

# THE CORRELATED HARTREE-FOCK EQUATIONS AND THE GENERALISED DENSITY MATRICES

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## 1. INTRODUCTION

ONE of the important problems of molecular chemistry concerns the evaluation of the correlation energy of molecules and the study, in general, of correlation effects in many-electron systems. The motions of the electrons in atomic or molecular systems are not independent of each other but are dependent on (or correlated with) the positions and spins of the other electrons. This correlation now is of two kinds—the first one arising from the limitations imposed by the Pauli Exclusion Principle which forbids two electrons of the same spin to stay in the same state, and the second kind arising from the strong Coulomb repulsion experienced by any two electrons when they try to approach each other closely.

The standard method of solving many-electron problems in quantum mechanics is by means of the Hartree-Fock equations, which are the variational equations of the Hamiltonian operator for a wave function that is a determinantal expression in the one-electron orbitals. Since the wave function is a determinant in the one-electron orbitals of the different electrons of the system, it will vanish when the co-ordinates of any two electrons having the same spin become identical and thus the Pauli Principle is implicit in this scheme. Or in other words, the Hartree-Fock equations suggest and bring within their scheme the correlation between electrons of the same spin, but because of the one-electron approximation they fail adequately to take into account of the Coulomb repulsion effects between the electrons. Experience has in fact shown that the H. F. equations give a much higher value for the energy of a molecular system than the experimentally observed one; this is to be expected because the H.F. equations neglect the Coulomb correlation between the electrons and would consequently contribute a much higher value for the repulsion energy of the system than is actually possible.

Coulomb correlation between the electrons can be brought into the theoretical formalism in several ways, but the simplest and most direct method

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of them all is to multiply the wave function by a correlation factor  $g(r_{12}, r_{13}, \dots)$  which is symmetric in the inter-electronic distances  $r_{12}, r_{13}, \dots$ , etc. Such a method has been found to be very effective for two electron systems like  $\text{He}^+$  ions and the hydrogen molecule, and it has been shown by Hylleraas, Löwdin and Redei that by using simple correlation factors of the type  $e^{ar_{12}}$  or  $(1 + ar_{12})$ , the energy for the Helium atom could be improved much beyond the value yielded by the H.F. equations. The introduction of the correlation factor modifies the field in which an electron is moving, and each electron moves in the average potential field of the remaining electrons subject to the condition that no two electrons can approach each other closely. The wave functions of the different electrons moving in such a correlated field will be different from the one electron orbitals obtained by solving the H.F. equations, and an important problem in the study of correlation effects is to determine the one-electron orbitals in this case. The equations determining these orbitals are given in Section 4 by making use of a formula given by Löwdin; in Section 8 we give the correlated Hartree-Fock equations for non-stationary systems. In Section 4, we have given the integro-differential equations satisfied by the generalised density matrices, and from these it is shown that one can obtain an expression for the energy matrix of the system which will be useful in determining a correlated Thomas-Fermi distribution. In Section 7, some remarks are made on the effects of correlation by a study of the general equations for the simple case of two electron systems.

## 2. DENSITY MATRICES

Let  $\Psi(x_1, x_2, \dots, x_N)$  be the normalised eigenfunction of the system so that we have

$$\int \Psi^* \Psi d\tau = 1 \quad (1)$$

where

$$\int d\tau = \int dx_1 dx_2 \dots dx_N$$

denotes integration over all space co-ordinates and summation over spin co-ordinates. The generalised density matrices have been defined by Löwdin as follows:

$$\begin{aligned} \Gamma(x_1' | x_1) \\ = N \int \Psi^*(x_1' x_2 \dots x_N) \Psi(x_1 x_2 \dots x_N) dx_2 \dots dx_N \end{aligned}$$

$$\begin{aligned}
 & \Gamma(x_1'x_2' \mid x_1x_2) \\
 &= \binom{N}{2} \int \Psi^*(x_1'x_2'x_3 \dots x_N) \Psi(x_1x_2 \dots x_N) dx_3 \dots dx_N \\
 & \Gamma(x_1'x_2' \dots x_p' \mid x_1x_2 \dots x_p) \\
 &= \binom{N}{p} \int \Psi^*(x_1'x_2' \dots x_p'x_{p+1} \dots x_N) \Psi(x_1 \dots x_N) \\
 & \quad \times dx_{p+1} \dots dx_N. \tag{2}
 \end{aligned}$$

For a system of N electrons,  $\Psi$  is an anti-symmetric function of the co-ordinates (space as well as spin) of the electrons and we choose for  $\Psi$  the following determinant:

$$\Psi = (N!)^{-1/2} \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \dots & \psi_N(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \dots & \psi_N(x_2) \\ \dots & \dots & \dots & \dots \\ \psi_1(x_N) & \psi_2(x_N) & \dots & \psi_N(x_N) \end{vmatrix}. \tag{3}$$

We assume for the sake of simplicity that the  $\psi$ 's form an ortho-normal system so that we have

$$\int \psi_i^*(x) \psi_k(x) dx = \delta_{ik}. \tag{4}$$

Now

$$\Psi^* \Psi = \frac{1}{N!} \rho = \frac{1}{N!} \det \parallel \rho_{ij} \tag{5}$$

where

$$\rho_{ij} = \sum_{k=1}^N \psi_k^*(x_i) \psi_k(x_j).$$

For future applications, we need also the quantity  $\rho'_{ij}$  defined by

$$\rho'_{ij} = \sum_{k=1}^N \psi_k^*(x_i') \psi_k(x_j). \tag{6}$$

Since the  $\psi$ 's form an ortho-normal set, we have

$$\int \rho'_{iN} \rho_{Nj} dx_N = \rho'_{ij}. \tag{7}$$

The integral of  $\rho$  over the co-ordinates of the various electrons has been given in Mott and Sneddon.<sup>5</sup> By adopting a similar procedure for the evaluation of the integrals and making use of (7), we can show that

$$\begin{aligned} \Gamma(x_1' | x_1) &= \rho'_{11} = \rho_1' \\ \Gamma(x_1'x_2' | x_1x_2) &= \frac{1}{2!} \begin{vmatrix} \rho'_{11} & \rho'_{12} \\ \rho'_{21} & \rho'_{22} \end{vmatrix} = \frac{1}{2!} \rho_2' \\ \Gamma(x_1'x_2' \dots x_p' | x_1 \dots x_p) &= \frac{1}{p!} \begin{vmatrix} \rho'_{11} & \dots & \rho'_{1p} \\ \dots & \dots & \dots \\ \rho'_{p1} & \dots & \rho'_{pp} \end{vmatrix} = \frac{1}{p!} \rho_p' \end{aligned} \quad (8)$$

where we have written  $\rho'_p$  for the determinant in the above line containing  $p$  rows and  $p$  co'umns.

There are several problems that deal with time-dependent processes, and the density matrices in such cases can be defined analogous to (2). Thus if  $\Psi(x_1x_2 \dots x_Nt)$  is the normalised time-dependent wave function for the system, we define the density matrix of order  $p$  as follows:—

$$\begin{aligned} \Gamma(x_1'x_2' \dots x_p't' | x_1x_2 \dots x_p t) \\ = \binom{N}{p} \int \Psi^*(x_1'x_2' \dots x_p'x_{p+1} \dots x_Nt') \Psi(x_1 \dots x_Nt) dx_{p+1} \dots dx_N. \end{aligned} \quad (2 a)$$

If as before we choose for  $\Psi$  a determinant built from one-electron orbitals so that

$$\Psi(x_1 \dots x_Nt) = (N!)^{-1} \det \{ \psi_1(x_1t) \dots \psi_N(x_Nt) \} \quad (3 a)$$

where the orbitals  $\psi_1, \psi_2, \dots, \psi_N$  satisfy the orthonormality conditions

$$\int \psi_i^*(xt) \psi_k^*(xt) dx = \delta_{ik} \quad (4 a)$$

then it follows that

$$\Gamma(x_1'x_2' \dots x_p't' | x_1 \dots x_p t) = \frac{\rho_p'}{p!}. \quad (8 a)$$

In the above

$$\rho_p' = \begin{vmatrix} \rho'_{11} & \rho'_{12} & \dots & \rho'_{1p} \\ \rho'_{21} & \rho'_{22} & \dots & \rho'_{2p} \\ \dots & \dots & \dots & \dots \\ \rho'_{p1} & \rho'_{p2} & \dots & \rho'_{pp} \end{vmatrix};$$

and

$$\rho'_{ij} = \rho'(x_i t'; x_j t) = \sum_k \psi_k^*(x_i t') \psi_k(x_j t) \tag{6 a}$$

Further if  $G(x_1 x_2 \dots x_l)$  is a symmetric function of the co-ordinates of  $l$  electrons, it can be shown (see Appendix I for proof) that

$$\begin{aligned} & \frac{\binom{N}{l}}{N!} \int G(x_1 x_2 \dots x_l) \frac{\partial \rho'_{l+1}}{\partial t} dx_1 \dots dx_N \\ &= \frac{1}{l!} \int G(x_1 \dots x_l) \frac{\partial \rho'_{l+1}}{\partial t} dx_1 \dots dx_{l+1} + \frac{(N-l-1)}{l!} \\ & \quad \times \int G(x_1 \dots x_l) \begin{vmatrix} \rho'_{11} & \dots & \rho'_{1l} & \rho'_{1l+1} \\ \dots & \dots & \dots & \dots \\ \rho'_{l1} & \dots & \rho'_{ll} & \rho'_{ll+1} \\ \frac{\partial \rho'_{l+1,1}}{\partial t} & \dots & \frac{\partial \rho'_{l+1,l}}{\partial t} & 0 \end{vmatrix} dx_1 \dots dx_{l+1}. \end{aligned} \tag{9}$$

### 3. THE ENERGY OF THE SYSTEM

The Hartree-Fock equations are the Euler differential equations of the variational principle

$$\delta \int \Psi^* H \Psi d\tau = 0. \tag{10}$$

In view of the one-electron approximation, the Hartree-Fock equations do not adequately take into account of the Coulomb correlation, and we shall, following Löwdin, take the correlated wave function of the system as the product of a correlation factor which is a symmetric function of the inter-electronic distances and the Slater determinant. The wave function  $\Phi$  for the system then becomes

$$\Phi = g(r_{12}, r_{13} \dots) \Psi. \tag{11}$$

For  $g$ , we shall choose the form

$$g(r_{12}, r_{13} \dots) = \alpha + \beta \sum_{i < j} f(r_{ij}) \tag{11 a}$$

where the functions  $f(r_{ij})$  are supposed to be known. The simple functions  $r_{12}$  or  $(e^{\alpha r_{12}} - 1)$  may be regarded as good choices for the correlation function  $f(r_{12})$ . One of the constants, say  $\alpha$ , can be determined from the condition

$$\int \Phi^* \Phi d\tau = 1 \tag{11 b}$$

and  $\beta$  can then be chosen as the best parameter minimising the energy. Now the best one-electron wave functions  $\psi_i(x)$  ( $i = 1, 2, \dots, N$ ) can be determined from the variational principle

$$\delta W = \delta \int \Phi^* H \Phi d\tau = \delta \int \Psi^* H_c \Psi d\tau = 0 \quad (12)$$

where

$$H_c = gHg. \quad (13)$$

Before writing down the variational equations we shall first fix the form of  $H_c$ .

Now

$$\begin{aligned} H_c &= \left\{ a + \beta \sum_{i < j} f(r_{ij}) \right\} \left\{ \sum_{i=1}^N E_i + \frac{1}{2} \sum'_{i,k} F(x_i, x_k) \right\} \\ &\quad \times \left\{ a + \beta \sum_{i < j} f(r_{ij}) \right\} \\ &= a^2 \left\{ \sum_{i=1}^N E_i + \frac{1}{2} \sum'_{i,k} F(x_i, x_k) \right\} \\ &\quad + a\beta \sum_{i=1}^N \sum_{\substack{s,t \\ s < t}} [f(r_{st}), E(i)] \\ &\quad + 2a\beta \sum_{\substack{st \\ s < t}} \sum_{\substack{ik \\ i < k}} f(r_{st}) F(x_i, x_k) \\ &\quad + \beta^2 \left\{ \sum_{\substack{st \\ s < t}} \sum_{i=1}^N \sum_{\substack{s't' \\ s' < t'}} f(r_{st}) E(i) f(r_{s't'}) \right. \\ &\quad \left. + \sum_{\substack{st \\ s < t}} \sum_{\substack{ik \\ i < k}} \sum_{\substack{s't' \\ s' < t'}} f(r_{st}) F(x_i, x_k) f(r_{s't'}) \right\} \\ &= T_1 + T_2 + T_3 + T_4. \end{aligned} \quad (14)$$

In the above  $[u, v]$  denotes the operator  $(uv + vu)$ . Consider now the term  $T_2$ . The summation here contains  $N^2(N-1)/2$  terms. Of these, the number of terms for which  $i, s$  and  $t$  are different is  $3 \binom{N}{3}$  while the number of terms involving two indices only is  $N(N-1)$ ,

Let us write

$$\begin{aligned} T_2(i, s) &= \alpha\beta [f(r_{is}), E(i) + E(s)] \\ T_2(i, s, t) &= \alpha\beta \{ [f(r_{st}), E(i)] + [f(r_{it}), E(s)] \\ &\quad + [f(r_{is}), E(t)] \}. \end{aligned} \tag{15 a}$$

Then

$$T_2 = \sum_{\substack{i, s \\ i < s}} T_2(i, s) + \sum_{\substack{i, s, t \\ i < s < t}} T_2(i, s, t). \tag{15 b}$$

Consider next  $T_3$ . The summation over  $i, k, (i < k)$  and  $s, t (s < t)$  contains  $N^2(N-1)^2/4$  terms. Of these, there are  $\binom{4}{2}\binom{N}{4}$  terms of the type  $r_{st} F(x_i, x_k)$  involving four different indices,  $6\binom{N}{3}$  terms of the type  $F(x_i, x_t)r_{is}$  involving three different indices and  $\binom{N}{2}$  terms of the type  $r_{ik} F(x_i, x_k)$  involving two indices only. If we write

$$\begin{aligned} T_3(i, s) &= 2\alpha\beta f(r_{is}) F(x_i, x_s) \\ T_3(i, s, t) &= 2\alpha\beta [F(x_i, x_t) (f(r_{is}) + f(r_{st})) + F(x_i, x_s) \\ &\quad \times (f(r_{it}) + f(r_{st})) + F(x_s, x_t) (f(r_{si}) + f(r_{ti}))] \\ T_3(i, k, s, t) &= 2\alpha\beta [f(r_{ik}) F(x_s, x_t) + \text{five similar terms arising} \\ &\quad \text{from the permutation of } i, k, s \text{ and } t], \end{aligned}$$

then

$$T_3 = \sum_{\substack{i, k \\ i < k}} T_3(i, s) + \sum_{\substack{i, k, s \\ i < k < s}} T_3(i, s, t) + \sum_{\substack{i, k, s, t \\ i < k < s < t}} T_3(i, k, s, t). \tag{16}$$

We shall finally consider  $T_4$ . The first term of  $T_4$ , involving the operators  $E_i$ , consists of  $N^3(N-1)^2/4$  terms and these can be split up into  $30\binom{N}{5}$  terms containing five different indices,  $48\binom{N}{4}$  terms containing four different indices,  $21\binom{N}{3}$  terms containing three different indices and  $2\binom{N}{2}$  terms containing two different indices. Similarly the second term of  $T_4$  involving the operators  $F(x_i, x_k)$  consists of  $N^3(N-1)^3/8$  terms and the terms involving 2, 3, ..., 6 different indices in this are given by the relation

$$\begin{aligned} \frac{N^3(N-1)^3}{8} &= 90\binom{N}{6} + 180\binom{N}{5} + 114\binom{N}{4} + 24\binom{N}{3} \\ &\quad + \binom{N}{2}. \end{aligned} \tag{17}$$

Let us denote by  $T_4(i, s), T_4(i, s, t), T_4(i, k, s, t) \dots T_4(i, k, s, t, s', t')$  the terms in  $T_4$  involving 2, 3, ..., 6 different indices. Then

$$T_4 = \sum_{\substack{i, s \\ i < s}} T_4(i, s) + \dots + \sum_{\substack{ik \\ i < k}} \sum_{\substack{st \\ s < t}} \sum_{\substack{s't' \\ s' < t'}} T_4(i, k, s, t, s', t'). \quad (18)$$

We shall now write

$$\begin{aligned} H_c^1 &= \alpha^3 E(i) \\ H_c^2(i, s) &= \alpha^2 F(x_i, x_s) + T_2(i, s) + T_3(i, s) + T_4(i, s) \\ H_c^3(i, s, t) &= T_2(i, s, t) + T_3(i, s, t) + T_4(i, s, t) \\ &\dots\dots\dots \\ H_c^6(i, k, s, t, s, t') &= T_4(i, k, s, t, s', t'). \end{aligned} \quad (19)$$

Then obviously

$$\begin{aligned} H_c &= \sum_{i=1}^N H_c^1(i) + \frac{1}{2!} \sum_{i, s} H_c^2(i, s) + \dots + \frac{1}{6!} \\ &\quad \times \sum_{ik,} \sum_{st,} \sum_{s't'} H_c^6(i, \dots, t'). \end{aligned} \quad (20)$$

We may note that the functions  $H_c^l(x_1, x_2, \dots, x_l)$  are symmetric in their arguments.

Now

$$W = \int \Phi^* H \Phi d\tau = \int \Psi^* H_c \Psi d\tau. \quad (21)$$

From (20) and (8) we have

$$\begin{aligned} W &= \int H_c^1(x_1) \Gamma(x_1' | x_1) dx_1 + \int H_c^2(x_1 x_2) \Gamma(x_1' x_2' | x_1 x_2) dx_1 dx_2 \\ &\quad + \dots + \int H_c^6(x_1 x_2 \dots x_6) \Gamma(x_1' \dots x_6' | x_1 \dots x_6) dx_1 \dots dx_6. \end{aligned} \quad (22)$$

where we are following the convention that, in the integrands, the operators  $H_c^1(x_1), H_c^2(x_1, x_2) \dots$  operate only on the unprimed co-ordinates  $x_1, \dots, x_6$  and that, after these operations have been carried out, we have to put  $x_1' = x_1; x_2' = x_2; \dots; x_6' = x_6$  before the integrations.

We see from (22) that the energy of the system is a functional of the density matrices alone.



#### 4. THE CORRELATED HARTREE-FOCK EQUATIONS

Löwdin has determined the one-electron functions  $\psi_1, \psi_2, \dots, \psi_N$  that make the determinant  $\Psi$  the 'best' approximation for the eigenvalue problem

$$\Omega_{op} \Psi = W\Psi \tag{23}$$

where  $\Omega_{op}$  is a many-particle operator expressible as

$$\Omega_{op} = \Omega_0 + \sum_i \Omega_i + \frac{1}{2!} \sum'_{ij} \Omega_{ij} + \frac{1}{3!} \sum'_{ijk} \Omega_{ijk} + \dots \tag{24}$$

The prime in the above indicates that the summation excludes terms having two or more indices equal.

The equations determining the functions  $\psi_1, \psi_2, \dots, \psi_N$  are given by

$$\begin{aligned} \Omega_1 \psi_k(x_1) + \int \Omega_{12} \begin{vmatrix} \psi_k(x_1) & \psi_k(x_2) \\ \rho(x_2', x_1) & \rho(x_2' x_2) \end{vmatrix} dx_2 \\ + \frac{1}{2!} \int \Omega_{123} \begin{vmatrix} \psi_k(x_1) & \psi_k(x_2) & \psi_k(x_3) \\ \rho(x_2' x_1) & \rho(x_2' x_2) & \rho(x_2' x_3) \\ \rho(x_3' x_1) & \rho(x_3' x_2) & \rho(x_3' x_3) \end{vmatrix} dx_2 dx_3 \\ = \sum_{i=1}^N \lambda_{ki} \psi_i(x_1). \end{aligned} \tag{25}$$

Now  $H_c$  is a many-particle operator similar to (24) and thus the best one-electron orbitals that minimise the energy of the system can be obtained from (25) by replacing  $\Omega_{op}$  by  $H_c$ . By expanding the determinants in (25) along the first row and denoting by  $\rho'_{l;ij}$  the co-factor of  $\rho'_{ij}$  in  $\rho'_l$ , we can write the integro-differential equations determining the correlated orbitals as

$$\begin{aligned} H_c^1(x_1) \psi_k(x_1) + \sum_{l=2}^6 \frac{1}{(l-1)!} \int H_c^l(x_1 x_2 \dots x_l) \\ \times \sum_{j=1}^l \rho'_{l;lj} \psi_k(x_j) dx_2 \dots dx_l \\ - \sum_{i=1}^N \lambda_{ki} \psi_i(x_1) = 0 \quad (k = 1, 2, \dots, N). \end{aligned} \tag{26}$$

The conjugate complex of the above equation is given by

$$\begin{aligned} & H_c^1(x_1) \psi_k^*(x_1) + \sum_{l=2}^6 \frac{1}{(l-1)!} \int H_c^l(x_1 \dots x_l) \\ & \times \sum_{j=1}^l \rho'^*_{l; 1j} \psi_k^*(x_j) dx_2 \dots dx_l \\ & - \sum_{i=1}^N \lambda_{ik} \psi_i^*(x_1) = 0 \end{aligned} \quad (27)$$

Equations (26) determine the correlated orbitals  $\psi_i(x_i)$ . They are a generalisation of the Hartree-Fock equations and since they explicitly take into account of correlation effects, they can be expected to give better theoretical values for physical parameters like energy, than the simple Hartree-Fock system of equations.

From (26) we have

$$\begin{aligned} \lambda_{ki} &= \sum_{l=1}^6 \frac{1}{(l-1)!} \int \psi_i^*(x_1) H_c^l(x_1 \dots x_l) \\ & \times \sum_{j=1}^l \rho'_{l; 1j} \psi_k(x_j) dx_1 \dots dx_l \end{aligned} \quad (28)$$

and from (27) we see that

$$\lambda_{ki} = \lambda^*_{ik}. \quad (29)$$

As in the H.F. scheme we see that the  $\lambda_{ki}$  are a set of arbitrary constants forming a Hermitean matrix. Again as in the H.F. scheme, the set of orbitals  $\psi_1, \psi_2, \dots, \psi_N$  are not uniquely determined as the equations (26) are invariant under an orthogonal transformation of these functions. The elements  $\rho'_{ij}$  of the density matrices (and consequently the density matrices themselves) are, however, uniquely determined.

Multiplying (26) by  $\psi_k^*(x_1')$ , summing over  $k$  and remembering that

$$\frac{1}{l!} \sum_{j=1}^l \rho'_{l; 1j} \rho'_{1j} = \Gamma(x_1' \dots x_l' | x_1 \dots x_l) \quad (30)$$

we get from (26), (28) and (30) that

$$\begin{aligned}
 & \sum_{l=1}^6 l \int H_c^l(x_1 \dots x_l) \Gamma(x_1', x_2', \dots, x_l' | x_1 \dots x_l) dx_2 \dots dx_l \\
 &= \sum_{l=1}^6 \frac{1}{(l-1)!} \int \rho_{\mu 1} H_c^l(x_\mu x_2 \dots x_l) \\
 & \quad \times \begin{vmatrix} \rho'_{1\mu} & \rho'_{12} & \dots & \rho'_{1l} \\ \rho'_{2\mu} & \rho'_{22} & \dots & \rho'_{2l} \\ \dots & \dots & \dots & \dots \\ \rho'_{l\mu} & \rho'_{l2} & \dots & \rho'_{ll} \end{vmatrix} dx_\mu dx_2 \dots dx_l. \tag{31}
 \end{aligned}$$

Multiplying (26) by  $\psi_{k^*}(x_a)$  and subtracting from it the corresponding equation for the conjugate of  $\psi_k(x_a)$  multiplied by  $\psi_k(x_1)$  and summing over  $k$ , one gets

$$\begin{aligned}
 & \sum_{l=1}^6 \frac{1}{(l-1)!} \int H_c^l(x_1 \dots x_l) \\
 & \quad \times \begin{vmatrix} \rho'_{a1} & \rho'_{a2} & \dots & \rho'_{al} \\ \rho'_{21} & \rho'_{22} & \dots & \rho'_{2l} \\ \dots & \dots & \dots & \dots \\ \rho'_{l1} & \rho'_{l2} & \dots & \rho'_{ll} \end{vmatrix} dx_2 \dots dx_l \\
 &= \sum_{l=1}^6 \frac{1}{(l-1)!} \int H_c^l(x_a \dots x_l) \\
 & \quad \times \begin{vmatrix} \rho'_{1a} & \rho'_{12} & \dots & \rho'_{1l} \\ \rho'_{2a} & \rho'_{22} & \dots & \rho'_{2l} \\ \dots & \dots & \dots & \dots \\ \rho'_{la} & \rho'_{l2} & \dots & \rho'_{ll} \end{vmatrix}^* dx_2 \dots dx_l. \tag{32}
 \end{aligned}$$

Equations (31) and (32) are integro-differential equations governing the density matrices. When correlation effects are neglected, we have  $g = 1$  and therefore  $a = 1$  and  $\beta = 0$ . It can easily be verified that in this case equations (26) reduce to the ordinary Hartree-Fock equations. Further, if we write

$F(x_1, x_2) = e^2 |r_{12}$  and  $B(x_1) = \int F(x_1, x_2) \rho(x_2, x_2) dx_2$ , then equation (32) reduces to the well-known equation.<sup>6</sup>

$$\{E(x) + B(x) - E(x') - B(x')\} \rho(x, x') - \int [F(x, x'') - F(x', x'')] \rho(x, x'') \rho(x'', x') dx'' = 0. \tag{33}$$

If we write

$$E(x) = \frac{p^2}{2m} + V(x) = -\frac{\hbar^2}{8\pi^2 m} \nabla_x^2 + V(x),$$

equation (31) becomes

$$\begin{aligned} & -\frac{\hbar^2}{8\pi^2 m} \int \delta(x - x') \nabla_x^2 \rho(x', x) dx' + (V + B) \rho(x, x) \\ & = \int F(x, x') |\rho(x, x')|^2 dx' + \int \rho(x', x) E(x') \rho(x, x') dx' \\ & \quad + \int F(x', x'') |\rho(x, x')|^2 \rho(x'', x'') dx' dx'' \\ & \quad - \int F(x', x'') \rho(x', x) \rho(x, x'') \rho(x'', x') dx' dx''. \end{aligned} \tag{34}$$

The above equation can be used to determine the charge density  $\rho(x, x)$  of the electron cloud of the atom.

### 5. THE ENERGY MATRIX

Let us now consider in greater detail the left-hand side of equation (32). We have

$$\begin{aligned} \text{L.H.S.} &= H_c^1(x_1) \rho'_{a1} + \sum_{l=2}^6 \frac{1}{(l-1)!} \int H_c^l(x_1 \dots x_l) \\ & \quad \times \begin{vmatrix} \rho'_{a1} & \rho'_{a2} & \dots & \rho'_{al} \\ \rho'_{21} & \rho'_{22} & \dots & \rho'_{2l} \\ \dots & \dots & \dots & \dots \\ \rho'_{l1} & \rho'_{l2} & \dots & \rho'_{ll} \end{vmatrix} \\ &= H_c^1(x_1) \rho'_{a1} + \sum_{l=2}^6 \frac{1}{(l-1)!} \int H_c^l(x_1 \dots x_l) \\ & \quad \times \left\{ \rho'_{a1} \rho'_{l; 11} + \sum_{k=2}^l \rho'_{ak} \rho'_{l; 1k} \right\} dx_2 \dots dx_l. \end{aligned} \tag{35}$$

Now since  $H_c^l(x_1 \dots x_l)$  is a symmetric function of  $x_1, x_2, \dots, x_l$ , it can be seen by simple transpositions  $(x_2, x_k)$  ( $k = 3, \dots, l$ ) of the integration variables  $x_2, x_3, \dots, x_k$  that the  $(l - 1)$  terms in the second summation of the above integral are all equal to  $\int H_c^l(x_1 \dots x_l) \rho'_{a2\rho' l; 12} dx_2 \dots dx_l$ .

Thus,

$$\begin{aligned} \text{L.H.S.} = & H_c^1(x_1) \rho'_{a1} + \frac{1}{(l-1)!} \int H_c^l(x_1 \dots x_l) \\ & \times \{ \rho'_{a1\rho' l; 11} + (l-1) \rho'_{a2\rho' l; 12} \} dx_2 \dots dx_l. \end{aligned} \quad (36)$$

Now  $\rho_{ij} = \rho(x_i, x_j) = \sum \psi_k^*(x_i) \psi_k(x_j)$  can be regarded as the  $(x_i, x_j)$ -th element of a continuous matrix  $\rho$ . We shall define a matrix  $K(x_2, x_1)$  by means of the following relation:

$$K(x_2, x_1) = K^1(x_2, x_1) + \sum_{l=2}^6 \frac{1}{(l-1)!} K^l(x_2, x_1) \quad (37)$$

where

$$\begin{aligned} K^1(x_2, x_1) &= \int \delta(x_2 - \eta) H_c^1(\eta, p_\eta) \delta(\eta - x_1) d\eta \\ K^l(x_2, x_1) &= \delta(x_2 - x_1) B^l(x_1) + (l-1) \int H_c^l(x_1 \dots x_l) \\ &\quad \times \rho'_{l; 12} dx_3 \dots dx_l; \end{aligned} \quad (38)$$

and

$$B^l(x_1) = \int H_c^l(x_1 \dots x_l) \rho'_{l; 11} dx_2 \dots dx_l. \quad (39)$$

We shall define the  $(a1)$ -th element of the product by  $\rho K^l$  by

$$(\rho K^l)_{a1} = \int K^l(x_2, x_1) \rho(x_a, x_2) dx_2. \quad (40)$$

The definition is the same as the usual matrix multiplication law, but we take care to write  $\rho(x_a, x_2)$  after the operator  $K(x_2, x_1)$  so that the latter can operate on  $\rho(x_a, x_2)$ . We can then show the left-hand side of equation (32) to be the  $(a1)$ -th element of  $\rho K$ . We have in fact

$$\begin{aligned} (\rho K^l)_{a1} &= \int \delta(x_1 - x_2) B^l(x_1) \rho(x_a, x_2) dx_2 \\ &\quad + (l-1) \int H_c^l(x_1 \dots x_l) \rho'_{l; 12} \rho'_{a2} \dots dx_2 \dots dx_l \\ &= B^l(x_1) \rho'_{a1} + \int H_c^l(x_1 \dots x_l) \sum_{k=2}^l \rho'_{l; 1k} \rho'_{ak} dx_2 \dots dx_l \\ &= \int H_c^l(x_1 \dots x_l) \begin{vmatrix} \rho'_{a1} & \rho'_{a2} & \dots & \rho'_{al} \\ \rho'_{21} & \rho'_{22} & \dots & \rho'_{2l} \\ \dots & \dots & \dots & \dots \\ \rho'_{l1} & \dots & \dots & \rho'_{ll} \end{vmatrix} dx_2 \dots dx_l. \end{aligned} \quad (41)$$

Further  $H_c^l(x_1) \rho'_{a1}$  is obviously the  $(a^l)$ -th element of  $\rho K^l$ . Thus the left-hand side of equation (32) is the  $(a^l)$ -th element of  $\rho K$ . Similarly

$$\begin{aligned}
 \text{R.H.S.} &= H_c^l(x_a) \rho'^*_{1a} + \sum_{l=2}^6 \frac{1}{(l-1)!} \int H_c^l(x_a \dots x_l) \\
 &\quad \times \begin{vmatrix} \rho'_{1a} & \rho'_{12} & \dots & \rho'_{1l} \\ \rho'_{2a} & \rho'_{22} & \dots & \rho'_{2l} \\ \dots & \dots & \dots & \dots \\ \rho'_{la} & \rho'_{l2} & \dots & \rho'_{ll} \end{vmatrix}^* \\
 &= H_c^l(x_a) \rho_{a1'} + \sum_{l=2}^6 \frac{N!}{(N-l)! (l-1)!} \\
 &\quad \times \int \Psi(x_1 x_2 \dots x_N) H_c^l(x_a x_2 \dots x_l) \\
 &\quad \times \Psi^*(x_a x_2 \dots x_N) dx_2 \dots dx_N \\
 &= H_c^l(x_a) \rho_{a1'} + \sum_{l=2}^6 \frac{N!}{(N-l)! (l-1)!} \\
 &\quad \times \int \Psi^*(x_a x_2 \dots x_N) H_c^l(x_a x_2 \dots x_l) \\
 &\quad \times \Psi(x_1 x_2 \dots x_N) dx_2 \dots dx_N \tag{42}
 \end{aligned}$$

since  $H_c^l$  is a real operator.

Thus we have

$$\begin{aligned}
 \text{R.H.S.} &= H_c^l(x_a) \rho_{a1'} + \sum \frac{1}{(l-1)!} \int H_c^l(x_a \dots x_l) \\
 &\quad \times \begin{vmatrix} \rho'_{a1} & \rho'_{a2} & \dots & \rho'_{al} \\ \rho'_{21} & \rho'_{22} & \dots & \rho'_{2l} \\ \dots & \dots & \dots & \dots \\ \rho'_{l1} & \dots & \dots & \rho'_{ll} \end{vmatrix}. \tag{43}
 \end{aligned}$$

Now

$$\begin{aligned}
 (K\rho)_{a1} &= \sum_{l=1}^6 \frac{1}{(l-1)!} \int K^l(x_a, x_2) \rho'(x_2, x_1) dx_2 \\
 &= \sum_{l=1}^6 \frac{1}{(l-1)!} \{B^l(x_a) \rho'_{a1} + (l-1) \int H_c^l(x_a x_2 \dots x_l) \\
 &\quad \times \rho'_{l; 2a} \rho'_{21} dx_2 \dots dx_l\} \\
 &= \text{R.H.S.} \tag{44}
 \end{aligned}$$

as can be seen by expanding the determinants in (43) along their first columns. Thus the equation (32) is the  $(\alpha 1)$ -th element of  $K\rho - \rho K$ . Hence we can write

$$K\rho - \rho K = 0. \quad (45)$$

The second term in  $K_l(x_2, x_1)$  subtracts from the matrix  $B(x_2, x_1) = \delta(x_2 - x_1) B(x_1)$  the physically irrelevant terms corresponding to the action of an electron upon itself and at the same time accounts for the exchange effect.

We can in fact express the energy of the system in terms of the matrices  $K^l(x_1, x_2)$  we have

$$W = D \left[ \rho \left( \sum_{l=1}^6 \frac{K^l}{l!} \right) \right] \quad (46)$$

where  $D$  denotes the diagonal sum or spur.

The matrix  $K$  is a generalisation of the matrix  $(E + B - A)$  (see Frenkel, pages 428–36) for the case when correlation is introduced into the theoretical formalism, and reduces to the latter when correlation is neglected. It can thus be regarded as the energy matrix for the system in analogy with the theory of the density matrix based on the Hartree-Fock equations. The importance of the energy matrix lies in the facility with which it enables one to pass on to a representation in the phase space and thus to obtain a semi-classical expression for the density of the charge cloud of the system. It is well known that by transforming the matrix  $K(x_1, x_2)$  into one  $\{K(x_1, p_1)\}$  involving the position and momentum of the particles, one can obtain the so-called Thomas-Fermi-Dirac equation that includes exchange effects besides. Thus the matrix  $K(x_1, x_2)$  defined in (37) can be used as a convenient starting-point to derive the equation governing the charge cloud of a molecular system; the details of this transformation theory leading to a correlated Thomas-Fermi charge distribution will be published separately in a different paper.

## 6. A GENERAL CORRELATION FACTOR

In the above discussion, we have chosen a correlation factor which is a linear function of  $f(r_{ij})$  where  $r_{ij}$  is the inter-electronic distance between the  $i$ -th and  $j$ -th electrons; each term of  $g$  thus contains the co-ordinates of two electrons only. While this type of correlation factor is the simplest to deal with and can certainly be expected to improve the H.F. equations, it does not take into account of the multiple correlations connecting the

positions of different electrons at the same time. A general correlation function is either a polynomial in the  $\binom{N}{2}$  inter-electronic distances or a convergent power series in them. Let us suppose that  $H_c (= gHg)$  is of the form

$$H_c = \sum_{l=1}^N \left\{ \sum_{s_1, \dots, s_l} \frac{1}{l!} H_c^l(x_1, x_2, \dots, x_l) \right\}. \quad (47)$$

The correlated H.F. equations in this case become

$$\begin{aligned} \sum_{l=1}^N \frac{1}{(l-1)!} \int H_c^l(x_1, x_2, \dots, x_l) \sum_{j=1}^l \rho'_{l;1j} \psi_k(x_j) dx_2 \dots dx_l \\ - \sum_{i=1}^N \lambda_{ki} \psi_i(x_1) = 0 \quad (k = 1, 2, \dots, N). \end{aligned} \quad (48)$$

The difference between (48) and (26) consists only in the summation for  $l$ ; while in (26) the summation for  $l$  runs from 1 to 6, in (48), it runs from 1 to  $N$ . The integro-differential equations satisfied by the density matrices in this case can be obtained from (31) and (32) by making the summation for  $l$  to run from 1 to  $N$ .

## 7. SPECIAL CASE

In this section, we write down the explicit form of the correlated H.F. equations for the case of the simplest two-electron system, namely the Helium atom. We do not propose to evaluate the energy of the system as this has been done by several authors, but give the form of the equations (26) as this might enable one to have some insight into the meaning of these equations. We have here

$$\begin{aligned} H_c^1 = a^2 E(x_1) &= a^2 \left\{ \frac{p_1^2}{2m} - \frac{Ze^2}{r_1} \right\} \\ H_c^2(x_1, x_2) &= a^2 F(x_1, x_2) + \alpha\beta [f(r_{12}), E(x_1) + E(x_2)] \\ &\quad + \frac{2\alpha\beta e^2 f(r_{12})}{r_{12}} + \beta^2 f(r_{12}) [E(x_1) + E(x_2)] f(r_{12}) \\ &\quad + \frac{\beta^2 e^2 f^2(r_{12})}{r_{12}}. \end{aligned} \quad (49)$$



Equations (28) become

$$\begin{aligned} H_c^1(x) \psi_1(x_1) + [ \int H_c^2(x_1, x_2) \psi_2^2(x_2) dx_2 ] \psi_1(x_1) \\ - [ \int H_c^2(x_1, x_2) \psi_2^*(x_2) \psi_1(x_2) dx_2 ] \psi_2(x_1) \\ = E_1 \psi_1(x_1) \end{aligned} \tag{50}$$

and a similar equation for electron 2 which may be obtained from the above by interchanging the indices 1 and 2. In the above we have chosen a diagonal representation for the matrix  $(\lambda_{ij})$ , and  $E_1$  and  $E_2$  denote the diagonal elements.  $H_c^1$  denotes the kinetic energy operator of the electron 1 plus its potential energy in the field of the nuclei. The second term in the bracket gives the average of the operator  $H_c^2(x_1, x_2)$  for all positions of the electron 2 and the third term gives the exchange effects. Since  $H_c^2(x_1, x_2)$  contains a term  $\alpha^2 F(x_1, x_2)$ , the part of it containing the factor  $\alpha^2$  can be interpreted as the potential energy of electron 1 moving in the average electric field of electron 2. The terms  $\alpha\beta [f(r_{12}), E(x_1) + E(x_2)]$  give the influence of correlation on the kinetic energies of the electrons. The term  $[\alpha\beta \int f(r_{12}) \psi_2^2(x_2) dx_2] E(x_1)$  especially shows that the kinetic energy of electron 1 is not independent of the motion of the electron 2, but is correlated with it. Since correlation reduces the chances of two electrons coming close to each other, it also reduces the fluctuations in the kinetic energies of the electrons and thus tends to make the distributions of the kinetic energies rather uniform. If we take  $f(r_{12}) = r_{12}$ , then  $\alpha\beta \int f(r_{12})/r_{12} \psi_2^2(x_2) dx_2 = \alpha\beta e^2$  and therefore the Hamiltonian for the electron 1 contains a constant term. By transferring this term to the right-hand side, the latter becomes  $(\epsilon_1 - \alpha\beta e^2) \psi_1$  and thus the influence of the correlation factor is to reduce the energy of the system. Since  $f(r_{12})$  is an increasing function of  $r_{12}$ , the effect of the term  $\beta^2 e^2 f^2(r_{12})/r_{12}$  in  $H_c^2(x_1, x_2)$  will be to increase the average inter-electronic distance and consequently to diminish the energy of the system.

### 8. NON-STATIONARY SYSTEMS

There are several problems of physical and chemical importance that depend for their solution on the time-dependent Schroedinger equation

$$\left( H + \frac{\hbar}{2\pi i} \frac{\partial}{\partial t} \right) \chi = 0. \tag{51}$$

In this section, we consider such non-stationary systems and find out the orbitals  $\psi_k(x, t)$  that make the function  $\Phi = g\Psi$ , where  $\Psi$  is given by

(3 a), the 'best' approximation for the equation (51). These orbitals are given by the variational principle

$$\delta \int \Phi^* \left( H + \frac{\hbar}{2\pi i} \frac{\partial}{\partial t} \right) \Phi d\tau = 0 \quad (52)$$

or

$$\delta \int \Psi^* \left( H_c - i\hbar G \frac{\partial}{\partial t} \right) \Psi d\tau = 0 \quad (52 a)$$

where

$$\begin{aligned} G &= g^2 \\ &= \alpha^2 + \frac{1}{2!} \sum'_{ij} G(i, j) + \frac{1}{3!} \sum'_{ijk} G(i, j, k) \\ &\quad + \frac{1}{4!} \sum'_{ijkl} G(i, j, k, l) \end{aligned} \quad (53)$$

$$G(i, j) = 2\alpha\beta f(r_{ij}) + \beta^2 f^2(r_{ij});$$

$$G(i, j, k) = 2\beta^2 \left[ f(r_{ij}) \{ (f(r_{jk}) + f(r_{ik})) + f(r_{jk})f(r_{ik}) \} \right];$$

$$G(i, j, k, l) = 2\beta^2 \{ f(r_{ij})f(r_{kl}) + f(r_{ik})f(r_{jl}) + f(r_{il})f(r_{jk}) \}. \quad (54)$$

We shall now evaluate the variation in (52 a) in two steps: first find out the variation of  $J_1 = \int \Psi^* H_c \Psi d\tau$  and secondly calculate the variation of

$$J_2 = \int G \Psi^* \frac{\partial \Psi}{\partial t} d\tau. \quad (55)$$

(a) First consider

$$\delta J_1 = \int \delta \Psi^* H_c \Psi d\tau + \int \delta \Psi H_c \Psi^* d\tau. \quad (56)$$

Now  $\int \Psi^* H_c \Psi d\tau$  is given by (22) and  $\int \delta \Psi^* H_c \Psi d\tau$  can be obtained from this by varying only the primed quantities (or the quantities with an asterisk) without varying  $\psi_1, \psi_2, \dots, \psi_N$ . We shall denote variations of this type by  $\delta^*$ . Similarly  $\int \delta \Psi H_c \Psi^* d\tau$  can be obtained by replacing the  $\Gamma$ 's in (22) by their complex conjugates and varying only the functions  $\psi_1, \psi_2, \dots, \psi_N$  in  $\Gamma^*(x'_1 x'_2 \dots x'_l | x_1 \dots x_l)$  ( $l = 1, 2, \dots, 6$ ). As mentioned earlier we follow the convention that the operators  $H_c^l$  and  $\partial/\partial t$  operate only on the unprimed quantities and that after these operations have been performed one should put  $x'_i = x_i$  ( $i = 1, 2, \dots, N$ ) and  $t' = t$  in the integrals.

Since by (8 a) the  $\Gamma$ 's are functions of  $\rho'_{ij}$ , we have

$$\begin{aligned}
 & \delta^* \Gamma(x_1' x_2' \dots x_l' | x_1 \dots x_l) \\
 &= \sum_{ij} \frac{\partial \Gamma(x_1' \dots x_l' | x_1 \dots x_l)}{\partial \rho'_{ij}} \delta^* \rho'_{ij} \\
 &= \frac{1}{l!} \sum_{i,j=1}^l \rho'_{i;ij} \left( \sum_{k=1}^N \delta \psi_k^*(x_i') \psi_k(x_j) \right) \quad (57)
 \end{aligned}$$

where  $\rho'_{i;ij}$  is the co-factor of  $\rho'_{ij}$  in  $\rho'_l$ .

Now

$$\begin{aligned}
 & \int \delta \Psi^* H_c \Psi d\tau \\
 &= \delta^* \sum_{i=1}^6 \int H_c^l(x_1 \dots x_l) \Gamma(x_1' \dots x_l' | x_1 \dots x_l) dx_1 \dots dx_l \\
 &= \sum_{i=1}^6 \int H_c^l(x_1 \dots x_l) \sum_{i,j=1}^l \rho'_{i;ij} \left\{ \sum_{k=1}^N \delta \psi_k^*(x_i') \psi_k(x_j) \right\} \\
 & \quad \times dx_1 \dots dx_l \\
 &= \sum_{i=1}^6 \frac{1}{l!} \int H_c^l(x_1 \dots x_l) \\
 & \quad \times \left\{ \sum_{j=1}^l \rho'_{i;ij} \sum_{k=1}^N \delta \psi_k^*(x_1') \psi_k(x_j) \right. \\
 & \quad \left. + \sum_{i=2}^l \sum_{j=1}^i \rho'_{i;ij} \sum_{k=1}^N \delta \psi_k^*(x_i') \psi_k(x_j) \right\}. \quad (58)
 \end{aligned}$$

Now the terms corresponding to the cases  $i = 2, 3, \dots, l$  can all be obtained from the first term of the above bracket by means of the cyclic permutations  $(x_1, x_2); (x_1, x_3); \dots (x_1, x_l)$  of the integration variables and thus the sums corresponding to the cases  $i = 2, 3, \dots, l$  are all identical with the sum corresponding to the case  $i = 1$ . Thus

$$\begin{aligned}
 & \int \delta \Psi^* H_c \Psi d\tau \\
 &= \sum_{i=1}^6 \frac{1}{(l-1)!} \int H_c^l(x_1 \dots x_l) \\
 & \quad \times \left\{ \sum_{j=1}^l \sum_{k=1}^N \rho'_{i;ij} \delta \psi_k^*(x_1') \psi_k(x_j) \right\} dx_1 \dots dx_l \quad (59)
 \end{aligned}$$

A similar expression follows for  $\int \delta\Psi H_c \Psi^* d\tau$  in which the variation acts on the unasterisked quantities alone. Thus

$$\begin{aligned} \delta J_1 = & \sum_{l=1}^6 \frac{1}{(l-1)!} \int \sum_{j=1}^l \sum_{k=1}^N \delta\psi_k^*(x_1) \\ & \times \{H_c^l(x_1 \dots x_l) \rho'_{lj}; \psi_k(x_j) dx_1 \dots dx_l\} \\ & + \int \delta\Psi H_c \Psi^* d\tau. \end{aligned} \tag{60}$$

(b) Next we have

$$\delta J_2 = \int G \delta\Psi^* \frac{\partial\Psi}{\partial t} d\tau - \int G \delta\Psi \frac{\partial\Psi^*}{\partial t} d\tau. \tag{61}$$

Now

$$\begin{aligned} & \delta^* \int G \Psi^* \frac{\partial\Psi}{\partial t} d\tau \\ & = \alpha^2 \sum_{k=1}^N \int \delta\Psi_k^*(x_1, t) \frac{\partial\Psi_k(x_1, t)}{\partial t} dx_1 \\ & \quad + \sum_{l=2}^4 \delta^* \frac{1}{l!} \int G(x_1 \dots x_l) \frac{\partial\rho'_{l+1}}{\partial t} dx_1 \dots dx_{l+1} \\ & \quad + \sum_{l=2}^4 \frac{(N-l-1)}{l!} \delta^* \int G(x_1 \dots x_l) Q_{l+1} dx_1 \dots dx_{l+1}, \end{aligned} \tag{62}$$

where

$$Q_{l+1} = \begin{vmatrix} \rho_{11} & \rho_{12} & \dots & \rho_{1l+1} \\ \rho_{21} & \rho_{22} & \dots & \rho_{2l+1} \\ \dots & \dots & \dots & \dots \\ \rho_{l1} & \rho_{l2} & \dots & \rho_{ll+1} \\ \frac{\partial\rho'_{l+1,1}}{\partial t} & \dots & \frac{\partial\rho'_{l+1,l}}{\partial t} & 0 \end{vmatrix} \tag{63}$$

$$= \alpha^2 \sum_{k=1}^N \int \delta\psi_k^*(x_1, t) \frac{\partial\psi_k(x_1, t)}{\partial t} dx_1 + t_2 + t_3 \tag{64}$$

where  $t_2$  and  $t_3$  denote respectively the second and third terms in the above expression. We shall first consider  $t_2$ . We have

$$\begin{aligned}
 t_2 &= \sum_{l=2}^4 \frac{1}{l!} \delta^* \int G(x_1 \dots x_l) \frac{\partial \rho'_{l+1}}{\partial t} dx_1 \dots dx_{l+1} \\
 &= \sum_{l=2}^4 \frac{1}{l!} \int G(x_1 \dots x_l) \frac{\partial}{\partial t} \delta^* \rho'_{l+1} dx_1 \dots dx_{l+1} \\
 &= \sum_{l=2}^4 \frac{1}{l!} \int G(x_1 \dots x_l) dx_1 \dots dx_{l+1} \\
 &\quad \times \frac{\partial}{\partial t} \left\{ \sum_{i=1}^{l+1} \sum_{j=1}^{l+1} \rho'_{l+1; ij} \sum_{k=1}^N \delta \psi_k^*(x_i) \psi_k(x_j) \right\}. \tag{65}
 \end{aligned}$$

Now the integrals of the sums corresponding to the cases  $i = 2, 3, \dots, l$  are all identical with the integral for the case  $i = 1$ . Further let us interchange the integration variables  $x_1$  and  $x_{l+1}$  in the sum corresponding to the case  $i = l + 1$ . Then we get

$$\begin{aligned}
 t_2 &= \sum_{l=2}^4 \frac{1}{l!} \int [lG(x_1 \dots x_l) + G(x_2 \dots x_{l+1}) \\
 &\quad \times \sum_{k=1}^N \delta \psi_k^*(x_1) \frac{\partial \rho^k_{l+1}}{\partial t} dx_1 \dots dx_{l+1}] \tag{66}
 \end{aligned}$$

where

$$\rho^k_{l+1} = \begin{vmatrix} \psi_k(x_1, t) & \psi_k(x_2, t) & \dots & \psi_k(x_{l+1}, t) \\ \rho'_{21} & \rho'_{22} & \dots & \rho'_{2l+1} \\ \dots & \dots & \dots & \dots \\ \rho'_{l+1, 1} & \rho'_{l+1, 2} & \dots & \rho'_{l+1, l+1} \end{vmatrix}. \tag{67}$$

Next

$$\begin{aligned}
 t_3 &= \sum_{l=2}^4 \frac{(N-l-1)}{l!} \int G(x_1 \dots x_l) dx_1 \dots dx_{l+1} \\
 &\quad \times \left\{ \sum_{i=1}^l \sum_{j=1}^{l+1} Q_{l+1; ij} \left( \sum_k \delta \psi_k^*(x_i) \psi_k(x_j) \right) \right. \\
 &\quad \left. + \sum_{i=1}^l Q_{l+1; l+1, j} \left( \sum_k \delta \psi_k^*(x_{l+1}) \frac{\partial \psi_k(x_j)}{\partial t} \right) \right\}. \tag{68}
 \end{aligned}$$

Now

$$Q_{l+1; l+1, j} = \rho_{l+1; l+1, j}. \quad (69)$$

Interchange as before the variables  $x_{l+1}$  and  $x_1$  in the second term in the bracket of the above integral. Then we get

$$\begin{aligned} t_3 = & \sum_{l=2}^4 \frac{(N-l-1)}{l!} \int \sum_{k=1}^N \delta\psi_k^*(x_1) dx_1 \dots dx_{l+1} \\ & \times \left\{ IG(x_1 \dots x_l) \sum_{j=1}^{l+1} Q_{l+1; lj} \psi_k(x_j) \right. \\ & \left. + G(x_2 \dots x_{l+1}) \sum_{j=1}^l \rho_{l+1; lj} \frac{\partial \psi_k(x_j)}{\partial t} \right\}. \quad (70) \end{aligned}$$

(c) Thirdly the orbitals  $\psi_i(x)$  satisfy the orthonormality conditions

$$\int \psi_k^*(x_1) \psi_i(x_1) dx_1 = 0 \quad (71)$$

or

$$\begin{aligned} \lambda_{ki} \int \delta\psi_k^*(x_1) \psi_i(x_1) dx_1 + \lambda_{ki} \int \psi_k^*(x_1) \delta\psi_i(x_1) dx_1 = 0 \\ (i, k = 1, 2, \dots, N) \quad (72) \end{aligned}$$

where  $\lambda_{ki}$  are arbitrary constants.

Subtracting (72) from  $\delta(J_1 - i\hbar J_2)$  which is given by (60), (64), (66) and (70) and equating to zero the coefficients of the variations  $\delta\psi_k^*(x_1)$ , we get

$$\begin{aligned} \left\{ H_c^1(x_1) - i\hbar a^2 \frac{\partial}{\partial t} \right\} \psi_k(x_1) + \sum_{l=2}^4 \frac{1}{(l-1)!} \\ \times \int H_c^l(x_1 \dots x_l) \sum_{j=1}^l \rho'_{l; lj} \psi_k(x_j) dx_2 \dots dx_l \\ - i\hbar \sum_{l=2}^4 \frac{1}{l!} \int \{ IG(x_1 \dots x_l) + G(x_2 \dots x_{l+1}) \} \\ \times \frac{\partial P_{l+1}^k}{\partial t} dx_2 \dots dx_{l+1} \\ - i\hbar \sum_{l=2}^4 \frac{(N-l-1)}{l!} \end{aligned}$$

$$\begin{aligned}
& \times \int \left\{ IG(x_1 \dots x_l) \sum_{j=1}^{l+1} Q_{l+1; 1j} \psi_k(x_j) \right. \\
& \left. + G(x_2 \dots x_{l+1}) \sum_{j=1}^l \rho_{l+1; 1j} \frac{\partial \psi_k(x_j)}{\partial t} \right\} dx_2 \dots dx_{l+1} \\
& = \sum_{i=1}^N \lambda_{ki} \psi_i(x_1) \tag{73}
\end{aligned}$$

and a similar equation for the complex conjugate of  $\psi_k(x_1)$ .

In the above equation, the Lagrangian multipliers  $\lambda_{ki}$  are functions of time; further when correlation is neglected, (21) reduces to the time-dependent H.F. equations as can be seen by putting  $\alpha = 1$  and  $\beta = 0$ .

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#### SUMMARY

The paper deals with a study of correlation effects in many-electron systems. Coulomb correlation is introduced into the theory by multiplying the Slater determinant formed from the one-electron orbitals by a correlation factor which is a symmetric and increasing function of the inter-electronic distances. The integro-differential equations satisfied by the best one-electron orbitals have then been deduced for non-stationary systems. From the extended Hartree-Fock equations given by Löwdin, the integro-differential equations satisfied by the density matrices have been derived. An expression for the energy-matrix of the system which is helpful in deriving a correlated Thomas-Fermi charge distribution, has also been given.

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## APPENDIX I

We shall here evaluate

$$T_l = \frac{\binom{N}{l}}{N!} \int G(x_1 x_2 \dots x_l) \frac{\partial \rho'_N}{\partial t} dx_1 \dots dx_N \quad (1)$$

and prove the relation (9) of Section 2. We have

$$T_l = \frac{\binom{N}{l}}{N!} \int G(x_1 x_2 \dots x_l) dx_1 \dots dx_N \times \left\{ \sum_{i=1}^l \sum_{j=1}^N \rho_{N;ij} \frac{\partial \rho'_{ij}}{\partial t} + \sum_{i=l+1}^N \sum_{j=1}^N \rho_{N;ij} \frac{\partial \rho'_{ij}}{\partial t} \right\} \quad (2)$$

$$= T_1 + T_2 \text{ (say)} \quad (3)$$

where  $T_1$  denotes the summation of  $i$  from 1 to  $l$  and  $T_2$  denotes the sum of terms for  $i = l + 1$  to  $N$ . Since  $G(x_1, \dots, x_l)$  is a symmetric function of  $x_1, \dots, x_l$ , the integrals of the sums corresponding to the terms  $i = 2, 3, \dots, l$  are all identical with the sum for the case  $i = 1$ . Thus

$$T_1 = \frac{\binom{N}{l}}{N!} \int l G(x_1 \dots x_l) \sum_{j=1}^N \rho_{N;1j} \frac{\partial \rho'_{1j}}{\partial t} dx_1 \dots dx_N. \quad (4)$$

Again the integrals corresponding to the cases  $j = l + 2, l + 3, \dots, N$  are all identical with the value of the integral for the case  $j = l + 1$ , as can be seen by the transpositions of the integration variables  $(x_{l+1}, x_{l+2}); (x_{l+1}, x_{l+3}), \dots, (x_{l+1}, x_N)$ . Further when  $j < (l + 2)$ ,

$$\int \rho_{N;1j} dx_{l+2} \dots dx_N = (N - l)! \rho_{l+1;1j}. \quad (5)$$

Thus

$$T_1 = \frac{1}{l!} \int l G(x_1 \dots x_l) dx_1 \dots dx_{l+1} \times \left\{ \sum_{j=1}^l \rho_{l+1;1j} \frac{\partial \rho'_{1j}}{\partial t} + (N - l) \rho_{l+1;1(l+1)} \frac{\partial \rho'_{1(l+1)}}{\partial t} \right\}. \quad (6)$$



We shall next consider  $T_2$ .

By means of the transpositions  $(x_{l+1} x_{l+2}) \dots (x_{l+1}, x_N)$  of the integration variables, one can see that the integrals corresponding to the cases  $i = l + 2$  to  $N$  are all identical with the value of the integral for  $i = l + 1$ . Thus

$$T_2 = \frac{\binom{N}{l}}{N!} (N - l) \int G(x_1 \dots x_l) \sum_{j=1}^N \rho_{N; l+1j} \frac{\partial \rho'_{l+1,j}}{\partial t} dx_1 \dots dx_N \quad (7)$$

$$\begin{aligned} &= \frac{\binom{N}{l}}{N!} (N - l) \int G(x_1 \dots x_l) \\ &\quad \times \left\{ \sum_{j=1}^{l+1} \rho_{N; l+1j} \frac{\partial \rho'_{l+1,j}}{\partial t} + (N - l - 1) \right. \\ &\quad \left. \times \rho'_{N; l+1, l+2} \frac{\partial \rho'_{l+1, l+2}}{\partial t} \right\} dx_1 \dots dx_N \quad (8) \end{aligned}$$

which follows again by the same argument of permutation of integration variables used above. Integrating the first term in the above with respect to the variables  $x_{l+2}$  to  $x_N$  and the second term with respect to the variables  $x_{l+3}$  to  $x_N$  one gets

$$\begin{aligned} T_2 &= \frac{1}{l!} \int G(x_1 \dots x_l) dx_{l+1} \\ &\quad \times \left\{ (N - l) \sum_{j=1}^{l+1} \rho_{l+1; l+1,j} \frac{\partial \rho'_{l+1,j}}{\partial t} + (N - l - 1) \right. \\ &\quad \left. \times \rho_{l+2; l+1, l+2} \frac{\partial \rho'_{l+1, l+2}}{\partial t} dx_{l+2} \right\}. \quad (9) \end{aligned}$$

Let us now consider the second term of the above expression and denote it by  $T_2^2$ . Expanding the determinant  $\rho_{l+2; l+1, l+2}$  along its last column, integrating with respect to the co-ordinate of the electron  $(l + 1)$  and changing the integration variable  $x_{l+2}$  into  $x_{l+1}$  in the resulting integral, one gets

$$T_2^2 = - \frac{(N - l - 1)}{l!} \int G(x_1 \dots x_l) dx_1 \dots dx_{l+1}$$

$$\times \left\{ l \rho_{l+1; 1l+1} \frac{\partial \rho'_{1l+1}}{\partial t} + \frac{\partial \rho'_{l+1, l+1}}{\partial t} \rho'_{l+1; l+2, l+1} \right\}. \quad (10)$$

From (9), (10) and (6), we get on summing  $T_1$  and  $T_2$  and grouping together like terms that

$$\begin{aligned} (T_1 + T_2) &= \frac{1}{l!} \int lG(x_1 \dots x_l) \\ &\times \left( \sum_{j=1}^{l+1} \rho_{l+1; ij} \frac{\partial \rho'_{ij}}{\partial t} \right) dx_1 \dots dx_{l+1} \\ &+ \frac{1}{l!} \int G(x_1 \dots x_l) \\ &\times \left\{ (N-l) \sum_{j=1}^l \rho'_{l+1; l+1, j} \frac{\partial \rho'_{l+1, j}}{\partial t} \right. \\ &\left. + \rho'_{l+1; l+1, l+1} \frac{\partial \rho'_{l+1, l+1}}{\partial t} \right\} \end{aligned} \quad (11)$$

or

$$\begin{aligned} T_l &= \frac{1}{l!} \int G(x_1 \dots x_l) dx_1 \dots dx_{l+1} \\ &\times \left\{ \sum_{i=1}^l \sum_{j=1}^{l+1} \rho_{l+1; ij} \frac{\partial \rho'_{ij}}{\partial t} + \sum_{j=1}^{l+1} \rho_{l+1; l+1, j} \frac{\partial \rho'_{l+1, j}}{\partial t} \right. \\ &\left. + (N-l-1) \sum_{j=1}^l \rho_{l+1; l+1, j} \frac{\partial \rho'_{l+1, j}}{\partial t} \right\}. \end{aligned} \quad (12)$$

On writing the summations in the above term in a determinantal form, we get the relation (9) of Section 2.