{\alpha}/R_{\alpha i}$ is the potential of electron 1 in the field of nucleus α , and atomic units (1 a.u. = 27.2 ev.) are used. H may be split into: $H = H_0 + H_1$ such that

$$H_0 = \sum_{i=1}^N (h_i^0 + V_1) \quad (11)$$

$$\text{and } H_1 = \sum_{1>j=1}^N g_{1j} - \sum_{i=1}^N V_1$$

V_1 is an average potential that acts on 1 and may be non-local. In the non-degenerate case the best choice for V_1 , i.e. one that leads to the smallest H_1 , is the Hartree-Fock potential:

$$V_1(x_1) = \int \frac{\rho(x_j, x_j)}{r_{1j}} d\tau_j - \int \frac{\rho(x_j, x_1)}{r_{1j}} P_{1j} d\tau_j \quad (12)$$

P_{1j} exchanges x_1 and x_j and $\rho(x_j, x_j)$ is the Fock-Dirac density (see e.g. Löwdin 1959)

$$\rho(x_1, x_j) = \sum_{n'=1}^{N'} n'^*(x_1) n'(x_j) \quad (13)$$

x_1 denotes both the spatial (r_1) and the spin coordinates (ξ_1); $n'(x_1)$ are the Hartree-Fock spin-orbitals[†] (in molecules MO SCF)

[†]Primes will be used to refer to the properties of H.F. orbitals as distinct from the solutions of h_i^0 .

with the orbital energies ϵ'_i , satisfying:

$$h_1^{\text{eff}} n'(\underline{x}_1) = \epsilon'_1 n'(\underline{x}_1) \quad (14)$$

where $h_1^{\text{eff}} = h_1^0 + V_1$. Formally the same V_1 acts on all the n' and 1.

The zero order W.F. is taken here as the normalized determinant

$$\Phi_0 = \frac{1}{\sqrt{N!}} \det \{ 1'(\underline{x}_1) 2'(\underline{x}_2) \cdots N'(\underline{x}_N) \} = A \{ 1' 2' 3' \cdots N' \} \quad (15)$$

A is the anti-symmetrizer:

$$A = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \quad (16)$$

Among the spin-orbitals $1'$ to N' , all odd integers refer to H.F. orbitals multiplied by spin α and all even ones to those with spin β ; e.g. in atoms $1' = 1s_\alpha$, $2' = 1s_\beta$, In equation (15), before A is applied, electron $\underline{x}_1$ occupies the spin-orbital $1'$.

From equation (11) we have:

$$(H_0 - E_0) = \sum_{i=1}^N (h_1^{\text{eff}} - \epsilon'_i) \quad (17)$$

$$E_1 = \langle \Phi_0, \left(\sum_{i,j} g_{ij} - \sum_{i=1}^N V_i \right) \Phi_0 \rangle = - \sum_{i>j=1}^N (J_{ij} - K_{ij}'') \quad (18)$$

where $J_{ij} = \langle 1'(\underline{x}_1) j'(\underline{x}_j), g_{ij} 1'(\underline{x}_1) j'(\underline{x}_j) \rangle = \langle 1' j', g_{12} 1' j' \rangle$
and $K_{ij}'' = \langle 1'(\underline{x}_1) j'(\underline{x}_j), g_{ij} j'(\underline{x}_1) 1'(\underline{x}_j) \rangle = \langle 1' j', g_{12} j' 1' \rangle$

$K_{ij}'' \neq 0$ only for $1'$ and j' of like spin.

The correction, X_1^i , to the H.F. Φ_0 of equation (15) must

be solved from equation (5)

$$L_0 X'_1 = (E_1 - H_1) \Phi_0 = \left\{ \sum_{1>j=1}^N (-J_{1j} + K''_{1j} - g_{1j}) + \sum_{i=1}^N V_i \right\} A(1'2' \dots N') \quad (19)$$

with $L_0 = H_0 - E_0$ of equation (17). Since L_0 is linear, X'_1 and equation (19) can be split into two parts

$$X'_1 = U' - W \quad (20)$$

such that

$$L_0 U' = \left\{ \sum_{1>j=1}^N (J_{1j} - K''_{1j} - g_{1j}) \right\} \Phi_0 \quad (21)$$

$$\text{and } L_0 W = \left\{ \sum_{1>j=1}^N 2(J_{1j} - K''_{1j}) - \sum_{i=1}^N V_i \right\} \Phi_0 \quad (22)$$

Subtracting equation (22) from (21), equation (19) is obtained. Each of these equations have solutions for non-degenerate Φ_0 , since they separately satisfy the existence condition, equation (8).

Equation (21) involves only the two electron repulsions, g_{1j} ; equation (22) only the one electron potentials, V_i . This is a very convenient result. Equation (21) has exactly the same form as the equation that gives the first order W.F., X_1 of an N-electron system when one takes the entire interelectronic repulsions, $\sum_{1>j=1}^N g_{1j}$ as the perturbation, H_1 , and uses bare nuclei orbitals (hydrogen-like orbitals in atoms) (Sinanoglu 1960b) instead of the H.F. Φ_0 . The main difference between equation (21) and an equation giving X_1 , with $H_1 = \sum_{1>j} g_{1j}$ lies

in L_0 which in the H.F. case contains the $h_1^{\text{eff}} = h_1^0 + V_1$ instead of just the h_1^0 [equation (14)]. Thus the methods developed previously (Sinanoglu 1960b) for obtaining X_1 in terms of pairs apply in exactly the same way to U' . Moreover, as we shall show first for a two electron system and then generally, once U' is determined W is obtained from it by simple orthogonalization procedures.

We give first the method of separating U' into pairs. This is based on the method that was used in the separation of X_1 with $H_1 = \sum_{i>j} g_{1j}$ (Sinanoglu 1960b).

The particular solution of equation (21) is obtained by inverting L_0 :

$$U' = L_0^{-1} \left\{ \sum_{i>j=1}^N (J_{1j} - K_{1j}'' - g_{1j}) \right\} A(1'2'\dots N') \quad (23)$$

L_0^{-1} is the Green's function operator and by equation (17):

$$L_0^{-1} = (H_0 - E_0)^{-1} = \frac{1}{e_1' + e_2' + \dots + e_N'} \quad (24)$$

where we have defined:

$$e_1' = h_1^{\text{eff}} - \epsilon_1' + (\text{spin part})_1 \quad (25)$$

and included the corresponding one electron spin part. In terms of the complete set of the anti-symmetrized eigenfunctions of H_0 , L_0^{-1} is given by:

$$L_0^{-1} = \sum_{n>\dots l>k>1}^{\infty} \frac{A(kl\dots n) \times A(kl\dots n)}{(\epsilon_k' + \epsilon_l' + \dots + \epsilon_n') - (\epsilon_1' + \epsilon_2' + \dots + \epsilon_N')} \quad (26)$$

L_0^{-1} is a self-adjoint, linear operator and commutes with A .

From $e'_1 1(x_1) = 0$ and equation (25) it follows that if e.g. $f_{12}(x_1, x_2)$ is any function of x_1 and x_2 only, then

$$\frac{1}{e'_1 + e'_2 + \dots + e'_N} \left\{ f_{12}(x_1, x_2) 3(x_3) 4(x_4) \dots N(x_N) \right\} = \left\{ 3(x_3) 4(x_4) \dots N(x_N) \right\} \frac{1}{e'_1 + e'_2} f_{12}(x_1, x_2) \quad (27)$$

Commuting A with $\sum_{i>j} m_{ij}$ ($m_{ij} \equiv J_{ij} - K_{ij} - g_{ij}$) and L_0^{-1} , this equation would allow U' in equation (23) to be written as a sum of terms each involving a two electron $q_{ij} \equiv$

$\frac{1}{e'_1 + e'_j} m_{ij} \left\{ 1'(x_1) j'(x_j) \right\}$ and multiplied by the remaining spin-orbitals $n'(x_n) \neq 1, j$. However, when each of the two electron inverse operators $\left(\frac{1}{e'_1 + e'_j} \right)$ is expanded as in equation (26), the expressions for q_{ij} become infinite. This is because q_{ij} does not correspond to a first order two electron W.F. obtainable as a solution of $(e'_1 + e'_j) q_{ij} = m_{ij} \left\{ 1'(x_1) j'(x_j) \right\}$ similar to equation (5). $\left\{ 1'(x_1) j'(x_j) \right\}$ will be degenerate with other two electron states, e.g. with $\left\{ 1'(x_j) j'(x_1) \right\}$, so that the q_{ij} equations do not satisfy the existence conditions, equation (8). In the overall U' , however, such pair degeneracies leading to infinities are removed when A is finally applied.

To obtain U' in terms of finite pair functions each one satisfying a two-electron non-homogeneous equation of the type, equation (5), the pair degeneracies must be removed before applying L_0^{-1} . This is accomplished by taking those linear combinations of $(i'j')$ pair products that belong to the

irreducible representations of the symmetry group of a two electron system. It is possible to find these combinations in a way leaving the overall $A\left\{\sum_{1>j} m_{1j}(1'2'\dots N')\right\}$ invariant (Sinanoglu 1960b) in the equation:

$$U' = L_0^{-1} A\left\{\sum_{1>j=1}^N m_{1j}(1'2'\dots N')\right\} \quad (28)$$

For instance if $1'$ and j' correspond to the same spatial orbital and differ only in spin, it is sufficient to make use of

$$\frac{1}{\sqrt{2}} AB_{1j} = A \quad (29)$$

where $B_{1j} = \frac{1}{\sqrt{2}!} (1 - P_{1j}) = \frac{1}{\sqrt{2}!} \det$, antisymmetrizes only $1'$ and j' by interchanging x_1 and x_j . Then from equations (27), (28) and (29) we get e.g. for the $(1'2')$ pair:

$$\begin{aligned} L_0^{-1} A\{(J_{12} - g_{12})(1'2'\dots N')\} = \\ L_0^{-1} \frac{A}{\sqrt{2}} \{(J_{12} - g_{12})B_{12}(1'2')3'(x_3)\dots N'(x_N)\} = \\ \frac{A}{\sqrt{2}} \{3'(x_3)4'(x_4)\dots N'(x_N)u'_{12}(x_1, x_2)\} \end{aligned} \quad (30)$$

where now $u'_{12}(x_1, x_2)$ is the particular solution† of

$$(e'_1 + e'_2)u'_{12}(x_1, x_2) = (J_{12} - g_{12})B_{12}\{1'(x_1)2'(x_2)\} \quad (31)$$

such that $\langle u'_{12}, B_{12}(1'2') \rangle = 0$. Before the last step of equation (29), L_0^{-1} and A have been commuted.

The total U' is given by

$$U' = \frac{1}{\sqrt{2}} A\left\{\sum_{1>j=1}^N (1'2'\dots [1-1]'[j+1]'\dots N')u'_{1j}\right\} \quad (32)$$

†The particular solution of equation (31) with the proper behaviour at $x_1, x_2 = 0$ and ∞ , must be made orthogonal to $B(1'2')$ before inserting it in equation (30).

where $l' = l'(x_1)$, $n' = n'(x_n)$ and $u'_{1j} = u'_{1j}(x_1, x_j)$. If for an $(l'j')$ pair, $B_{1j}(l'j')$ already belongs to an irreducible representation (or to one of its rows) of the two electron symmetry group (a "closed shell" pair) the corresponding u'_{1j} will be the particular solution of

$$(e'_1 + e'_j)u'_{1j} = m_{1j}B_{1j}(l'j') \quad (33)$$

such that $\langle u'_{1j}, B_{1j}(l'j') \rangle = 0$; $m_{1j} = J_{1j} - K_{1j}'' - g_{1j}$. If on the other hand B_{1j} is not sufficient to remove the degeneracy of an $(l'j')$ pair, then, in the equation

$$U' = L_0^{-1} \frac{A}{\sqrt{2}} \left\{ \sum_{1 \leq j=1}^N m_{1j} B_{1j}(l'2' \dots N') \right\} \quad (34)$$

obtained from equations (28) and (29), $m_{1j}B_{1j}(l'j')$ must be written as a linear combination of terms that belong to the mentioned irreducible representations and hence satisfy equation (8) individually.

Suppose there are r such terms, ϕ_{1j}^s , for a given $(l'j')$,

$$\frac{A}{\sqrt{2}} \left\{ m_{1j} B_{1j}(l'2' \dots l'j' \dots N') \right\} = \frac{1}{r} A \left\{ (l' \dots [1 - 1]' [j + 1]' \dots N') \right. \\ \left. \times \sum_{s=1}^r m_{1j}^s \phi_{1j}^s(x_1, x_j) \right\} \quad (35)$$

then

$$u'_{1j} = \frac{\sqrt{2}}{r} \sum_{s=1}^r u_{1j}^s \quad (36a)$$

where u_{1j}^s are the solutions of

$$(e'_1 + e'_j)u_{1j}^s = m_{1j}^s \phi_{1j}^s \quad (36b)$$

and $m_{1j}^s = \langle \phi_{1j}^s, g_{12} \phi_{1j}^s \rangle - g_{1j}$. The u_{1j}^s must be made orthogonal

to ϕ_{ij}^B before inserting in equations (36a) and (32). This procedure for obtaining the proper u_{ij} has been illustrated in detail before for the case of Li atom with $H_1 = \sum_{i>j} g_{ij}$ (Sinanoglu 1960b) where the $\frac{1}{\sqrt{2}} \det (1s_\beta 2s_\alpha)$ pair leads to the u_{ij} of the $(1s2s)^1S$ and 3S states of Li^+ .

Now each u'_{ij} occurring in equation (32) can be obtained by solving several two electron equations, equations (33) or (36b), e.g. by variational principles/such as equation (9).
(Sinanoglu 1960c)

The number of independent pair functions in U' , in general will be less than the total number of pairs. In the next sections, the complete X'_1 will be obtained by relating W (equation (20)) to U' .

a) Two-Electron System

Consider a non-degenerate two electron system such as the ground state of He or H_2 . Then $1'$ and $2'$ are the H.F. SCF spin-orbitals, e.g. $1s_\alpha$, $1s_\beta$ or $(\sigma_g 1s)_\alpha$, $(\sigma_g 1s)_\beta$. Now $U' = u'_{12}$ satisfies equation (31) and $X'_1 = u'_{12} - w_{12}$. Equation (22) becomes

$$(e'_1 + e'_2)w_{12}(x_1, x_2) = [(J_{12} - V_1) + (J_{12} - V_2)]B_{12}(1'2') \quad (37)$$

We have written the perturbation appearing on the right hand side of this equation as the sum of two terms: $(J_{12} - V_1)$ and $(J_{12} - V_2)$. Each one of these is a one electron function. Changing the notation of equation (22) slightly and letting the subscripts denote the orbitals producing the potential,

$V_1 \equiv V_1(x_2)$ and from equation (12):

$$V_1(x_2) = \langle 1'(x_1), g_{12} 1'(x_1) \rangle_{x_1} = \int dx_1 g_{12}(x_1, x_2) |1'(x_1)|^2 \quad (38)$$

Inverting $(e_1' + e_2')$, we have

$$w_{12} = \frac{1}{e_1' + e_2'} B_{12} [(J_{12} - V_1(x_2)) + (J_{12} - V_2(x_1))] (1'(x_1) 2'(x_2))$$

or using equation (27):

$$w_{12} = B_{12} \{ 1'(x_1) t_2(x_2) \} + B_{12} \{ t_1(x_1) 2'(x_2) \} \quad (39a)$$

where e.g.

$$t_2(x_2) = \frac{1}{e_2'} (J_{12} - V_1(x_2)) 2'(x_2) \quad (39b)$$

In equation (39) t_1 and t_2 are related to $u'_{12}(x_1, x_2)$ simply by:

$$\begin{aligned} t_1(x_1) &= \sqrt{2!} \langle 2'(x_2), u'_{12}(x_1, x_2) \rangle_{x_2} \\ t_2(x_2) &= \sqrt{2!} \langle 1'(x_1), u'_{12}(x_1, x_2) \rangle_{x_1} \end{aligned} \quad (40)$$

where, as in equation (38), $\langle \rangle_{x_1}$ denotes an integration over only x_1 . To prove this we substitute the particular solution of equation (31) into equation (40):

$$\langle 2', u'_{12} \rangle_{x_2} = \langle 2'(x_2), \frac{1}{e_1' + e_2'} (J_{12} - g_{12}) B_{12} (1' 2') \rangle_{x_2}$$

The operations $(e_1')^{-1}$ and $\langle \rangle_{x_2}$ commute and $(e_1' + e_2')^{-1}$ is self-adjoint with respect to $\langle \rangle$ as well as $\langle \rangle_{x_2}$. Thus

$$\begin{aligned} \langle 2', u'_{12} \rangle_{x_2} &= \langle \frac{1}{e_1' + e_2'} 2'(x_2), (J_{12} - g_{12}) B_{12} (1' 2') \rangle_{x_2} \\ &= \frac{1}{e_1'} \langle 2'(x_2), (J_{12} - g_{12}) B_{12} (1' 2') \rangle_{x_2} \end{aligned} \quad (41)$$

Equation (27) has been used in the last step. Since $1'$ and $2'$

are orthonormal and $\langle 2'(\underline{x}_2), g_{12} 2'(\underline{x}_2) \rangle = V_2(\underline{x}_1)$, equation (41) leads to the desired result, equation (40):

$$\langle 2', u'_{12} \rangle_{\underline{x}_2} = \frac{1}{\sqrt{2!} e_1} (J_{12} - V_2(\underline{x}_1)) 1'(\underline{x}_1) = \frac{1}{\sqrt{2!}} t_1(\underline{x}_1)$$

Note also that

$$\langle t_1(\underline{x}_1), 1'(\underline{x}_1) \rangle = \langle t_2(\underline{x}_2), 2'(\underline{x}_2) \rangle = 0 \quad (42)$$

Equations (19), (20), (39a) and (40) show that the first order correction, X'_1 , to the H.F. solution is given by u'_{12} orthogonalized (by the Schmidt process) to the H.F. spin-orbitals $1'$ and $2'$; i.e.

$$\begin{aligned} X'_1(\underline{x}_1, \underline{x}_2) = u'_{12} - \det \left\{ 1'(\underline{x}_1) \langle 1'(\underline{x}_1), u'_{12}(\underline{x}_1, \underline{x}_2) \rangle_{\underline{x}_1} \right\} \\ - \det \left\{ 2'(\underline{x}_2) \langle 2'(\underline{x}_2), u'_{12}(\underline{x}_1, \underline{x}_2) \rangle_{\underline{x}_2} \right\} \end{aligned} \quad (43)$$

so that

$$\langle X'_1, 1' \rangle_{\underline{x}_1} = \langle X'_1, 2' \rangle_{\underline{x}_2} = 0 \quad (44)$$

Substituting this result in equation (6) with $\langle X'_1, B_{12}(1'2') \rangle = 0$ and using equation (11) we get:

$$E_2 = \langle \frac{1}{\sqrt{2!}} \det(1'2'), g_{12} X'_1 \rangle \quad (45)$$

The $\sum_1 V_1$ part of H_1 has vanished because of the orthogonalization conditions, equation (44). If $G_{12} B_{12}(1'2') = g_{12} X'_1(\underline{x}_1, \underline{x}_2)$ is written in equation (45) and the $\underline{x}_1$ integration carried out first, E_2 becomes the expectation value, $\langle 2'(\underline{x}_2), V_p(\underline{x}_2) 2'(\underline{x}_2) \rangle$, of the correlation or fluctuation (Sinanoglu 1960a) potential, $V_p(\underline{x}_2) = \langle 1', G_{12} 1' \rangle_{\underline{x}_1}$ acting on the electron $\underline{x}_2$.

the usual

In the language of/Schrödinger perturbation theory, i.e. when equation (32) is solved using equation (26), u'_{12} contains all the double and the single virtual excitations from $\Phi_0 = B_{12}(1'2')$. To get the complete solution X'_1 to equation (5), the contribution of the single excitations are subtracted out from u'_{12} by orthogonalization to $1'$ and $2'$ (equation (43)). Thus when Φ_0 is a Hartree-Fock solution, X'_1 consists only of the "dispersion" (double excitations) part, the "orbital average polarization" (single excitations) part does not appear because it is already implicit in the S.C.F. nature of Φ_0 . (See e.g. Sinanoglu 1960a).

b) N-electron System

In the case of an N-electron system, as in the previous case, the complete first order correction, X'_1 to the H.F. Φ_0 is obtained by orthogonalizing each u'_{ij} in equation (32) to its H.F. orbitals $1'$ and j' .

To show this, we first split the sum of the H.F. potentials, $\sum_{i=1}^N V_i(x_i)$ appearing as the perturbation in equation (22) into the coulomb and exchange potentials of individual orbitals $1'$ acting on electrons x_j . Substituting equation (13) in (12)

$$\sum_{k=1}^N V_k(x_k) = \sum_{1 \geq j=1}^N \left[\left(S_1(x_j) + S_j(x_1) \right) - \left(R_1''(x_j) + R_j''(x_1) \right) \right] \quad (46)$$

$S_1(x_j)$ is the coulomb and $R_1(x_j)$ the exchange potential of the orbital $1'$. In $\Phi_0 = A(1'2' \cdots N')$, $1'$ is occupied by the

electron x_1 before A is applied.

$$S_1(x_j) = \langle 1'(x_1), g_{1j} 1'(x_1) \rangle_{x_1} \quad (47a)$$

$$\begin{aligned} R_1''(x_j) j'(x_j) &= \langle 1'(x_1), g_{1j} 1'(x_1) P_{1j} \rangle_{x_1} j'(x_j) \\ &= \langle 1'(x_1), g_{1j} j'(x_1) \rangle_{x_1} 1'(x_j) \end{aligned} \quad (47b)$$

We write the perturbation in equation (22) as the sum of pair terms using equation (46), after commuting it with A :

$$L_0 W = A \left\{ \sum_{1 \leq j=1}^N k_{1j} \right\} (1' 2' 3' \dots N') \quad (48a)$$

where

$$k_{1j} = \left[J_{1j} - K_{1j}'' - S_1(x_j) + R_1''(x_j) \right] + \left[J_{1j} - K_{1j}'' - S_j(x_1) + R_j''(x_1) \right] \quad (48b)$$

The form of this equation is exactly the same as equation (28) which gave U' ; only k_{1j} has replaced the m_{1j} . Thus W is obtained in terms of the corresponding pair functions, w_{1j} , in the same way that U' was related to u'_{1j} , except now the use of $A = \frac{1}{\sqrt{2}} AB_{1j}$ suffices to do this. For reasons that will be apparent shortly, it is not necessary to resolve some of the $B_{1j}(1' j')$ further in terms of ϕ_{1j}^S (cf. equation (35)). We get

$$W = L_0^{-1} \frac{A}{\sqrt{2}} \left\{ \sum_{1 \leq j=1}^N k_{1j} B_{1j} (1' 2' \dots 1' j' \dots N') \right\} \quad (49)$$

Then, commuting A and L_0^{-1} and using equation (27) for each k_{1j} term,

$$W = \frac{1}{\sqrt{2}} A \left\{ \sum_{1 \geq j=1}^N (1' 2' \dots [1-1]' [j+1]' \dots N') w_{1j} \right\} \quad (50)$$

where $w_{1j} = \frac{1}{e_1' + e_2'} k_{1j} B_{1j}(1' j')$ (cf. equations (34)).

The w_{1j} 's are related to the "immersed pair" functions u_{1j}' in the same way as we showed in the two electron system. B_{1j} (i.e. $\frac{1}{\sqrt{2}!} \det$) commutes with k_{1j} and $(e_1' + e_2')^{-1}$, so that using equation (27) and the definition of k_{1j} , equation (48b),

$$w_{1j} = B_{1j} \left\{ i'(\underline{x}_1) t_j(\underline{x}_j) \right\} + B_{1j} \left\{ t_1(\underline{x}_1) j'(\underline{x}_j) \right\} \quad (51a)$$

$$t_1(\underline{x}_1) = \frac{1}{e_1'} \left[J_{1j} - K_{1j}'' - S_j(\underline{x}_1) + R_j''(\underline{x}_1) \right] i'(\underline{x}_1) \quad (51b)$$

i and j are interchanged to get $t_j(\underline{x}_j)$. These equations are the generalization of equations (39) to any pair. Again we have:

$$\begin{aligned} t_1(\underline{x}_1) &= \sqrt{2!} \langle j'(\underline{x}_j), u_{1j}'(\underline{x}_1, \underline{x}_j) \rangle_{\underline{x}_j} \\ t_j(\underline{x}_j) &= \sqrt{2!} \langle i'(\underline{x}_1), u_{1j}'(\underline{x}_1, \underline{x}_j) \rangle_{\underline{x}_1} \end{aligned} \quad (52)$$

Equation (52) is valid for any w_{1j} whether its u_{1j}' is obtained just from $B_{1j}(1' j')$, (equation (33)), or from pair symmetry states, ϕ_{1j}^S by equations (36). The proof of the first case with $B_{1j}(1' j')$ follows in exactly the same way as in the two electron system by substituting $u_{1j}' = (e_1' + e_j')^{-1} m_{1j} B_{1j}(1' j')$ in equation (52) and noting that $\langle i'(\underline{x}_1), (S_j(\underline{x}_1) - R_j''(\underline{x}_1)) i'(\underline{x}_1) \rangle = J_{1j} - K_{1j}''$. The other case is similarly verified by substituting $u_{1j}' =$

$\frac{\sqrt{2}}{r} \sum_{s=1}^r (e_i' + e_j')^{-1} m_{ij}^s \phi_{ij}^s$ and writing out ϕ_{ij}^s in terms of the appropriate $B_{ij}(1'j')$'s at the last step.

$$\begin{aligned} \langle 1'(\underline{x}_1), u_{ij}'(\underline{x}_1, \underline{x}_j) \rangle_{\underline{x}_1} &= \frac{\sqrt{2}}{r} \sum_{s=1}^r \langle 1'(\underline{x}_1), \frac{1}{e_i' + e_j'} m_{ij}^s \phi_{ij}^s \rangle_{\underline{x}_1} \\ &= \frac{\sqrt{2}}{r} \sum_{s=1}^r \frac{1}{e_j'} \langle 1'(\underline{x}_1), m_{ij}^s \phi_{ij}^s \rangle_{\underline{x}_1} = \frac{1}{\sqrt{2}} \frac{1}{e_j'} (J_{ij} - K_{ij}'' - S_1 + R_1'') j'(\underline{x}_j) \\ &= \frac{1}{\sqrt{2}} t_j(\underline{x}_j) \end{aligned}$$

Finally the overall first order W.F., X_1' is obtained by combining the U' given by equation (32) and the W of equation (50). The result is:

$$X_1' = U' - W = \frac{1}{\sqrt{2}} A \left\{ \sum_{i>j=1}^N (1'2' \cdots [i-1]'[j+1]' \cdots N') \bar{u}_{ij} \right\} \quad (53)$$

expressed in terms of $\bar{u}_{ij}$, the "immersed pair" functions orthogonalized to the H.F. orbitals $1'$ and j' :

$$\begin{aligned} \bar{u}_{ij}(\underline{x}_1, \underline{x}_j) &= u_{ij}' - \det \left\{ 1'(\underline{x}_1) \langle 1'(\underline{x}_1), u_{ij}'(\underline{x}_1, \underline{x}_j) \rangle_{\underline{x}_1} \right. \\ &\quad \left. - \det \left\{ j'(\underline{x}_j) \langle j'(\underline{x}_j), u_{ij}'(\underline{x}_1, \underline{x}_j) \rangle_{\underline{x}_j} \right\} \right\} \quad (54) \end{aligned}$$

$\bar{u}_{ij}$ corresponds to only the "dispersion" part of u_{ij}' . Note that since the particular solutions, u_{ij}' , were obtained such that

$$\langle u_{ij}', B_{ij}(1'j') \rangle = 0 \quad (55)$$

we have $\langle \Phi_0, X_1' \rangle = 0$. Also

$$\langle \bar{u}_{ij}, 1' \rangle_{\underline{x}_1} = \langle \bar{u}_{ij}, j' \rangle_{\underline{x}_j} = 0 \quad (56)$$

The second order energy of the system is given from

equations (6), (11), (53) and (55) by:

$$E_2 = \sqrt{\frac{N!}{2}} \langle A(1'2' \dots N'), (\sum_{1>j} g_{1j}) [3'(x_3)4'(x_4) \dots N'(x_N) \bar{u}_{12}(x_1, x_2) + 1'(x_1)2'(x_2)5'(x_5) \dots N'(x_N) \bar{u}_{34}(x_3, x_4) + \dots] \rangle \quad (57)$$

where we have used the self-adjoint property of A and $A^2 = \sqrt{N!} A$.

The $\sum_1 V_1$ terms of H_1 vanished because of equation (56). The E_2 just given is simply the sum of "dispersion" energies of pairs of electrons $(1'j')$ immersed in the N electron medium, plus three and four body Fermi correlation terms ("exclusion effects"). To see this examine e.g. the first part of equation (57) with $\bar{u}_{12}$. Out of all the permutations in $A = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P$ only those P that interchange the electrons x_1, x_j, x_1, x_2 in $1'(x_1)j'(x_j)\bar{u}_{12}(x_1, x_2)$ contribute to the part of this term involving g_{1j} . We have:

$$\begin{aligned} & \frac{\sqrt{N!}}{\sqrt{2}} \langle A(1'2' \dots N'), (\sum_{1>j=1}^N g_{1j}) 3'(x_3)4'(x_4) \dots \bar{u}_{12}(x_1, x_2) \rangle \\ &= \langle B_{12}(1'2'), g_{12} \bar{u}_{12} \rangle - 2 \sum_{m>2}^N \langle m'(x_2) B_{1m} \{ 1'(x_1)2'(x_m) \}, \\ & \quad g_{1m}^{m'}(x_m) \bar{u}_{12}(x_1, x_2) \rangle + \sum_{\ell>k>2}^N \langle B_{12}(k'\ell'), \bar{u}_{12} \rangle \\ & \quad \langle B_{12}(1'2'), g_{12} B_{12}(k'\ell') \rangle \end{aligned} \quad (58)$$

The first term on the right is the dispersion energy of the pair $(1'2')$; it depends on the other electrons of the system only through the H.F. S.C.F. potential. The second term gives the "exclusion effect" of the occupied orbital m' on the correlation of $(1'2')$. In the usual perturbation theory it arises

because the virtual excitations of $(1'2')$ to m' ($2' < m' < N'$) are forbidden by the Pauli principle. The last term of equation (58) similarly represents four-body "exclusion effects" (effect of $k'l'$ on $(1'2')$). There are no other many-body effects. Terms such as $\langle 1'(x_1) 2'(x_2) 3'(x_3) \bar{u}_{12}(x_1, x_2) \rangle$ which we have called "cross-polarization" (Sinanoglu 1960b) vanish due to equation (56) in this case, where Φ_0 was chosen as the Hartree-Fock solution.

From equations (57) and (58) we thus have:

$$E_2 = \sum_{n>m>1}^N \langle B_{mn}(m'n'), g_{mn} \bar{u}_{mn} \rangle + (\text{Exclusion Effects}) \quad (59)$$

This is a rigorous result that had been obtained approximately before (Sinanoglu 1960a).

Equation (59) can be put into a very compact form by orthogonalizing $\bar{u}_{mn}$ to all the other occupied H.F. orbitals of the system. Equation (58) is equivalent to

$$\begin{aligned} \frac{\sqrt{N!}}{\sqrt{2}} \langle A(1'2' \dots N'), (\sum_{1>j} g_{1j}) 3'(x_3) 4'(x_4) \dots N'(x_N) \bar{u}_{12}(x_1, x_2) \rangle \\ = \langle B_{12}(1'2'), g_{12} \hat{u}_{12} \rangle \end{aligned} \quad (60)$$

where:

$$\begin{aligned} \hat{u}_{12} = \bar{u}_{12}(x_1, x_2) - \sum_{m'>2}^N \det \left\{ m'(x_1) \langle m'(x_1), \bar{u}_{12}(x_1, x_2) \rangle_{x_1} \right\} \\ + \sum_{b>k>2}^N \langle B_{12}(kl), \bar{u}_{12} \rangle B_{12}(kl) \end{aligned} \quad (61)$$

so that $\langle \hat{u}_{12}(x_1, x_2), m'(x_1) \rangle_{x_1} = 0$ for $2' < m' < N'$. Thus equation (57) or (59) becomes

$$E_2 = \sum_{n>m>1}^N \langle B_{mn}(m'n'), E_{mn} \hat{u}_{mn} \rangle \quad (62)$$

and $\langle \hat{u}_{mn}(x_m, x_n), k'(x_m) \rangle_{x_m} = 0$ for $N \gg k' \neq m', n'$.

The X'_1 , equation (53), that gave this E_2 , also gives the E_3 by equation (7), which can be analyzed in a similar way.

SUMMARY OF THE NON-EMPIRICAL PROCEDURE

The steps involved in a purely non-empirical calculation of the corrections to the Hartree-Fock energy and W.F. of an N electron system by the method given above are the following:

1) Determine all the unique u'_{ij} equations as in equations (33), (35) and (36). (See also Sinanoğlu 1960b). u'_{ij} 's belong to the irreducible representations of the symmetry group of a two electron system. The number of u'_{ij} 's to be solved for, will usually be less than the total number of pairs, $N(N-1)/2$, due to the multiplicity of some of the pair states. For example in Be, the only u'_{ij} 's needed are for $(1s^2) 1s$, $(1s2s) 1s$ and $3s$, and $(2s^2) 1s$.

2) Obtain each u'_{ij} from equation (33) or from equations (36), either by a special variational principle such as equation (9) or by other approximate ways of solving these non-homogeneous two-electron partial differential equations. Orthogonalize u'_{ij} to $B(1'j')$ or ϕ_{1j}^S . Many of the pairs will correspond to the excited states of a two-electron system. These can be obtained by the modified minimum principle (Sinanoğlu 1960c).

3) Orthogonalize each u'_{ij} to its own i' and j' , so that the new pair function, $\bar{u}_{ij}$, satisfies $\langle \bar{u}_{ij}, i'(x_i) \rangle_{x_i} = \langle \bar{u}_{ij}, j'(x_j) \rangle_{x_j} = 0$.

4) The complete first order W.F., X_1' is given by equation (53). The use of this X_1' leads to E_2 as the sum of pair dispersion interactions and three- and four-body exclusion effects (equations (57) and (59)). Alternatively, $\bar{u}_{1j}$ may be orthogonalized by equation (61) to all the other H.F. orbitals different from $1'$ and j' and occupied in Φ_0 . This gives the same E_2 , but expressed as a sum of effective pair energies, equation (62).

5) X_1' also determines E_3 by equation (7). The total energy calculated will be an upper limit to the exact E only if E_3 is added to $E_0 + E_1 + E_2$.

DISCUSSION

We have seen in the previous sections that in an N-electron system each $(1'j')$ pair of orbitals is associated with one u_{1j}' . This means that even when electron correlation can no longer be neglected there will be some validity to talking about the orbitals $1'$ and j' which merely serve as labels and imply u_{1j}' as well. Thus many of the cruder and qualitative concepts of quantum chemistry which were based on the orbital approximation and neglected correlation can be justified on this basis.

The theory developed above does not have to be used in a purely non-empirical way. Its usefulness even for large molecules depends on the possibility of its semi-empirical application. The "immersed pairs" of X_1' are almost independent

of the other electrons of the system. The u'_{ij} equations are just like those that determine the first order W.F. of an actual two electron system taking $H_1 = g_{12}$, except that the electrons of u'_{ij} move in the H.F. S.C.F. of all N electrons rather than only in the field of nuclei. Often some of the i' , j' orbitals, e.g. inner shells, will be quite unchanged in going from one atom or molecule to another. Then provided the change in V_i is also small, the corresponding u'_{ij} , the $\bar{u}_{ij}$ and the pair energy $\langle B_{ij}(i'j'), g_{12}\bar{u}_{ij} \rangle$ as well as the orbitals i' , j' can be transferred from one system to the other.

When a pair of electrons occupy the same orbital, the solution of their u'_{ij} e.g. by equation (9) will be similar to the He or H_2 problem and should be greatly aided by the use of r_{12} in the trial function, $(u'_{ij})_{\text{trial}}$.

If the electrons of a pair occupy different orbitals their correlation error will be much smaller and may be obtained by other approximate methods. When the different orbitals are equivalent to two orbitals around different centers the resulting pair interaction may be described as a generalized London force within the same molecule. On the other hand one of the orbitals may belong to an inner and the other to an outer shell. Then we may describe the outer electron as moving in a core-polarization potential. Both of these weaker correlation effects can be obtained by the adiabatic approximation or by the use of mean excitation energies (Sinanoglu 1960a).

We considered above a system with a single H.F. determinant Φ_0 . Many molecular problems, e.g. involving π -electrons however will have degeneracies. These cases can also be treated by the formalism of this article. The $L_0^{-1} = (\sum_i e_i^i)^{-1}$ (equations (24) to (27)) acting on Φ_0 would separate X_1^i into a closed shell part and the degenerate outer shell part. The degeneracy of the latter may then be resolved so as to satisfy equation (8). The rest of the method then applies as before.

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REFERENCES

- Bethe, H. A. and Salpeter, E. E. 1957 Encyclopedia of Physics, vol. 35. Berlin: Springer-Verlag.
- Brueckner, K. A. 1959 The Many Body Problem; Grenoble Université, École d'été de physique theorique, Les Houches. Methuen, Wiley.
- Eden, R. J. 1958 Nuclear Reactions, I. Amsterdam: North Holland Publishing Company.
- Hurley, A. C., Lennard-Jones, J. E. and Pople, J. A. 1953 Proc. Roy. Soc. A220, 446.
- Löwdin, P. O. 1959 Advances in Chemical Physics, vol. II, pp. 207 ff. Interscience Publishers.
- Lykos, P. G. and Parr, R. B. 1956 J. Chem. Phys. 24, 1166.
- McWeeny, R. 1959 Proc. Roy. Soc. A253, 242.
- Morse, P. M. and Feshbach, H. 1953 Methods of Theoretical Physics, vol. II, pp. 1119-20. New York: McGraw Hill.
- Sinanoğlu, O. 1960a J. Chem. Phys. (in press).
- Sinanoğlu, O. 1960b Phys. Rev. (to be published); also: University of California, Lawrence Radiation Laboratory Report UCRL-
- Sinanoğlu, O. 1960c Phys. Rev. (to be published); also: University of California, Lawrence Radiation Laboratory Report UCRL-9316.