

THE STRUCTURE OF CORRELATION AMPLITUDES IN MANY-FERMION SYSTEMS*

by

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ABSTRACT

The structure of the correlation functions appearing in Sinanoğlu's many-electron theory is analyzed. It is shown how these functions lead naturally to the definitions of correlation amplitudes satisfying a set of coupled integro-differential equations. Approximate solutions to a subset of these equations - the two-particle equations - correspond with solutions of the "exact pair" equations proposed by Sinanoğlu. The relationship of these correlation amplitudes with those employed by Clark and Westhaus in cluster expansion techniques is also explored, and the equivalence of Sinanoğlu's "exact pair" theory with their truncated factor-cluster formalism is demonstrated.

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In his formulation of the problem of determining the electronic eigenstates

$$H\Psi = E\Psi \quad (1)$$

Sinanoğlu^{1,2,3} has proposed that for a particular state m Ψ_m be written

$$\Psi_m = Q(N) \left[\frac{1}{i!} \prod_{i=1}^N \varphi_{m_i}(x_i) + \sum_{p \neq i} \frac{1}{i!p} \prod_{i \neq p} \varphi_{m_i}(x_i) U_{m_p}(x_p) + \right. \\ \left. \frac{1}{\sqrt{2!}} \sum_{p < q} \frac{1}{i!p!q} \prod_{i \neq p, q} \varphi_{m_i}(x_i) U_{m_p m_q}(x_p, x_q) + \dots \frac{1}{N!} \prod_{i=1}^N \varphi_{m_i}(x_i) \right] \quad (2)$$

with the antisymmetrizer defined as

$$Q(N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^S P \quad (3)$$

Here, $\varphi_{m_1}(x_1), \varphi_{m_2}(x_2), \dots, \varphi_{m_N}(x_N)$ are a particular set of N single particle functions (orbitals) chosen from among the elements of an orthonormal basis $\{\varphi_i\}$ which we shall assume satisfy

$$h(x_i) \varphi_i(x_i) = \epsilon_i \varphi_i(x_i), \quad (x_i = r_i, s_i) \quad (4)$$

The electronic Hamiltonian can then be resolved into an "unperturbed" and a "perturbed" part in the usual fashion:

$$H = H_0 + (H - H_0) \\ = H_0 + V, \quad (5)$$

where

$$H_0(1 \dots N) = \sum_{i=1}^N h(i) \quad (6)$$

The orbitals $\varphi_{m_i}, i=1, \dots, N$ and $h(i)$ may, for example, be chosen self-consistently as in the Hartree-Fock Scheme with the remaining elements of $\{\varphi_i\}$ determined in accordance with (4).

In any event, we may choose $\varphi_{m_1}, \varphi_{m_2}, \dots, \varphi_{m_N}$ in some optimal fashion, so that this configuration has the largest amplitude in a determinantal expansion of Ψ_m in terms of $\{\varphi_i\}$ and normalize

Ψ_m such that this amplitude is unity. The correlation functions $U_{m_1 \dots m_N}^{(x_1 \dots x_N)}$ can be expressed in terms of the configuration interaction (CI) amplitudes

$$U_{m_1 \dots m_N}^{(x_1 \dots x_N)} = \frac{1}{\sqrt{n!}} \sum_{\lambda_1 \dots \lambda_n} C_{m_N \dots x_n \dots x_1 \dots m_1 \dots m_1 \dots m_2 \dots m_N} \det[\varphi_{\lambda_1}^{(x_1)} \dots \varphi_{\lambda_n}^{(x_n)}] \quad (7)$$

The sum is over all combinations of n orbitals omitted from the set $\{m_1, m_2, \dots, m_N\}$, and $C_{m_N \dots x_n \dots x_1 \dots m_1 \dots m_1 \dots m_2 \dots m_N}$ is the coefficient of the configuration obtained by replacing orbitals

$\varphi_{m_1}, \dots, \varphi_{m_n}$ in $\det[\varphi_{m_1}^{(x_1)} \varphi_{m_2}^{(x_2)} \dots \varphi_{m_N}^{(x_N)}]$ by orbitals $\varphi_{\lambda_1}, \dots, \varphi_{\lambda_n}$ respectively. (Here, $[\varphi_{p_1}^{(x_1)} \dots \varphi_{p_p}^{(x_p)}]$ denotes a $p \times p$ matrix whose i, j th element is $\varphi_{p_i}^{(x_j)}$.) In practice these

coefficients are to be determined via some perturbative or variational calculation but formally are given in terms of the sought-for

eigenstate Ψ_m by

$$C_{m_1 \dots m_N} = \frac{1}{\sqrt{N!}} \int \prod_{i=1}^N dx_i \det[\varphi_{m_i}^{(x_i)}] \Psi_m^* \quad (8)$$

We hope to point out some interesting properties of these correlation functions and the "correlation amplitudes" to which they naturally lead. Although the derivations given here are original and the implications regarding Sinanoglu's formalism have not been fully explored previously⁴, much of the following leans heavily upon the work of Primas⁵ and, although not contained in his work, is inspired by it.

Substitution of (8) into (7) followed by the interchange of the sums over orbital indices with the integrations over particle coordinates allows us to write

$$U_{m_1, \dots, m_N}^{(x_1, \dots, x_N)} =$$

$$\frac{1}{\sqrt{N!n!}} \int \prod_{i=1}^N dx'_i \sum_{x'_1 < \dots < x'_N} \begin{vmatrix} \varphi_{m_1}^*(x'_1) & \dots & \varphi_{x'_1}^*(x'_1) & \dots & \varphi_{x'_n}^*(x'_1) & \dots & \varphi_{m_N}^*(x'_1) \\ \vdots & & \vdots & & \vdots & & \vdots \\ \varphi_{m_1}^*(x'_N) & \dots & \varphi_{x'_1}^*(x'_N) & \dots & \varphi_{x'_n}^*(x'_N) & \dots & \varphi_{m_N}^*(x'_N) \end{vmatrix} \begin{vmatrix} 1 & \dots & 0 & \dots & 0 & \dots & 0 \\ 0 & 1 & \vdots & & \vdots & & \vdots \\ \vdots & & \varphi_{x'_1}^{(x_1)} & \dots & \varphi_{x'_n}^{(x_1)} & \dots & 0 \\ \vdots & & \vdots & & \vdots & & \vdots \\ 0 & \dots & 0 & \dots & 0 & \dots & 1 \end{vmatrix} \times \Psi_{\underline{m}}^{(x_1, \dots, x_N)}$$

$$= \frac{1}{\sqrt{N!n!}} \int \prod_{i=1}^N dx'_i \sum_{x'_1 < \dots < x'_N} \begin{vmatrix} \varphi_{m_1}^*(x'_1) & \dots & \sum_{\ell=1}^n \varphi_{x'_\ell}^*(x'_1) \varphi_{x'_\ell}^{(x_1)} & \dots & \sum_{\ell=1}^n \varphi_{x'_\ell}^*(x'_1) \varphi_{x'_\ell}^{(x_n)} & \dots & \varphi_{m_N}^*(x'_1) \\ \vdots & & \vdots & & \vdots & & \vdots \\ \varphi_{m_1}^*(x'_N) & \dots & \sum_{\ell=1}^n \varphi_{x'_\ell}^*(x'_N) \varphi_{x'_\ell}^{(x_1)} & \dots & \sum_{\ell=1}^n \varphi_{x'_\ell}^*(x'_N) \varphi_{x'_\ell}^{(x_n)} & \dots & \varphi_{m_N}^*(x'_N) \end{vmatrix} \times \Psi_{\underline{m}}^{(x_1, \dots, x_N)}$$

$$= \frac{1}{\sqrt{N!n!}} \int \prod_{i=1}^N dx'_i \sum_{x'_1 < \dots < x'_N} \det W_{\substack{(x'_1, \dots, x'_N; x_1, \dots, x_n) \\ m_1, \dots, m_N; x_1, \dots, x_n}} \cdot$$

A particular determinant appearing in the sum in the integrand depends upon N orbitals $\varphi_{m_1}, \dots, \varphi_{m_{j-1}}, \varphi_{x_1}, \dots, \varphi_{x_n}, \varphi_{m_{(j+n+1)}}, \dots, \varphi_{m_N}$ with the q - p th element of the corresponding matrix $W_{m_1, \dots, x_1, \dots, x_n, m_N}$ being given by

$$\varphi_{m_p}^*(x_q), \quad \text{if } p \notin \{j_1, \dots, j_n\}, \tag{10}$$

$$(W_{m_1, \dots, x_1, \dots, x_n, m_N})_{qp} = \sum_{\ell=1}^n \varphi_{x_\ell}^*(x_q) \varphi_{x_\ell}(x_i), \quad \text{if } p=j_i, i=1, \dots, n.$$

That is, to construct $W_{m_1, \dots, x_1, \dots, x_n, m_N}$ we take $[\varphi_{m_1}, \dots, \varphi_{m_j}, \dots, \varphi_{m_n}, \dots, \varphi_{m_N}]$ and replace the q row of the j_i column by $\sum_{\ell=1}^n \varphi_{x_\ell}^*(x_q) \varphi_{x_\ell}(x_i)$, $q=1, \dots, N$, $i=1, \dots, n$. Moreover, the sum of all such determinants may be expressed as a single determinant:

$$\sum_{x_1 < \dots < x_n} \det W_{m_1, \dots, x_1, \dots, x_n, m_N} = \sum_{x_1 < \dots < x_n} \left\{ \begin{matrix} x_n & x_n & \dots & x_n \\ \sum_{\ell=1}^n & \sum_{\ell=2}^n & \dots & \sum_{\ell=n}^n \end{matrix} \begin{matrix} \varphi_{m_1}^*(x_1) & \dots & \varphi_{x_1}^*(x_1) \varphi_{x_1}(x_1) & \dots & \varphi_{x_n}^*(x_1) \varphi_{x_n}(x_1) & \dots & \varphi_{m_N}^*(x_1) \\ \vdots & & \vdots & & \vdots & & \vdots \\ \varphi_{m_1}^*(x_n) & & \varphi_{x_1}^*(x_n) \varphi_{x_1}(x_n) & \dots & \varphi_{x_n}^*(x_n) \varphi_{x_n}(x_n) & \dots & \varphi_{m_N}^*(x_n) \end{matrix} \right\} \tag{11}$$

$$= \sum_{t_1} \sum_{t_2} \cdots \sum_{t_n} \begin{vmatrix} \varphi_{m_1}^*(x'_1) \cdots \varphi_{t_1}^*(x'_1) \varphi_{t_1}(x_1) \cdots \varphi_{t_n}^*(x'_1) \varphi_{t_n}(x_n) \cdots \varphi_{m_N}^*(x'_1) \\ \vdots \\ \varphi_{m_1}^*(x'_N) \cdots \varphi_{t_1}^*(x'_N) \varphi_{t_1}(x_N) \cdots \varphi_{t_n}^*(x'_N) \varphi_{t_n}(x_n) \cdots \varphi_{m_N}^*(x'_N) \end{vmatrix} \cdot$$

(11) cont'd

In the last line of (11) each of the n sums runs independently over all orbital labels excluding m_1, m_2, \dots, m_N , but whenever $t_p = t_q$, $p \neq q$, the particular contribution vanishes due to the proportionality of two columns of the determinant. Expanding $\det W_{m_1, \dots, x'_1, \dots, x'_n, m_N}$ as the sum of determinants is a consequence of repeatedly applying the identity

$$\begin{vmatrix} a_{11} + b_{11} & c_{12} & c_{13} & \cdots & c_{1N} \\ a_{21} + b_{21} & c_{22} & c_{23} & \cdots & c_{2N} \\ \vdots & \vdots & \vdots & \cdots & \vdots \\ a_{N1} + b_{N1} & c_{N2} & c_{N3} & \cdots & c_{NN} \end{vmatrix} = \begin{vmatrix} a_{11} & c_{12} & c_{13} & \cdots & c_{1N} \\ a_{21} & c_{22} & c_{23} & \cdots & c_{2N} \\ \vdots & \vdots & \vdots & \cdots & \vdots \\ a_{N1} & c_{N2} & c_{N3} & \cdots & c_{NN} \end{vmatrix} + \begin{vmatrix} b_{11} & c_{12} & c_{13} & \cdots & c_{1N} \\ b_{21} & c_{22} & c_{23} & \cdots & c_{2N} \\ \vdots & \vdots & \vdots & \cdots & \vdots \\ b_{N1} & c_{N2} & c_{N3} & \cdots & c_{NN} \end{vmatrix} \cdot$$

(12)

Now using this identity in the sense of going from right to left, we can contract the second expansion appearing in (11), to one determinant:

$$\sum_{x_1, \dots, x_n} \det W_{m_1, \dots, x_1, \dots, x_n, \dots, m_N} = \quad (13)$$

$$\begin{vmatrix} \varphi_{m_1}^*(x'_1) \cdots \sum_{t \notin m_1} \varphi_t^*(x'_1) \varphi_t(x_1) \cdots \sum_{t \notin m_1} \varphi_t^*(x'_1) \varphi_t(x_n) \cdots \varphi_{m_N}^*(x'_1) \\ \vdots \\ \varphi_{m_1}^*(x'_N) \cdots \sum_{t \notin m_1} \varphi_t^*(x'_N) \varphi_t(x_1) \cdots \sum_{t \notin m_1} \varphi_t^*(x'_N) \varphi_t(x_n) \cdots \varphi_{m_N}^*(x'_N) \end{vmatrix}$$

The single determinant which results from these operations is most simply described as the determinant of that matrix constructed by taking $[\varphi_{m_1}, \dots, \varphi_{m_j}, \dots, \varphi_{m_j}, \dots, \varphi_{m_N}]$ and replacing the j th row of the j th column by $\sum_{t \notin m_j} \varphi_t^*(x'_j) \varphi_t(x_i)$ where the index t assumes all orbital labels except m_1, m_2, \dots, m_N . Since $\{\varphi_i\}$ form a complete orthonormal set of orbitals, we find, according to the closure property, that

$$\sum_{t \notin m_j} \varphi_t^*(x'_j) \varphi_t(x) = \delta(x', x) - \sum_{i=1}^N \varphi_{m_i}^*(x'_j) \varphi_{m_i}(x). \quad (14)$$

However, when (14) is inserted into (13), of the N terms occurring

in each sum over $i = m_1, m_2, \dots, m_N$ only those for which

$i = m_{j_1}, m_{j_2}, \dots, m_{j_n}$ need be kept, since only they would give rise

to non-vanishing contributions if the resulting determinant were

expanded in the fashion of (12). Therefore, defining

$$\Delta_{m_j, \dots, m_{j_n}}^{(x'_j, x)} = \delta(x'_j, x) - \sum_{i=1}^n \varphi_{m_{j_i}}^*(x'_j) \varphi_{m_{j_i}}(x), \quad (15)$$

we arrive at a compact formula for Sinanoğlu's correlation functions:

$$\begin{aligned} U_{m_j, \dots, m_{j_n}}^{(x_1, \dots, x_n)} &= \\ &= \frac{1}{\sqrt{N! n!}} \int \prod_{i=1}^N dx'_i \begin{vmatrix} \varphi_{m_{j_1}}^*(x'_1) & \dots & \Delta_{m_{j_1}, \dots, m_{j_n}}^{(x'_1, x_1)} & \dots & \Delta_{m_{j_1}, \dots, m_{j_n}}^{(x'_1, x_n)} & \dots & \varphi_{m_{j_1}}^*(x'_1) \\ \vdots & & \vdots & & \vdots & & \vdots \\ \varphi_{m_{j_n}}^*(x'_n) & \dots & \Delta_{m_{j_n}, \dots, m_{j_n}}^{(x'_n, x_1)} & \dots & \Delta_{m_{j_n}, \dots, m_{j_n}}^{(x'_n, x_n)} & \dots & \varphi_{m_{j_n}}^*(x'_n) \end{vmatrix} \Psi_m(x'_1, \dots, x'_N) \\ &= \sqrt{\frac{N!}{n!}} \int \prod_{i=1}^N dx'_i \{ \varphi_{m_{j_1}}^*(x'_1) \cdot \dots \cdot \Delta_{m_{j_1}, \dots, m_{j_n}}^{(x'_1, x_1)} \cdot \dots \cdot \Delta_{m_{j_n}, \dots, m_{j_n}}^{(x'_n, x_n)} \cdot \dots \cdot \varphi_{m_{j_n}}^*(x'_n) \} \Psi_m(x'_1, \dots, x'_N) \end{aligned} \quad (16)$$

The collapse of the determinant to a simple product is a consequence of the required antisymmetry of $\Psi_m(x'_1, \dots, x'_N)$.

Although it appears that this result has only a formal significance since the eigenfunction $\Psi_m(x'_1, \dots, x'_N)$ is not known, we may bypass the derivation of (16) and alternatively view this formula as a starting point for the analysis of a given trial wave function $\tilde{\Psi}_m$ into its correlation function components $\tilde{U}_{m_j, \dots, m_{j_n}}$. When seen in this spirit Eq. (16) simply provides a somewhat more elegant formulation of the technique proposed by Sinanoğlu³. It might prove interesting to apply this analysis to various proposed trial wave

functions, e.g. spin-projected Hartree-Fock⁶ or Jastrow^{7,8} correlated wave functions.

These correlation functions are interrelated with the elements of other methods for attacking the many-body problem. In particular, we shall see that the exact correlation functions serve to define the solutions of a hierarchy of coupled equations considered by Brenig⁹, Brout¹⁰, Nesbet¹¹, and Kumar¹². We shall call these solutions "correlation amplitudes".¹³ In addition, a set of trial correlation functions may be used to define a set of trial correlation amplitudes which play a key role in the cluster expansion developments of Iwamoto and Yamada¹⁴ and Clark and Westhaus.^{8,15}

We define the correlation amplitude $\Psi_{m_1 \dots m_n}^{(x_1 \dots x_n)}$ by analogy with Sinanoğlu's decomposition (2) in terms of the correlation functions $U_{m_1 \dots m_k}$ derived from Ψ_{m_i} via (16). (Here we understand Ψ_{m_i} to be either the exact or a trial wave function.) Thus we write

$$\Psi_{m_1 \dots m_n}^{(x_1 \dots x_n)} = \sqrt{\frac{n!}{N!}} A(n) \left[\prod_{i=1}^n \varphi_{m_i}(x_i) + \sum_{p=1}^n \prod_{i \neq p} \varphi_{m_i}(x_i) U_{m_i m_p}^{(x_p)} \right. \\ \left. + \frac{1}{\sqrt{2!}} \sum_{p < q} \prod_{i \neq p, q} \varphi_{m_i}(x_i) U_{m_i m_p m_q}^{(x_p, x_q)} + \dots \frac{1}{\sqrt{n!}} U_{m_1 \dots m_n}^{(x_1 \dots x_n)} \right]. \quad (17)$$

with $(A(n))^2 = \sqrt{n!} A(n)$.

Then upon explicitly inserting (16) and collecting terms, we obtain a very simple expression for the correlation amplitude:

$$\begin{aligned}
\Psi_{m_{j_1} \dots m_{j_n}}^{(x_1 \dots x_n)} &= \sqrt{\frac{n!}{N!}} Q(n) \left[\prod_{i=1}^n \varphi_{m_{j_i}}^{(x_i)} + \right. \\
&\quad \sqrt{N!} \sum_p \prod_{i \neq p} \varphi_{m_{j_i}}^{(x_i)} \int \prod_{b=1}^n dx'_b \{ \varphi_{m_{j_1}}^*(x'_1) \dots \Delta_{m_{j_p} j_p}^{(x'_p, x_p)} \dots \varphi_{m_{j_n}}^*(x'_n) \} \Psi_{\underline{m}}^{(x'_1 \dots x'_n)} \\
&\quad + \frac{\sqrt{N!}}{2!} \sum_{p < q} \prod_{i \neq p, q} \varphi_{m_{j_i}}^{(x_i)} \int \prod_{b=1}^n dx'_b \{ \varphi_{m_{j_1}}^*(x'_1) \dots \Delta_{m_{j_p} j_p}^{(x'_p, x_p)} \dots \Delta_{m_{j_q} j_q}^{(x'_q, x_q)} \dots \varphi_{m_{j_n}}^*(x'_n) \} \Psi_{\underline{m}}^{(x'_1 \dots x'_n)} \\
&\quad + \dots \left. \frac{\sqrt{N!}}{n!} \int \prod_{b=1}^n dx'_b \{ \varphi_{m_{j_1}}^*(x'_1) \dots \Delta_{m_{j_1} j_1}^{(x'_1, x_1)} \dots \Delta_{m_{j_n} j_n}^{(x'_n, x_n)} \dots \varphi_{m_{j_n}}^*(x'_n) \} \Psi_{\underline{m}}^{(x'_1 \dots x'_n)} \right] \\
&= \int \prod_{b=1}^n dx'_b \prod_{i=1}^n \delta(x'_{j_i}, x_i) \prod_{p \neq j_1 \dots j_n} \varphi_{m_p}^*(x'_p) \Psi_{\underline{m}}(x'_1 \dots x'_N)
\end{aligned}
\tag{18}$$

This result is obtained by noting that, upon expanding all the

$\Delta_{m_{l_1} \dots m_{l_k}}$'s, the term in square brackets

$$\prod_{\substack{p \in \{j_1 \dots j_n\} \\ p \notin \{l_1 \dots l_q\}}} \varphi_{m_p}^{(x_p)} \cdot \int \prod_{b=1}^n dx'_b \{ \varphi_{m_{j_1}}^*(x'_1) \dots \delta(x'_{j_1}, x_{j_1}) \dots \delta(x'_{j_2}, x_{j_2}) \dots \varphi_{m_{j_n}}^*(x'_n) \} \\
\times \Psi_{\underline{m}}(x'_1 \dots x'_N)$$

in which orbitals labeled with the particular set $m_{l_1}, m_{l_2}, \dots, m_{l_q}$

$\{l_1 \dots l_q\} \subset \{j_1 \dots j_n\}$, do not occur, enters with a coefficient

$$\begin{aligned}
& \sqrt{N!} \sum_{s=q}^n \frac{1}{s!} (-1)^{s-q} \frac{s!}{q!(s-q)!} \times (s-q)! \times \frac{(n-q)!}{(s-q)!(n-s)!} \\
&= \frac{\sqrt{N!}}{q!} \sum_{s'=0}^{n-q} (-1)^{s'} \frac{(n-q)!}{s'!(n-q-s')!} \\
&= \frac{\sqrt{N!}}{n!} \delta_{qn}
\end{aligned}$$

(Here we have used the fact that the product of an appropriately signed particle permutation operator with the antisymmetrizer again generates $Q(n)$.)

Thus, when the operator $\sqrt{N!}/N! A(n)$ is applied to these brackets the final line in (18) follows immediately. Aside from a normalization factor the correlation amplitudes $\Psi_{m_1, \dots, m_n}^{(x_1, \dots, x_n)}$ defined in terms of Sinanoğlu's correlation functions are equivalent to those found, for instance, in the work of Primas⁵ and Kumar.¹²

If Ψ_m is the solution of (1), a hierarchy of coupled integro-differential equations is satisfied by the correlation amplitudes obtained with Sinanoğlu's correlation functions. A somewhat different form of these equations than that developed by Kumar is found by observing

$$\begin{aligned}
E \Psi_{m_{j_1} \dots m_{j_n}}^{(x_1 \dots x_n)} &= \int \prod_{b=1}^N dx'_b \left\{ \varphi_{m_1}^*(x'_1) \dots \delta(x'_1, x_1) \dots \delta(x'_{j_n}, x_n) \dots \varphi_{m_n}^*(x'_n) \right\} \times \\
&\quad H(1' \dots N') \Psi_{\tilde{m}}^{(x'_1 \dots x'_N)} \\
&= \int \prod_{b=1}^N dx'_b \prod_{i=1}^n \delta(x'_{j_i}, x_i) \prod_{p \neq j_1 \dots j_n} \varphi_{m_p}^*(x'_p) [H_0 + V] \Psi_{\tilde{m}}^{(x'_1 \dots x'_N)} \\
&= \left[\sum_{i=1}^n h(i) \right] \Psi_{m_{j_1} \dots m_{j_n}}^{(x_1 \dots x_n)} + \left[\sum_{K \neq j_1 \dots j_n} \epsilon_{m_K} \right] \Psi_{m_{j_1} \dots m_{j_n}}^{(x_1 \dots x_n)} \\
&\quad + \int \prod_{b=1}^N dx'_b \prod_{i=1}^n \delta(x'_{j_i}, x_i) \prod_{p \neq j_1 \dots j_n} \varphi_{m_p}^*(x'_p) V(1' \dots N') \Psi_{\tilde{m}}^{(x'_1 \dots x'_N)}.
\end{aligned} \tag{19}$$

Here we have appealed to the Hermiticity of $h(i)$ in order to write

$$\begin{aligned}
\int dx'_K \varphi_{m_K}^*(x'_K) h(K') \Psi_{\tilde{m}}^{(x'_1 \dots x'_N)} &= \\
\int dx'_K \left\{ h(K') \varphi_{m_K}^*(x'_K) \right\} \Psi_{\tilde{m}}^{(x'_1 \dots x'_N)} &= \\
\epsilon_{m_K} \int dx'_K \varphi_{m_K}^*(x'_K) \Psi_{\tilde{m}}^{(x'_1 \dots x'_N)} &
\end{aligned} \tag{20}$$

Henceforth we shall assume that the perturbation may be written as the symmetric sum of velocity-independent, two-body operators

$$\mathcal{V}(ij) \quad \text{so that in general}$$

$$\left[\sum_{i=1}^n h(i) + \sum_{1 \leq i < j \leq n} V(ij) - \sum_{i=1}^n \epsilon_{m_j} - \Delta E \right] \Psi_{m_1 \dots m_n}(x_1, \dots, x_n) =$$

$$- \sum_{p \neq j_1 \dots j_n} \int dx_1 \varphi_{m_p}^*(x_1) \left\{ \sum_{i=1}^n V(i, i') \right\} \Psi_{m_1 \dots m_p \dots m_n}(x_1, \dots, x_{i'} \dots x_n) \quad (21)$$

$$- \sum_{p < q} \int dx_1' dx_2' \varphi_{m_p}^*(x_1') \varphi_{m_q}^*(x_2') V(i', i'') \Psi_{m_1 \dots m_p \dots m_q \dots m_n}(x_1, \dots, x_{i'} \dots x_{i''} \dots x_n)$$

with ΔE the difference between the exact eigenvalue and the orbital energies

$$\Delta E = E - \sum_{i=1}^N \epsilon_{m_i} \quad (22)$$

(Obvious modifications in the form of (21) are obtained for those specific cases with $\eta = 1$, $\eta = N-1$, $\eta = N$ (cf. Eq. (23)).)

Eq. (21) resembles a Schrödinger equation for the n-particle

amplitude $\Psi_{m_1 \dots m_n}(x_1, \dots, x_n)$ save for the coupling through the perturbation

to all $(\eta+1)$ - and $(\eta+2)$ - particle correlation amplitudes

with sets of indices containing $\{m_1, \dots, m_n\}$ as a subset. There

are $2^N - 1$ such coupled equations, the N-particle equation

being the Schrödinger equation for $\Psi_{m_1 \dots m_N} = \Psi_m$.

An expression for the exact energy E follows directly upon

consideration of the equation for Ψ_{m_1} :

$$\left\{ h(x_1) - \epsilon_{m_1} - \left(E - \sum_{i=1}^N \epsilon_{m_i} \right) \right\} \Psi_{m_1}(x_1) = \quad (23)$$

$$- \sum_{p=2}^N \int dx' \varphi_{m_p}^*(x') V(x, x') \Psi_{m_1, m_p}(x, x') - \sum_{2 \leq p < q \leq N} \int dx' dx'' \left[\varphi_{m_p}^*(x') \varphi_{m_q}^*(x'') \times \right. \\ \left. V(x, x') \Psi_{m_1, m_p, m_q}(x, x', x'') \right]$$

Using the fact that for any set of $p+1$ indices, m_1, \dots, m_{p+1} which contains the given index m_2 ,

$$\Psi_{m_2, \dots, m_p}^{(x_2, \dots, x_{p+1})} = (-1)^{1 - \delta_{q,2}} \int dx_1 \varphi_{m_q}^*(x_1) \Psi_{m_1, \dots, m_{p+1}}^{(x_1, \dots, x_{p+1})} \quad (24)$$

where $m_2 \in \{m_1, \dots, m_{p+1}\} - m_q$, we obtain upon multiplying (23) from the left by $\varphi_{m_1}^*(x_1)$ and integrating

$$E = \sqrt{N!} \left\{ \sum_{p=1}^N \int dx \varphi_{m_p}^*(x) h(x) \Psi_{m_p}^{(x)} + \sum_{1 \leq p < q \leq N} \int dx dx_2 \varphi_{m_p}^*(x) \varphi_{m_q}^*(x_2) V(x, x_2) \Psi_{m_p, m_q}^{(x, x_2)} \right\} \quad (25)$$

Note that we have written $\epsilon_{m_i} \int \varphi_{m_i}^* \Psi_{m_i} dx_i = \int \varphi_{m_i}^* h(x_i) \Psi_{m_i} dx_i$. Thus, as is well-known, only the one and two particle correlation amplitudes are explicitly required to evaluate the energy; of course, they in turn depend via Eqs. (21) upon the many-body correlation amplitudes.

The point to be emphasized here is that with Sinanoğlu's correlation amplitudes as defined in (17) satisfying (21), certain approximations upon this hierarchy of equations immediately generate the corresponding two particle functions examined by Sinanoğlu. Thus,

the origin of his "exact pair" equation and "Bethe-Goldstone-like" equation becomes clearer.² Also important is the realization that the $\Psi_{m_j, m_{j_2}}$ are simply a subset of the correlation amplitudes which satisfy (21) and the entire Many-Electron theory can, in fact, be equivalently formulated in terms of these amplitudes as opposed to the correlation functions $U_{m_{j_1} \dots m_{j_n}}$. We shall return to these considerations later.

Let us now point out that, in contrast to (25), even were we to have all the exact correlation amplitudes, the factor-cluster-decomposition proposed by Clark and Westhaus¹⁵ for expanding the expectation value of H ,

$$\begin{aligned}
 E = \langle H \rangle &= \frac{\int \prod_{b=1}^N dx_b \Psi_m^* H \Psi_m}{\int \prod_{b=1}^N dx_b \Psi_m^* \Psi_m} \\
 &= \sum_{i=1}^N \epsilon_{m_i} + \sum_{n=2}^N \sum_{\langle j_1 \dots j_n \rangle} Z_{m_{j_1} \dots m_{j_n}} \quad (26)
 \end{aligned}$$

still contains explicitly many-particle correlations. The notation

$\langle k_1 \dots k_p | l_1 \dots l_q \rangle$ $p \leq q$, denotes a particular combination of p indices $k_1 \dots k_p$ chosen from the set $\{l_1 \dots l_q\}$.

When $\{l_1 \dots l_q\} \equiv \{1, 2, \dots, N\}$, the notation assumes the abbreviated form $\langle k_1 \dots k_p \rangle$. Briefly we recall that

$$Z_{m_{j_1}} = Q_{m_{j_1}} - \tilde{Q}_{m_{j_1}} \quad (27)$$

and

$$Z_{m_{j_1} \dots m_{j_n}} = \sum_{p=1}^n (-1)^{n-p} \sum_{\langle l_1 \dots l_p | j_1 \dots j_n \rangle} Q_{m_{l_1} \dots m_{l_p}}, \quad n \geq 2, \quad (27) \text{ (cont'd)}$$

with $Q_{m_{l_1} \dots m_{l_p}}$ and $\tilde{Q}_{m_{j_1}}$ given respectively by the quotients

$$Q_{m_{l_1} \dots m_{l_p}} = \frac{\int \prod_{b=1}^p dx_b \Psi_{m_{l_1} \dots m_{l_p}}^*(x_1 \dots x_p) \left\{ \sum_i^p h(c_i) + \sum_{i,j}^p v(c_{ij}) \right\} \Psi_{m_{l_1} \dots m_{l_p}}(x_1 \dots x_p)}{\int \prod_{b=1}^p dx_b \Psi_{m_{l_1} \dots m_{l_p}}^*(x_1 \dots x_p) \Psi_{m_{l_1} \dots m_{l_p}}(x_1 \dots x_p)}$$

and

(28)

$$\tilde{Q}_{m_{j_1}} = \frac{\int dx_1 \varphi_{m_{j_1}}^*(x_1) h(c_1) \varphi_{m_{j_1}}(x_1)}{\int dx_1 \varphi_{m_{j_1}}^*(x_1) \varphi_{m_{j_1}}(x_1)} = \epsilon_{m_{j_1}}$$

If the occupied orbitals are chosen self-consistent in the Brueckner sense, i.e. $U_{m_i}^{(x)} = 0$ so that

$$\Psi_{m_i}^{(x)} = \frac{1}{\sqrt{N_i}} \varphi_{m_i}^{(x)}, \quad (29)$$

then we have

$$\tilde{Q}_{m_i} = Q_{m_i} = \frac{\int \Psi_{m_i}^*(x_1) h(c_1) \Psi_{m_i}(x_1) dx_1}{\int \Psi_{m_i}^*(x_1) \Psi_{m_i}(x_1) dx_1} = \epsilon_{m_i}, \quad (30)$$

and thus every one-indexed Z_{m_i} vanishes. On the other hand, if (29) does not hold -- e.g. if the Ψ_{m_i} are self-consistent only in the Hartree-Fock sense - then as a consequence of (27), (28), and (23) we obtain the formal expression

$$Z_{m_{j_1}} = \Delta E - \tag{31}$$

$$\frac{\left[\sum_{\substack{p=1 \\ p \neq j_1}}^N \int dx_1 dx_2 \Psi_{m_{j_1}}^*(x_1) \Psi_{m_p}^*(x_2) V_{(12)} \Psi_{m_{j_1}}(x_1) \Psi_{m_p}(x_2) + \sum_{\substack{p < q \\ p, q \neq j_1}}^N \int dx_1 dx_2 dx_3 \Psi_{m_{j_1}}^*(x_1) \Psi_{m_p}^*(x_2) \Psi_{m_q}^*(x_3) V_{(23)} \Psi_{m_{j_1}}(x_1) \Psi_{m_p}(x_2) \Psi_{m_q}(x_3) \right]}{\int dx_1 \Psi_{m_{j_1}}^*(x_1) \Psi_{m_{j_1}}(x_1)}$$

which explicitly contains the sought-for energy via (22). Whether or not (29) holds, however, since the exact n -body correlation amplitudes are assumed to be known, the remaining $Z_{m_{j_1} \dots m_{j_n}}$ also may be expressed in terms of ΔE and quantities which contain neither the single-particle energies $\epsilon_{m_{j_i}}$ nor the operator $h_{(i)}$ explicitly. To see this, again consider that, directly from (28) and (21)

$$Q_{m_{R1} \dots m_{Rp}} = \sum_{i=1}^p E_{m_{Ri}} + \Delta E$$

$$- p \left[\frac{\sum_{\substack{1 \leq i_1 \dots i_p \\ 1 \leq i_1 \dots i_p}} \int dx'_1 \dots dx'_p \prod_{b=1}^p dx_b \Psi_{m_{R1} \dots m_{Rp}}^*(x_1 \dots x_p) \varphi_{m_{Ri_1}}^*(x'_{i_1}) \dots \varphi_{m_{Ri_p}}^*(x'_{i_p}) \mathcal{U}(i_1, i_2) \Psi_{m_{R1} \dots m_{Rp}}(x_1 \dots x_1' \dots x_p)}{\int \prod_{b=1}^p dx_b \Psi_{m_{R1} \dots m_{Rp}}^*(x_1 \dots x_p) \Psi_{m_{R1} \dots m_{Rp}}(x_1 \dots x_p)} \right]$$

$$- \left[\frac{\sum_{\substack{1 \leq i_1 \dots i_p \\ 1 \leq i_1 \dots i_p}} \int dx'_1 dx'_2 \dots \prod_{b=1}^p dx_b \Psi_{m_{R1} \dots m_{Rp}}^*(x_1 \dots x_p) \varphi_{m_{Ri_1}}^*(x'_{i_1}) \varphi_{m_{Ri_2}}^*(x'_{i_2}) \dots \varphi_{m_{Ri_p}}^*(x'_{i_p}) \mathcal{U}(i_1, i_2) \Psi_{m_{R1} \dots m_{Rp}}(x_1 \dots x_1' \dots x_2' \dots x_p)}{\int \prod_{b=1}^p dx_b \Psi_{m_{R1} \dots m_{Rp}}^*(x_1 \dots x_p) \Psi_{m_{R1} \dots m_{Rp}}(x_1' \dots x_p)} \right] \quad (32)$$

When this result is inserted into the second equation of (27), the sum of the single particle energies vanishes¹⁵ and, in general, one obtains

$$Z_{m_{j_1} \dots m_{j_n}} = (-1)^{n-1} \Delta E \cdot +$$

$$\sum_{p=1}^n (-1)^{n-p-1} \sum_{\langle i_1 \dots i_p | j_1 \dots j_n \rangle} \left\{ \frac{p \sum_{\substack{1 \leq i_1 \dots i_p \\ 1 \leq i_1 \dots i_p}} \int dx'_1 \dots dx'_p \prod_{b=1}^p dx_b \Psi_{m_{R1} \dots m_{Rp}}^*(x_1 \dots x_p) \varphi_{m_{Ri_1}}^*(x'_{i_1}) \dots \varphi_{m_{Ri_p}}^*(x'_{i_p}) \mathcal{U}(i_1, i_2) \Psi_{m_{R1} \dots m_{Rp}}(x_1 \dots x_1' \dots x_p)}{\int \prod_{b=1}^p dx_b \Psi_{m_{R1} \dots m_{Rp}}^*(x_1 \dots x_p) \Psi_{m_{R1} \dots m_{Rp}}(x_1 \dots x_p)} \right.$$

$$\left. + \frac{\sum_{\substack{1 \leq i_1 \dots i_p \\ 1 \leq i_1 \dots i_p}} \int dx'_1 dx'_2 \dots \prod_{b=1}^p dx_b \Psi_{m_{R1} \dots m_{Rp}}^*(x_1 \dots x_p) \varphi_{m_{Ri_1}}^*(x'_{i_1}) \varphi_{m_{Ri_2}}^*(x'_{i_2}) \dots \varphi_{m_{Ri_p}}^*(x'_{i_p}) \mathcal{U}(i_1, i_2) \Psi_{m_{R1} \dots m_{Rp}}(x_1 \dots x_1' \dots x_2' \dots x_p)}{\int \prod_{b=1}^p dx_b \Psi_{m_{R1} \dots m_{Rp}}^*(x_1 \dots x_p) \Psi_{m_{R1} \dots m_{Rp}}(x_1 \dots x_p)} \right\} \quad (33)$$

Clearly, there is no reason to suspect the vanishing of such a

$$Z_{m_{j_1} \dots m_{j_n}}$$

These manipulations, in which knowledge of the exact correlation amplitudes has been assumed, are purely formal and have only served to indicate the explicit presence of many-body terms in the cluster expansion of $\langle H \rangle$ even in this ideal situation. We now point out, however, an approximation to $\langle H \rangle$ based upon summing all the terms in (26) with ν or less indices. For the moment we again assume that the exact correlation amplitudes are known. We see from (22) and (26) that $\Delta E = \sum_{n=1}^N \sum_{\langle j_1 \dots j_n \rangle} Z_{m_{j_1} \dots m_{j_n}}$ and hence for a " ν th order approximation" we write

$$\Delta E \approx \sum_{n=1}^{\nu} \sum_{\langle j_1 \dots j_n \rangle} Z_{m_{j_1} \dots m_{j_n}}, \quad \nu \leq N. \quad (34)$$

Regrouping the ΔE terms which occur explicitly in every $Z_{m_{j_1} \dots m_{j_n}}$ we see that

$$\Delta E \approx \sum_{n=1}^{\nu} \frac{(-1)^{n-1} N! \Delta E}{n! (N-n)!} + \sum_{n=1}^{\nu} \sum_{\langle j_1 \dots j_n \rangle} Z'_{m_{j_1} \dots m_{j_n}}, \quad (35)$$

so that using the combinatorial analysis result,

$$\sum_{n=1}^{\nu} \frac{(-1)^{n-1} N!}{n! (N-n)!} = (-1)^{\nu-1} \left[\frac{(N-1)!}{\nu! (N-1-\nu)!} \right] + 1, \quad (36)$$

we arrive at an approximate expression for ΔE ,

$$\Delta E \approx \frac{V!(N-1-V)!}{(N-1)!} \sum_{n=1}^V \sum_{\langle j_1 \dots j_n \rangle} \sum_{m_{j_1} \dots m_{j_n}} \quad (37)$$

Here, solely in terms of the orbitals, correlation amplitudes, and perturbation potential,

$$\sum_{m_{j_1} \dots m_{j_n}} \sum_{\langle j_1 \dots j_n | j_1 \dots j_n \rangle} \left\{ \frac{p \cdot \sum_{s \neq l_1 \dots l_p} \int \prod_{b=1}^p dx'_b \Psi_{m_{l_1} \dots m_{l_p}}^*(x_1 \dots x_p) \varphi_{m_s}^*(x'_1) \varphi_{m_s}^*(x'_2) V(l_1, l_2) \Psi_{m_{j_1} \dots m_{j_n}}(x_1 \dots x_p)}{\int \prod_{b=1}^p dx_b \Psi_{m_{l_1} \dots m_{l_p}}^*(x_1 \dots x_p) \Psi_{m_{l_1} \dots m_{l_p}}(x_1 \dots x_p)} \right. \\ \left. \frac{\sum_{s \subset t} \int \prod_{b=1}^p dx'_b \prod_{b=1}^p dx_b \Psi_{m_{l_1} \dots m_{l_p}}^*(x_1 \dots x_p) \varphi_{m_s}^*(x'_1) \varphi_{m_t}^*(x'_2) V(l_1, l_2) \Psi_{m_{j_1} \dots m_{j_n}}(x_1 \dots x_p)}{\int \prod_{b=1}^p dx_b \Psi_{m_{l_1} \dots m_{l_p}}^*(x_1 \dots x_p) \Psi_{m_{l_1} \dots m_{l_p}}(x_1 \dots x_p)} \right\} \quad (38)$$

Eq. (37) is meaningful only for $V < N$. To be practical, of course, it is required that $V \ll N$. It is proposed that substituting thoughtfully chosen trial forms for the correlation amplitudes in (38) may provide practical means of carrying out this approximation to a fruitful conclusion.

The correlation amplitude $\Psi_{m_{j_1} m_{j_2}}(x_1, x_2)$ may be looked upon as more accurately depicting the distribution of two particles which, in the independent particle approximation, occupy orbitals $\varphi_{m_{j_1}}$ and $\varphi_{m_{j_2}}$. Let us consider an effective Hamiltonian which, at least intuitively, governs the motion of these two particles and consequently generates approximate solutions for $\Psi_{m_{j_1} m_{j_2}}$. We shall find that with the most straightforward form for this effective Hamiltonian a variation performed upon the terms through second order

in the factor cluster-expansion¹⁵ (26) leads to Sinanoğlu's "exact-pair" equations². Thus we will see the equivalence of the Many-Electron-Theory and the factor cluster expansions. Employing the variational principle with other truncated cluster expansions generates further approximations to the "exact pair" theory. In particular, we shall discover the connection between the Iwamoto-Yamada¹⁴ cluster formalism and Sinanoğlu's Bethe-Goldstone-like pairs. In all these cluster expansion formalisms, however, it is the correlation amplitudes

ψ_{m_1, \dots, m_n} as opposed to the correlation functions U_{m_1, \dots, m_n} which play the central role. It appears to be intuitively simpler to assign some physical status to the former quantities, and thus perhaps to say something significant concerning their transfer from one molecular species to another.

We now specialize to the case in which the independent-particle model is constructed according to the Hartree-Fock scheme so that the orbitals satisfy

$$h(i) \varphi_i(x_i) = \left[-\frac{\hbar^2}{2m} \nabla_i^2 + \sum_{\text{nuclei } \alpha} \frac{-Z_\alpha e^2}{|r_i - r_\alpha|} + V(i) \right] \varphi_i = \epsilon_i \varphi_i(x_i) \quad (39)$$

Here, following the remarks of Geller, Taylor, and Levine,^{16,17} we define the non-local potential

$$V(i) = \sum_{j=1}^N S_{m_j(i)} = \sum_{j=1}^N \left[\bar{S}_{m_j(i)} - R_{m_j(i)} \right] \quad (40)$$

where in terms of the usual Coulomb and exchange operators of Hartree-Fock theory

$$\bar{S}_{m_i}^{(1)} \varphi_{m_j}^{(x_1)} \equiv \int dx_2 \varphi_{m_i}^{*(x_2)} \frac{1 \cdot e^2}{|r_1 - r_2|} \varphi_{m_i}^{(x_2)} \varphi_{m_j}^{(x_1)} \quad (41)$$

and

$$R_{m_i}^{(1)} \varphi_{m_j}^{(x_1)} \equiv \int dx_2 \varphi_{m_i}^{*(x_2)} \frac{1 \cdot e^2}{|r_1 - r_2|} \varphi_{m_j}^{(x_2)} \varphi_{m_i}^{(x_1)} .$$

Now focusing on orbitals m_{j_1} and m_{j_2} in the Hartree-Fock model we ask what effective Hamiltonian may be constructed to approximate more realistically the motion of the "electrons" occupying these orbitals. We propose the following Hamiltonian which, in addition to the mutual Coulomb repulsion of the electrons in the chosen orbitals, includes the effective interaction of each of these two electrons with the "background" particles:

$$H_{m_{j_1} m_{j_2}}^{(1,2)} = \left[-\frac{\hbar^2}{2M} \nabla_1^2 - \frac{\hbar^2}{2M} \nabla_2^2 + \sum_a Z_a e^2 \left\{ \frac{1}{r_{1a}} + \frac{1}{r_{2a}} \right\} + \frac{e^2}{r_{12}} \right] + \left[\sum_{i=1}^2 \{ V(i) - \bar{S}_{m_{j_i}}^{(i)} - S_{m_{j_2}}^{(i)} \} \right] . \quad (42)$$

The one-body operators appearing in the second group of terms approximate the effective interaction of each chosen electron with the background as the difference between the total Hartree-Fock potential and that part contributed by quasiparticles occupying orbitals m_{j_1} and m_{j_2} . (Notice that this latter term is defined to be in accord with the Hartree-Fock potential of Geller

Taylor and Levine.^{16,17)} One might then look upon Ψ_{m_1, m_2} which satisfies

$$H_{m_1, m_2}^{(1,2)} \Psi_{m_1, m_2}^{(1,2)} = E_{m_1, m_2} \Psi_{m_1, m_2}^{(1,2)} \quad (43)$$

as an approximation to the two body correlation amplitude defined in (17). More to the point of the present discussion, however, we can redefine, as the basic ingredients of the factor cluster expansion,

$$\begin{aligned} \tilde{Q}_{m_1} &= \frac{\int dx_1 \varphi_{m_1}^*(x_1) h(1) \varphi_{m_1}(x_1)}{\int dx_1 \varphi_{m_1}^*(x_1) \varphi_{m_1}(x_1)} = E_{m_1}, \\ Q_{m_1} &= \frac{\int dx_1 \tilde{\Psi}_{m_1}^*(x_1) \{h(1) - S_{m_1}^{(1)}\} \tilde{\Psi}_{m_1}(x_1)}{\int dx_1 \tilde{\Psi}_{m_1}^*(x_1) \tilde{\Psi}_{m_1}(x_1)}, \\ Q_{m_1, m_2} &= \frac{\int dx_1 dx_2 \tilde{\Psi}_{m_1, m_2}^*(x_1, x_2) H_{m_1, m_2}^{(1,2)} \tilde{\Psi}_{m_1, m_2}(x_1, x_2)}{\int dx_1 dx_2 \tilde{\Psi}_{m_1, m_2}^*(x_1, x_2) \tilde{\Psi}_{m_1, m_2}(x_1, x_2)}, \end{aligned} \quad (44)$$

where $\tilde{\Psi}_{m_1}$ and $\tilde{\Psi}_{m_1, m_2}$ are trial correlation amplitudes defined as in (17) in terms of trial correlation functions \tilde{U}_{m_1} , \tilde{U}_{m_2} and \tilde{U}_{m_1, m_2} . These latter quantities may be obtained from a trial form for $\tilde{\Psi}_{m_1}$ via (16) but also may simply be postulated functional forms containing variational parameters. In the definition of Q_{m_1} we have introduced a new effective one-body Hamiltonian to replace the Hartree Fock operator. This is, of course, not necessary (cf. (30))

but it may prove convenient as explained in the following paragraph. Thus, in general, to use the factor cluster expansion through second order we need

$$\tilde{\Psi}_{m_{j_1}}^{(x_1)} = \frac{1}{\sqrt{N!}} \left[\varphi_{m_{j_1}}^{(x_1)} + \tilde{U}_{m_{j_1}}^{(x_1)} \right] \quad (45)$$

$$\tilde{\Psi}_{m_{j_1} m_{j_2}}^{(x_1, x_2)} = \sqrt{\frac{2}{N!}} Q(2) \left[\varphi_{m_{j_1}}^{(x_1)} \varphi_{m_{j_2}}^{(x_2)} + \varphi_{m_{j_1}}^{(x_1)} \tilde{U}_{m_{j_2}}^{(x_2)} + \tilde{U}_{m_{j_1}}^{(x_1)} \varphi_{m_{j_2}}^{(x_2)} + \tilde{U}_{m_{j_1}}^{(x_1)} \tilde{U}_{m_{j_2}}^{(x_2)} + \frac{1}{\sqrt{2}} \tilde{U}_{m_{j_1} m_{j_2}}^{(x_1, x_2)} \right]$$

We shall assume in the forthcoming discussion, however, that the one-body correlation functions are negligibly small throughout all space¹, so that $\tilde{\Psi}_{m_{j_1}} = \frac{1}{\sqrt{N!}} \varphi_{m_{j_1}}$ and thus, because $\int dx_i \varphi_{m_{j_1}}^*(x_i) S_{m_{j_1}}^{(x_i)} \varphi_{m_{j_1}}(x_i) = 0$ in accordance with (27) the one-index cluster integrals $Z_{m_{j_1}}$ vanish.

Let us briefly take time to note that although the one- and two-body effective Hamiltonians depend explicitly upon the corresponding Hartree-Fock orbitals under consideration and thus are very much unlike the operators proposed previously¹⁵, the factor-cluster-formalism proceeds in the same fashion as before. This is because the factor - cluster decomposition - like all cluster decompositions - leads to an expansion for the expectation value of an operator S which, if completely summed, results identically in $\langle S \rangle$. Thus, were we to continue to define state-dependent effective Hamiltonians in the manner of (42) we would obtain

$$H_{m_{j_1} \dots m_{j_n}}^{(1, \dots, n)} = \left[\sum_{i=1}^n \left(-\frac{\hbar^2}{2M} \nabla_i^2 + \sum_{\text{nuclei } a} \frac{-Z_a e^2}{|r_i - r_a|} \right) + \sum_{i < j} \frac{e^2}{|r_i - r_j|} \right] + \left[\sum_{i=1}^n (V(i) - \sum_{K=1}^n S_{m_{j_K}}^{(i)}) \right] \quad (46)$$

$$H_{m_{j_1} \dots m_{j_N}}^{(1, \dots, N)} = \left[\sum_{i=1}^N \left(-\frac{\hbar^2}{2M} \nabla_i^2 + \sum_{\text{nuclei } a} \frac{-Z_a e^2}{|r_i - r_a|} \right) + \sum_{i < j} \frac{e^2}{|r_i - r_j|} \right] + \left[\sum_{i=1}^N (V(i) - \sum_{K=1}^N S_{m_{j_K}}^{(i)}) \right] = H(1, \dots, N)$$

in which the N-particle effective Hamiltonian is identically the given Hamiltonian, the expectation value of which with respect to

$\tilde{\Psi}_{m_{j_1} \dots m_{j_N}}^{(x_1, \dots, x_N)} = \tilde{\Psi}_{m_{j_1} \dots m_{j_N}}^{(x_1, \dots, x_N)}$ is the sole surviving term in the completely summed cluster expansion.

Inserting $H_{m_{j_1} m_{j_2}}^{(1, 2)}$ and $\tilde{\Psi}_{m_{j_1} m_{j_2}}^{(x_1, x_2)}$ as defined above into (44) and after regrouping the terms in the effective Hamiltonian taking advantage of the fact that

$$\begin{aligned} & \left\{ -\frac{\hbar^2}{2M} \nabla_1^2 - \frac{\hbar^2}{2M} \nabla_2^2 + \sum_a \frac{-Z_a e^2}{r_a} \left(\frac{1}{r_{1a}} + \frac{1}{r_{2a}} \right) + V(1) + V(2) \right\} \left[\varphi_{m_{j_1} j_1}^{(x_1)} \varphi_{m_{j_2} j_2}^{(x_2)} - \varphi_{m_{j_1} j_1}^{(x_2)} \varphi_{m_{j_2} j_2}^{(x_1)} \right] \\ & = (E_{m_{j_1}} + E_{m_{j_2}}) \left[\varphi_{m_{j_1} j_1}^{(x_1)} \varphi_{m_{j_2} j_2}^{(x_2)} - \varphi_{m_{j_1} j_1}^{(x_2)} \varphi_{m_{j_2} j_2}^{(x_1)} \right] \\ & = (E_{m_{j_1}} + E_{m_{j_2}}) \tilde{\Psi}_{m_{j_1} m_{j_2}}^{(x_1, x_2)} \end{aligned} \quad (47)$$

We find that

$$\begin{aligned} Z_{m_j, m_{j_2}} &= Q_{m_j, m_{j_2}} - Q_{m_{j_1}} - Q_{m_{j_2}} \\ &= Q_{m_j, m_{j_2}} - E_{m_{j_1}} - E_{m_{j_2}} \end{aligned}$$

$$\begin{aligned} &= \left[\frac{(\Phi_{m_j, m_{j_2}}^{(x_1, x_2)} + \tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)}) \frac{e^2}{r_{12}} - S_{m_{j_1}}^{(1)} - S_{m_{j_2}}^{(1)} - S_{m_{j_1}}^{(2)} - S_{m_{j_2}}^{(2)}}{(\Phi_{m_j, m_{j_2}}^{(x_1, x_2)} + \tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)})} \left| \Phi_{m_j, m_{j_2}}^{(x_1, x_2)} + \tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)} \right. \right] \\ &+ \left[\frac{(\tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)}) \left[-\frac{\hbar^2}{2M} \nabla_1^2 - \frac{\hbar^2}{2M} \nabla_2^2 + V_{(1)} + V_{(2)} + \sum_{\substack{i=1 \\ i \neq j}}^2 -Z e^2 \left(\frac{1}{r_{1i}} + \frac{1}{r_{2i}} \right) - E_{m_{j_1}} - E_{m_{j_2}} \right]}{(\Phi_{m_j, m_{j_2}}^{(x_1, x_2)} + \tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)})} \left| \tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)} \right. \right] \end{aligned} \quad (48)$$

Let us now add and subtract the difference between the Coulomb and exchange integrals, $J_{m_j, m_{j_2}} - K_{m_j, m_{j_2}}$, to $Z_{m_j, m_{j_2}}$ and thereby obtain

$$\begin{aligned} Z_{m_j, m_{j_2}} &= - (J_{m_j, m_{j_2}} - K_{m_j, m_{j_2}}) \\ &+ \left[\frac{(\Phi_{m_j, m_{j_2}}^{(x_1, x_2)} + \tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)}) \left[\frac{e^2}{r_{12}} \right]}{(\Phi_{m_j, m_{j_2}}^{(x_1, x_2)} + \tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)})} \left| \Phi_{m_j, m_{j_2}}^{(x_1, x_2)} + \tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)} \right. \right] \\ &+ \left[\frac{(\tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)}) \left[\sum_{i=1}^2 \left[-\frac{\hbar^2}{2M} \nabla_i^2 + V_{(i)} - \sum_{\substack{j=1 \\ j \neq i}}^2 \frac{Z e^2}{r_{ij}} - E_{m_{j_1}} \right] \right]}{(\Phi_{m_j, m_{j_2}}^{(x_1, x_2)} + \tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)})} \left| \tilde{U}_{m_j, m_{j_2}}^{(x_1, x_2)} \right. \right] \end{aligned} \quad (49)$$

where in the terminology of Geller, Taylor, and Levine

$$\mathcal{M}_{m_1, m_2}^{(1,2)} = \frac{e^2}{r_{12}} - S_{m_1}^{(1)} - S_{m_2}^{(1)} - S_{m_1}^{(2)} - S_{m_2}^{(2)} + J_{m_1, m_2} - K_{m_1, m_2} \quad (50)$$

Then, since

$$\left(\Phi_{m_1, m_2}^{(x_1, x_2)} \mid \mathcal{M}_{m_1, m_2}^{(1,2)} \mid \Phi_{m_1, m_2}^{(x_1, x_2)} \right) = 0, \quad (51)$$

we have simply

$$\begin{aligned} Z_{m_1, m_2} &= - \left[J_{m_1, m_2} - K_{m_1, m_2} \right] + \quad (52) \\ &\quad \frac{\left(\Phi_{m_1, m_2}^{(x_1, x_2)} \mid \mathcal{M}_{m_1, m_2}^{(1,2)} \mid \tilde{U}_{m_1, m_2}^{(x_1, x_2)} \right) + \left(\tilde{U}_{m_1, m_2}^{(x_1, x_2)} \mid \mathcal{M}_{m_1, m_2}^{(1,2)} \mid \Phi_{m_1, m_2}^{(x_1, x_2)} \right)}{\left(\Phi_{m_1, m_2}^{(x_1, x_2)} + \tilde{U}_{m_1, m_2}^{(x_1, x_2)} \mid \Phi_{m_1, m_2}^{(x_1, x_2)} + \tilde{U}_{m_1, m_2}^{(x_1, x_2)} \right)} \\ &\quad + \frac{\left(\tilde{U}_{m_1, m_2}^{(x_1, x_2)} \mid \sum_{i=1}^2 \left(-\frac{\hbar^2 \nabla_i^2}{2m_i} + V_{ei} \right) - \sum \frac{ze^2}{r_{ei}} - \epsilon_{m_1} \right) + \mathcal{M}_{m_1, m_2}^{(1,2)} \mid \tilde{U}_{m_1, m_2}^{(x_1, x_2)} \right)}{\left(\Phi_{m_1, m_2}^{(x_1, x_2)} + \tilde{U}_{m_1, m_2}^{(x_1, x_2)} \mid \Phi_{m_1, m_2}^{(x_1, x_2)} + \tilde{U}_{m_1, m_2}^{(x_1, x_2)} \right)} \end{aligned}$$

But upon inserting this expression for the Z_{m_1, m_2} 's into the cluster expansion we obtain

$$\begin{aligned} E &\approx \sum_{i=1}^N \epsilon_{m_i} + \sum_{i < j} Z_{m_i, m_j} \\ &\approx \left[\sum_{i=1}^N \epsilon_{m_i} - \sum_{i < j} (J_{m_i, m_j} - K_{m_i, m_j}) \right] + \\ &\quad \sum_{i < j} \left\{ \frac{\left(\Phi_{m_i, m_j} \mid \mathcal{M}_{m_i, m_j} \mid \tilde{U}_{m_i, m_j} \right) + \left(\tilde{U}_{m_i, m_j} \mid \mathcal{M}_{m_i, m_j} \mid \Phi_{m_i, m_j} \right) + \right. \\ &\quad \left. \left(\tilde{U}_{m_i, m_j} \mid \sum_{i=1}^2 \left(-\frac{\hbar^2 \nabla_i^2}{2m_i} + V_{ei} \right) - \sum \frac{ze^2}{r_{ei}} - \epsilon_{m_i} - \epsilon_{m_j} + \mathcal{M}_{m_i, m_j} \mid \tilde{U}_{m_i, m_j} \right)}{\left(\Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j} \mid \Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j} \right)} \right\} \\ &\approx E_{HF} + \sum_{i < j} \tilde{\epsilon}'_{m_i, m_j} \quad (53) \end{aligned}$$

where, in the final expression, we recognize that the sum of terms in square brackets in the intermediate equation is the Hartree-Fock energy. To correspond with Sinanoğlu's notation we have defined

$$\tilde{\epsilon}_{m_i m_j} = \frac{(\Phi_{m_i m_j} | H L_{m_i m_j} | \tilde{U}_{m_i m_j}) + C.C. + (\tilde{U}_{m_i m_j} | h_{(1)} + h_{(2)} - \epsilon_{m_i} - \epsilon_{m_j} + H_{m_i m_j} | \tilde{U}_{m_i m_j})}{(\Phi_{m_i m_j} + \tilde{U}_{m_i m_j} | \Phi_{m_i m_j} + \tilde{U}_{m_i m_j})} \quad (54)$$

The form of (54) is similar to that of the corresponding expression in Sinanoğlu's "exact pair" theory. However, an important distinction exists. In arriving at (53) we have nowhere invoked the so-called strong orthogonality conditions,

$$\int dx_1 \varphi_{m_k}^*(x_1) U_{m_i m_j}^{(x_1, x_2)} = 0, \quad i, j, k = 1, \dots, N. \quad (55)$$

To avoid the "Nightmare of inner shells", these conditions must be imposed upon trial correlation functions;¹ they are, unfortunately, a source of great complexity in practical calculations as attested by Geller, Taylor, and Levine¹⁷ in their application of Many-Electron-Theory to Be. When these conditions are imposed, we find that the denominator in (54) becomes

$$(\Phi_{m_i m_j} + \tilde{U}_{m_i m_j} | \Phi_{m_i m_j} + \tilde{U}_{m_i m_j}) = 1 + (\tilde{U}_{m_i m_j} | \tilde{U}_{m_i m_j}), \quad (56)$$

and then the two approaches are strictly identical: The correlation functions, or equivalently, the correlation amplitudes which result upon minimizing the above truncated factor cluster expansion term by

term are the same as those which emerge via Sinanoğlu's procedure. On the other hand the fact that the former method results in the same form as Sinanoğlu's without the imposition of (55) suggest that one should not carry out an unrestricted variational calculation upon the truncated factor cluster expansion in the many electron problem. A similar conclusion would appear to be valid in using this method to construct a theory of finite nuclei.¹⁸

Thus we see that the results of Sinanoğlu's Many-Electron-Theory can be equivalently obtained within the framework of the correlation amplitudes and the factor cluster expansion. The latter approach is easily (in principle) extended to higher order through the introduction of n -particle correlation amplitudes $\tilde{\Psi}_{m_1, \dots, m_n}$ ¹⁵. The few-body correlation amplitudes, say $n \leq 3$, play an essential role in this formulation and thus supplant the correlation functions $\tilde{U}_{m_1, \dots, m_n}$ in considering such questions as the transferability of entire regions of electrons from one molecule to another.

To examine the significance of the normalization factors $\langle \Phi_{ij} + \tilde{U}_{ij} | \Phi_{ij} + \tilde{U}_{ij} \rangle$ let us consider the Iwamoto-Yamada (IY) cluster formalism.^{8, 14, 15, 19} Once again assuming that the one-body correlation functions can be neglected and retaining explicitly only those second order terms which are linear in the IY cluster integrals, we can approximate the expectation value of the Hamiltonian by

$$E \approx \sum_{i=1}^N E_{m_i} + \sum_{i < j} \tilde{J}_{m_i m_j} \quad (57)$$

Under these assumptions, it turns out that

$$\begin{aligned} Z_{m_i, m_j} &= (\Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j} | \Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j}) [Q_{m_i, m_j} - Q_{m_i} - Q_{m_j}] \\ &= (\Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j} | \Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j}) Z_{m_i, m_j} \end{aligned} \quad (58)$$

so that performing the same manipulations with J_{m_i, m_j} and K_{m_i, m_j} which led to (53), we obtain

$$E = E_{HF} + \sum_{i < j} \tilde{e}'_{m_i, m_j} \quad (59)$$

with

$$\begin{aligned} \tilde{e}'_{m_i, m_j} &= \tilde{e}'_{m_i, m_j} [(\Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j} | \Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j})] \\ &\quad - (J_{m_i, m_j} - K_{m_i, m_j}) [(\Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j} | \Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j}) - 1] \\ &= \tilde{e}'_{m_i, m_j} (J_{m_i, m_j} - K_{m_i, m_j}) [(\Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j} | \Phi_{m_i, m_j} + \tilde{U}_{m_i, m_j}) - 1]. \end{aligned} \quad (60)$$

The first term is simply the numerator of the corresponding term in (53). The second is essentially a normalization correction to the truncated Iwamoto-Yamada expansion. Indeed, it follows immediately from the order by order equivalence¹⁵ of the factor and the Iwamoto-Yamada cluster expansions and the structure of Z_{m_i, m_j} as seen in (58) that the role of the remaining second order terms

involving higher powers of the IY cluster integrals is simply to incorporate all the second order normalization effects possessed by the denominators in (54).

When the strong orthogonality conditions are imposed the second term in (60) is $O((\tilde{U}_{m_i m_j} | \tilde{U}_{m_i m_j}))$. Neglecting all such terms occurring in his denominators, Sinanoğlu has arrived at an approximation to his "exact pairs" which he terms "Bethe-Goldstone-like pairs".² Clearly, by employing the IY cluster expansion truncated as in (57) and then neglecting terms $O((\tilde{U}_{m_i m_j} | \tilde{U}_{m_i m_j}))$, we arrive at an identical result. Thus, the variational principle applied to the truncated energy expression

$$E \approx E_{HF} + \sum_{i,j} \tilde{E}_{m_i m_j} \quad (61)$$

also yields Sinanoğlu's Bethe-Goldstone-like equations for the approximate two-body correlation amplitudes. Another theory of correlated wave functions which, through "third order", leads to a result similar to (61) in that the denominator in (54) is replaced by unity has recently been given by Steiner²⁰. It might be pointed out that without imposing the strong orthogonality conditions an unrestricted variation upon each of the $\tilde{E}_{m_i m_j}$ in (61) can lead to infinitely negative energies. This catastrophic result was first pointed out by Emery²¹ in connection with the nuclear matter binding energy problem. A similar difficulty was also found by Steiner²² in calculations on Be. The resolution of this difficulty in the nuclear

matter problem was obtained by imposing restrictions upon the trial correlation function; one of the most common restrictions imposed has recently been shown by Clark²³ to include the strong orthogonality conditions.

These considerations indicate the close connection between the cluster expansion formalisms and Sinanoğlu's Many-Electron Theory. It is hoped that the emphasis placed upon the correlation amplitudes as opposed to the correlation functions will bring about a clearer physical insight into atomic and molecular processes. Numerical work on the correlation problem within the cluster expansion formalisms should get under way in the near future.

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