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Many-Body Approach to Electron Correlation in Atoms and Molecules*

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Many-body perturbation theory (MBPT) is used to investigate the energy, wave function, and two-electron density matrix of a closed-shell atom or molecule when the initial approximation to the wave function is taken in the Hartree-Fock approximation. Since, as Kelly has found in his calculations using MBPT, certain classes of terms *dominate* in all orders of perterbation theory, models are investigated in which certain types of terms are summed to all orders of perturbation theory. The diagrams which are summed are explicitly chosen to provide results in the form of inhomogeneous integrodifferential equations which are as similar as possible to the models used by Kelly, Sinanoǧlu, and Nesbet, thereby enabling some comparison to be made between these theories and indicating some of the corrections to them.

It is proven that the diagrams approximated by Kelly to all orders of perturbation theory, which have only two electrons excited at a given time, could be calculated from a knowledge of what Sinanoǧlu calls Bethe-Goldstone (BG) pairs, which represent the perturbative corrections for correlation for a pair of electrons moving in the field of the remaining electrons, which are in their ground-state Hartree-Fock (HF) orbitals. The uncoupled linear inhomogeneous equations for the pairs could be solved by the use of a correlated basis set, and their solution can be found variationally, along with the individual pair correlation energies, by varying part of the energy of a simple cluster-type wave function. However, as in the case of the other models presented in this work, certain variations of part of the energy are shown to be equivalent to the summation of particular classes of diagrams to all orders of perturbation theory.

The doubly excited diagrams omitted by the BG pairs arise from the fact that when a pair of electrons are excited out of the HF "sea," the Pauli principle no longer prohibits the remaining electrons from occupying the space left behind by the excited electrons. The inclusion of these exclusion effects results in coupled *linear* inhomogeneous equations for the new pair-correlation correction functions. Single and triple excitations modify the pair equations by the inclusion of a two-body potential, respectively, describing the virtual de-excitation of one of the two correlating electrons and virtual excitations of a third electron in the field of the two correlating electrons. Alternatively, coupled *linear* inhomogeneous equations can be written for the one-, two-, and three-electron cluster functions, and these equations may be solved variationally.

The generalization of the above results to cover the case in which the zeroth-order wave function is a single Slater determinant of *arbitrary* orthonormal spin orbitals (as well as a treatment of the higher excitations) is presented in the following paper. In the appendix, a discussion is presented to indicate the connection between what Sinanoǧlu calls "unliked clusters" and the diagrams of MBPT.

I. INTRODUCTION

At present there is great interest in the role of electron correlation in the description of atoms and molecules. Approaches to this problem have been made using the methods of configuration interaction (CI),[1-3] cluster-type wave functions,[4-13] and many-body perturbation theory (MBPT).[14-18] Approximate calculations have been attempted using all three methods, but the relationship between approximations made in some of these different approaches still remains to be clarified, especially in the case of the latter two methods.[19]

MBPT, which is just a diagrammatic representation of ordinary Rayleigh-Schrödinger perturbation theory,[20] can be used to investigate the part electron correlation plays in the energy,[14-18] wave function, and/or reduced density matrices of many-electron atoms and molecules. Because of its pictorial form, MBPT can also aid in giving some physical insight into the nature of electron correlation.

Our interest in electron correlation has been stimulated by the availability and ease of calculation of HF wave functions for atoms and small molecules.[21-26] As we know, the HF equations describe an independent particle model in which each electron moves in the average field of all the other electrons. The HF equations, aside from being soluble for atoms and small molecules, have the virtue of providing us with simple physical pictures, namely the orbital picture and the concept of exchange interactions, which are lost when CI or MBPT are used.

Errors in HF calculations, i.e., the difference between predictions made with HF wave functions and experimentally determined quantities, are due to electron correlation. Although HF calculations do provide on the order of 99% of the electronic energy of small molecules, they only provide about 50% of the binding energy of small diatomic molecules. For the fluorine molecule, HF calculations do not predict binding.[27] Thus, in order to properly account for energetics to the chemical accuracy of 1 kcal/mole, some description of electron correlation must be included in any calculation.[28] Furthermore, it must be remembered that electron correlation also affects properties other than energies, and some of these properties are often more difficult to measure experimentally than the energy.

In his calculations of the correlation energy of closed-shell atoms[14,15] (as well as in the open-shell case[16]), Kelly found that certain classes of diagrams contributed *significantly* to all orders of perturbation theory. Some diagrams were therefore summed through infinite order, and the magnitude of other diagrams in successive orders of perturbation theory were approximated so these contributions could approximately be summed to all orders of perturbation theory. In this paper the process of summation of diagrams to all orders of perturbation theory is discussed in a systematic manner. The discussion is applicable to the study of electron correlation in atoms and molecules.[29] It is shown that the majority of the diagrams evaluated to all orders of perturbation theory by Kelly[14,15] (i.e., the dominant diagrams) can be expressed in terms of what Sinanoğlu calls Bethe-Goldstone (BG) pair correlation functions.[5,6,30] This connection, thereby, provides a basis for the comparison of results obtained from MBPT calculations[14-18] with those obtained from cluster-type or Nesbet's BG-type wave functions.[31]

For simplicity, the discussion in this work is restricted to closed-shell atoms and molecules where the zeroth-order approximation is given by a HF wave function.[13,32,33] One of the virtues of using MBPT is that we can automatically separate those diagrams which can contribute to one-, two-, three-, $\cdots$, and N-body cluster-type correlation functions, and in fact, these diagrams could, in principle, be summed to give the differential equations determining all the correlation functions contained in the cluster-type wave functions.[33,34]

The process of diagram summation is then continued beyond those classes that Kelly found are dominant[14] in order to investigate the effects of the coupling between the pairs[35] and of single and triple excitations upon the pair correlations. It is shown that these phenomena can be discussed, respectively, in terms of localized orbitals and "self-energy operators" describing the virtual deexcitation and excitation of an electron in the field of a pair of correlating electrons and the remaining HF "sea."

In the next section we briefly review some of the various approaches to the treatment of electron correlation in closed-shell atoms and molecules.[32] The discussion is not meant to be all inclusive; rather it is used in order to introduce the notation, termonology, and ideas in terms of which the above-mentioned results are presented. In Sec. III the equations for the BG pairs are derived from MBPT. The coupled pair equations are derived in Sec. IV, and in Sec. V the single and triple excitations are also included. Appendix A discusses what Sinanoğlu calls "unlinked clusters"[4,5] in relation to MBPT.[36]

II. VARIOUS APPROACHES TO THE DESCRIPTION OF ELECTRON CORRELATION

For simplicity, the discussion is applied to closed-shell systems.[32] We assume that our initial approximation Φ_0 to the nondegenerate ground-state wave function ψ of an N-electron system is a HF wave function.[37] ψ is the solution to the nonrelativistic Schrödinger equation

$$H\psi = E\psi, \tag{2.1}$$

where H is the Hamiltonian. (For molecules, the Born-Oppenheimer approximation is assumed.)

We can decompose H as $H = H_0 + H_1$, (2.2)

where H_0 is the HF Hamiltonian, and (in a.u.)

$$H_0 = \sum_{i=1}^{N} H_0(i), \quad H_0\Phi_0 = E_0\Phi_0, \tag{2.3}$$

$$E_{\mathrm{HF}} = E_0 + E_1 = \langle\Phi_0|H|\Phi_0\rangle, \tag{2.4}$$

$$H_1 = \sum_{i>j}\frac{1}{r_{ij}} - \sum_{l\ \mathrm{occ}}\sum_{i=1}^{N}\langle l(\mu)|\frac{1-P_{i\mu}}{r_{i\mu}}|l(\mu)\rangle = \sum_{i>j} v_{ij} - \sum_i V_i. \tag{2.5}$$

$P_{i\mu}$ is a permutation operator, and $\{l\}$'s are the N lowest spin-orbitals which are eigenfunctions of $H_0(i)$,

$$H_0(i)l(i) = \epsilon_l l(i), \tag{2.6}$$

defining the HF orbital energies ϵ_l. In terms of the $\{l\}$, Φ_0 can be written as

$$\Phi_0 = \mathcal{A}\varphi_0, \tag{2.7}$$

where $\mathcal{A} = (N!)^{-\frac{1}{2}}\sum_P(-1)^P P$ is the N-body normalized antisymmetrizer and

$$\varphi_0 = \prod_{j=1}^{N} l_j(j). \tag{2.8}$$

Thus

$$E_0 = \sum_{l\ \mathrm{occpd}} \epsilon_l, \quad E_1 = -\sum_{(l>l')\ \mathrm{occpd}} \langle l(1)l'(2)\,|\frac{(1-P_{12})}{r_{12}}|\,l(1)l'(2)\rangle, \tag{2.9}$$

where the spin-orbital indices are considered to be ordered in some manner, e.g., $l_1 > l_2 > l_3 > \cdots > l_N$.

One of the earliest methods of including correlation was via the technique of configuration interaction.[1-3] Here we consider CI as written in terms of a complete set of HF spin-orbitals in order to introduce some of the notation and to give a simple discussion of CI. Any basis set could, of course, be chosen. Let the set of spin-orbitals $\{m\}$ be the eigenfunctions of the HF one-particle operator $H_0(i)$ via

$$H_0(i)m(i) = \epsilon_m m(i), \tag{2.6b}$$

where the unoccupied (or virtual) HF spin-orbitals $\{m\}$ along with the HF ground-state spin-orbitals $\{l\}$ form a complete set of spin-orbitals, and

$$\epsilon_m > \epsilon_l \quad \text{all } l \text{ and } m. \tag{2.6c}$$

Since all possible Slater determinants formed from the complete set of HF spin-orbitals give a complete set of N-particle wave functions, the exact wave function ψ can be written as a superposition of these Slater determinants,

$$\psi = \mathfrak{a}\Big(\varphi_0 + \sum_{l,m} C_l{}^m \varphi_l{}^m + \sum_{l>l',\,m>m'} C_{ll'}{}^{mm'} \varphi_{ll'}{}^{mm'} + \cdots\Big), \tag{2.10a}$$

where $\langle\psi\,|\,\Phi_0\rangle \equiv 1$. The expansion has been separated into singly, doubly, $\cdots$, N-fold excited configurations and the excited spin-orbitals are ordered in some arbitrary manner, e.g., $m_1 > m_2 > m_3 \cdots$.

$$\Phi_{l_j;\,m} = \mathfrak{a}\varphi_{l_j}{}^m = \mathfrak{a}[\varphi_0 m(j)/l_j(j)], \tag{2.11a}$$

$$\Phi_{l_j l_k;\,mm'} = \mathfrak{a}\varphi_{l_j l_k}{}^{mm'} = \mathfrak{a}[\varphi_0 m(j)m'(k)/l_j(j)l_k(k)] \tag{2.11b}$$

describe singly and doubly excited Slater determinants. The excited Slater determinants are prescribed by enumerating which of the N spin-orbitals are occupied. The vacated spin-orbitals are called "holes," while the excited occupied spin-orbitals are called "particles." Thus Φ_0 in (2.7) and (2.8) contains neither holes nor particles and is often called the "vacuum state." The Slater determinant $\Phi_{l,m}$ contains the hole l and the particle m. The coefficients $C_l{}^m$, $C_{ll'}{}^{mm'}$, $C_{ll'l''}{}^{mm'm''}$, $\cdots$ can be obtained by minimizing $\langle\psi\,|H - E_{\mathrm{HF}}\,|\psi\rangle/\langle\psi\,|\,\psi\rangle$ with respect to these coefficients, which yields an infinite secular equation. In practice, we are forced to truncate this expression in some manner, obtaining approximate coefficients and an approximate wave function.[28,31,35]

We can also attempt to evaluate these coefficients by using perturbation theory. MBPT is just a convenient representation of Rayleigh-Schrödinger perturbation theory and enables the separation of contributions to the various $C_l{}^m$, $C_{ll'}{}^{mm'}$, etc.

We shall briefly review some of the presentation of Goldstone[20] in order to introduce some of the notation. $\eta_k{}^\dagger$ and η_k are the "second quantized" creation and annihilation operators for an electron in the HF orbital k (k may be either an occupied or virtual orbital), and these operators obey the usual fermion anticommutation relations. Matrix elements of v and V are written as

$$\langle rs\,|v|\,mn\rangle = \int r^*(1)s^*(2)v_{12}m(1)n(2)d(12), \tag{2.12a}$$

$$\langle r\,|V|\,s\rangle = \int r^*(1)V_1 s(1)d(1), \tag{2.12b}$$

and in terms of this second-quantized notation, (2.5) and (2.6) are rewritten as

$$H_0 = \textstyle\sum_n \epsilon_n \eta_n{}^\dagger \eta_n, \tag{2.13a}$$

$$H_1 = \textstyle\sum \langle rs\,|v|\,mn\rangle \eta_r{}^\dagger \eta_s{}^\dagger \eta_n \eta_m - \sum_{r,s} \langle r\,|V|\,s\rangle \eta_r{}^\dagger \eta_s\,. \tag{2.13b}$$

The first sum in (2.13b) is over distinct matrix elements, i.e., $\langle sr\,|v|\,mn\rangle$ is distinct from $\langle sr\,|v|\,nm\rangle$, but $\langle rs\,|v|\,mn\rangle$ is not. Although the perturbation (2.13b) is time-independent, the perturbed ground-state wave function ψ_0 can be obtained from the unperturbed ground state Φ_0 by using time-dependent perturbation theory and adiabatically switching on the interaction H_1 from time $t = -\infty$ to time $t = 0$. Let (in units where $\hbar = 1$)

$$H_1(t) = e^{iH_0 t} H_1 e^{-iH_0 t} e^{\alpha t}, \tag{2.14}$$

and

$$U_\alpha = \sum_{n=0}^{\infty} (-i)^n \int_{0>t_1>t_2>\cdots t_n} H_1(t_1)H_1(t_2)\cdots H_1(t_n)dt_1\cdots dt_n. \tag{2.15}$$

As $\alpha \to 0$, we obtain the perturbed ground state at time $t=0$

$$\psi_0 = \lim_{\alpha \to 0} U_\alpha \Phi_0 / \langle \Phi_0 | U_\alpha | \Phi_0 \rangle \tag{2.16}$$

and the ground-state energy

$$E - E_0 = \langle \Phi_0 | H_1 | \psi_0 \rangle = \lim_{\alpha \to 0} \langle \Phi_0 | H_1 U_\alpha | \Phi_0 \rangle / \langle \Phi_0 | U_\alpha | \Phi_0 \rangle . \tag{2.17}$$

Ordinary Rayleigh-Schrödinger perturbation theory with the unlinked clusters[36] canceled is obtained from (2.16) and (2.17) once the time integrations are performed. Equations (2.16) and (2.17) are ratios of power series in the perturbation H_1. In both cases, however, the denominator is an exact factor of the numerator, and therefore $E-E_0$ may be expressed as a single power series in H_1. This factorization is easily established (Goldstone's theorem) when the results of the time integrations (2.15) are expressed in terms of Feynman diagrams, but can also be derived without the use of a time-dependent formalism.[38] The rules for obtaining all of the diagrams contributing to ψ_0 and $E-E_0$ are described by Goldstone and need not be repeated here. However, the diagrams needed will be presented and evaluated as they are used in the discussion.

Perturbative calculations of the wave function or energy can be performed in two manners: either we calculate the contributions for successively higher orders of the perturbation H_1[39] (i.e., starting with zeroth-, first-, second-, $\cdots$ order wave functions, energies, etc.) or, as is presented in this work, we can choose a model in which certain contributions (hopefully the dominant ones) are calculated to all orders in H_1; e.g., we calculate all contributions to the correlation energy arising from doubly-excited configurations. Kelly's Be calculation is of just this modellistic nature.[14,15] The graphical representation of Rayleigh-Schrödinger perturbation theory is not necessary for the treatment of the lowest orders of perturbation theory, but is very helpful in enumerating which contributions have been included in a given model.

In (2.10a) if we let

$$\textstyle\sum_m C_l{}^m m(j) \equiv U_l(j), \tag{2.18a}$$

$$(2)^{-\frac{1}{2}}(1-P_{12}) \sum_{m>m'} C_{ll'}{}^{mm'} m(j) m'(k) \equiv \bar{U}_{ll'}(jk), \tag{2.18b}$$

$$\varphi_{lj} = \varphi_0 / l_j(j), \tag{2.18c}$$

$$\psi = \mathfrak{A}[\varphi_0 + \textstyle\sum_l \varphi_l U_l + (2)^{-1/2} \displaystyle\sum_{l>l'} \varphi_{ll'} \bar{U}_{ll'} + \cdots], \tag{2.10b}$$

where U_l, $\bar{U}_{ll'}$, $\bar{U}_{ll'l''}$ are cluster or orbital correlation functions which are strongly orthogonal to the HF ground-state spin-orbitals.[40] Following Sinanoğlu,[4] we can decompose these cluster functions into "linked" and "unlinked" parts via[36,41]

$$\bar{U}_{ll'}(12) = (2)^{-1/2}(1-P_{12}) U_l(1) U_{l'}(2) + U_{ll'}(12), \tag{2.19a}$$

$$\begin{aligned}\bar{U}_{ll'l''}(123) = {}& (6)^{-1/2}(1-P_{13}-P_{23})(1-P_{12})[U_l(1)U_{l'}(2)U_{l''}(3) \\ & + (2)^{-1/2}(U_l(3)U_{l'l''}(12) + U_{ll''}(12)U_{l'}(3) + U_{ll'}(12)U_{l''}(3))] + U_{ll'l''}(123) \text{ etc.,}\end{aligned} \tag{2.19b}$$

where U_l, $U_{ll'}$, $U_{ll'l''}$, $\cdots$ are the S-type unlinked clusters.[36,41] If (2.10b) is truncated to include only $\{U_l, U_{ll'}\}$ (see Sec. VII), and the energy from such a wave function is varied by making arbitrary variations in the spin-orbitals of Φ_0 as well as the cluster functions (in order to maintain self-consistency), subject to the orthonormality of the ground-state spin-orbitals and their strong orthogonality to the cluster functions, then the *nonlinear* coupled eigenvalue equations of Szaz for the $\{l, U_l, U_{ll'}\}$ are obtained.[9]

In order to avoid obtaining nonlinear coupled equations, as well as for physical reasons to be discussed below, Sinanoğlu kept the $\{l_i\}$ fixed as the HF spin-orbitals in the approximate wave function

$$\psi_{\text{CL}} \sim \mathfrak{A}[\varphi_0 + (2)^{-1/2} \sum_{l>l'} \varphi_{ll'} \tilde{U}_{ll'}], \tag{2.10c}$$

and varied the $\{\tilde{U}_{ll'}\}$ in only part of the energy expression.[4-8] These two-particle correlation functions were used to construct the four-, six-, $\cdots$ body S-type unlinked clusters[36,41] in (2.10a), e.g., the four-body correlations were approximated by only the "unlinked" parts[4,36,41]

$$\begin{aligned}\tilde{U}_{ll'l''l'''}(1234) \simeq {}& (3\,!)^{-1/2}(1-P_{13}-P_{14}-P_{23}-P_{24}+P_{23}P_{14})[\tilde{U}_{ll'}(12)\tilde{U}_{l''l'''}(34) \\ & + \tilde{U}_{ll''}(12)\tilde{U}_{l'l'''}(34) + \tilde{U}_{ll'''}(12)\tilde{U}_{l'l''}(34)],\end{aligned} \tag{2.19c}$$

where the tildes on the orbital correlation functions indicate that these are approximate functions.[42]

In the next section the basic features of the technique of diagram summation are illustrated by restricting attention to the two-body diagrams, which (together with S-type unlinked contributions which can be evaluated from the resulting pair functions[41]) Kelly found gave better than 90% of the correlation energy for Be.[14,15] It is proven that the evaluation of these diagrams is equivalent to the solution of perturbative Bethe-Goldstone equations.[30] As opposed to the direct summation of diagrams, which requires the use of a complete orbital basis, the BG equations may be solved by the use of correlated pair functions whose convergence is expected to be much more rapid.[11,43,44]

III. DERIVATION OF THE BG PAIR EQUATIONS

It is well known (Brillouin's theorem) that for a closed shell HF wave function all matrix elements of the perturbation H_1 between Φ_0 and singly excited states (e.g., $\alpha\varphi_l^m$, all l and m) vanish. Thus, the lowest-order correction to the true wave function is due to double excitations. It has long been believed that corrections due to double excitations represent the major corrections for correlation to the wave functions and energies of closed-shell systems which are initially described by HF wave functions.[4,32] Thus, it is not surprising to find a number of theories in which these double excitations play the central role.[4-18,28,31,45]

In this section as was suggested in part by the diagrams evaluated by Kelly,[14,15] a subset of all the diagrams involving *only* double excitations are summed to all orders of perturbation theory, while the remaining diagrams of this type are considered in the next section.

In MBPT, to each diagram in nth-order perturbation theory there corresponds 2^n-1 "exchange diagrams."[20] Much labor is saved if all these 2^n diagrams are considered to be equivalent, but the matrix elements are taken as the direct minus the exchange term at each vertex in the diagram. Only one of the equivalent class of 2^n diagrams must then be counted, and the overall sign of this "antisymmetrized" diagram is just that which the ordinary diagram of this form would have [i.e., $(-1)^{h+l}$ where h is the number of hole lines and l is the number of loops].[46] Thus the usual second-order energy diagrams are replaced by the single "antisymmetrized" diagram given in Fig. 1. This diagram has the value $E^{(2)}$, where

$$E^{(2)} = \sum_{\substack{(l>l')\,\text{occpd}\\(m>m')\,\text{unoccpd}}} \frac{|\langle l(1)l'(2)|(1-P_{12})/r_{12}|m(1)m'(2)\rangle|^2}{\epsilon_{ll'}-\epsilon_{mm'}}, \tag{3.1a}$$

P_{12} permutes the coordinates (space and spin) of particles 1 and 2, and $\epsilon_{ll'}=\epsilon_l+\epsilon_{l'}$, $\epsilon_{mm'}=\epsilon_m+\epsilon_{m'}$ are sums of Hf spin-orbital energies. In (3.1)

$$\sum_{m>m'} = \tfrac{1}{2}\sum_{\text{all } m,m'}, \tag{3.2}$$

since the contribution with $m=m'$ vanishes because the direct and exchange matrix elements are identical. Furthermore, we can use the equality

$$\sum_{m,m'} \frac{|m(1)m'(2)\rangle\langle m(1)m'(2)|}{\epsilon_{ll'}-\epsilon_{mm'}} = \sum_{m,m'} \frac{|m(1)m'(2)\rangle\langle m(1)m'(2)|}{\epsilon_{ll'}-H_0(12)}, \tag{3.3a}$$

where $H_0(12)=H_0(1)+H_0(2)$. (3.3b)

$$\text{Setting } Q_1 = \sum_{m\ \text{unoccpd}} |m(1)\rangle\langle m(1)| = \hat{1}(1) - \sum_{l\ \text{occpd}} l(1)\rangle\langle l(1)|, \tag{3.3c}$$

then (3.3a) becomes $Q_1Q_2/[\epsilon_{ll'}-H_0(12)]$.

Let

$$|[ll']_{12}\rangle = 2^{-1/2}(1-P_{12})\,|l(1)l'(2)\rangle, \tag{3.4a}$$

$$Q_{12}=Q_1Q_2=Q_2Q_1, \tag{3.4b}$$

then (3.1a) can be rewritten as

$$E^{(2)} = \sum_{l>l',\,\text{occpd}} \langle [ll']_{12}|\frac{1}{r_{12}}\frac{Q_{12}}{\epsilon_{ll'}-H_0(12)}\frac{1}{r_{12}}|[ll']_{12}\rangle, \tag{3.1b}$$

which is the sum of contributions from each of the HF pairs.[47]

Define the antisymmetric pair functions $U_{ll'}^{(1)}(12)$ by

$$U_{ll'}^{(1)}(12) = \{Q_{12}/[\epsilon_{ll'}-H_0(12)]\}(1/r_{12})\,|[ll']_{12}\rangle. \tag{3.5a}$$

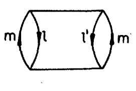


FIG. 1. The "antisymmetrized" diagram for the second order energy of a closed-shell HF system involving the excited state $\Phi_{ll';mm'}$.

Note that Q_{12} is a projection operator which makes any pair function strongly orthogonal to the ground-state spin-orbitals.[40] Since $Q_{12}^2 = Q_{12}$, the integral equation (3.5a) is equivalent to the differential equation

$$[\epsilon_{ll'} - H_0(12)]Q_{12}U_{ll'}^{(1)}(12) - Q_{12}(1/r_{12})\,|\,[ll']_{12}\rangle = 0. \tag{3.5b}$$

Equation (3.5b) should be recognized as the equation defining the first-order pair functions from which the first-order wave function

$$\psi^{(1)} = 2^{-1/2}\mathfrak{a}\sum_{l>l'}\varphi_{ll'}U_{ll'}^{(1)}$$

is constructed.[5,6,48] In terms of these first-order pairs,

$$E^{(2)} = \sum_{l>l'} E_{ll'}^{(2)} = \sum_{l>l'}\langle [ll']_{12}\,|\,\frac{1}{r_{12}}\,|\,U_{ll'}^{(1)}(12)\rangle, \tag{3.1c}$$

where $E_{ll'}^{(2)}$ is the second-order correlation energy of the spin-orbital pair ll'. Thus (3.5b) and hence (3.1c) can be evaluated by expansion in any basis set, including a correlated basis set of the James-Coolidge or Hylleraas variety.

Equation (3.5b) can be solved variationally for each first-order pair function and second-order correlation energy. The functional[5,6,48]

$$\begin{aligned} F_{ll'}^{(1)}(\tilde{U}_{ll'}^{(1)}) = {} & \langle [ll']_{12}\,|\,(1/r_{12})Q_{12}\,|\,\tilde{U}_{ll'}^{(1)}(12)\rangle \\ & + \langle \tilde{U}_{ll'}^{(1)}(12)\,|\,Q_{12}(1/r_{12})\,|\,[ll']_{12}\rangle + \langle \tilde{U}_{ll'}^{(1)}(12)\,|\,Q_{12}(H_0(12) - \epsilon_{ll'})\,|\,\tilde{U}_{ll'}^{(1)}(12)\rangle \end{aligned} \tag{3.6}$$

is stationary with respect to variations of the $\tilde{U}_{ll'}^{(1)}$ or $\tilde{U}_{ll'}^{(1)*}$ about the first-order pairs which are the solutions to (3.5b), and the stationary value of $F_{ll'}^{(1)}(\tilde{U}_{ll'}^{(1)})$ is just $E_{ll'}^{(2)}$. The variational principle for $U_{ll'}^{(1)}$ is merely the familiar second-order variation-perturbation theory applied to a closed-shel HF Φ_0.[39]

Some of the third-order "antisymmetrized" energy diagrams are given in Fig. 2. The two remaining third-order diagrams are obtained from Figs. 2(c) and (d) by taking mirror images in a plane perpendicular to the page and the vertices. The new vertex in Fig. 2(a) is a "particle-particle interaction," while in (b) it is a "hole-hole interaction," and in (c) and (d) there are "hole-particle interactions." In this section only diagrams with diagonal-hole lines are considered (the ones with nondiagonal-hole lines are treated in the next section). Thus, with regard to Fig. 2(b) only the terms with $l = l''$ and $l' = l'''$ are considered in this section, while in Figs. 2(c) and (d) the diagrams with $l' = l'''$ are diagonal-hole-line diagrams.

Writing the Coulomb and exchange operators for two electrons (1 and 2)

$$K_{ll'} = \sum_{l=1,2}\langle l(\mu)\,|\,\frac{1-P_{i\mu}}{r_{i\mu}}\,|\,l'(\mu)\rangle = \sum_{i=1,2}K_{ll'}(i) \tag{3.7}$$

and the two-particle potential

$$V_{ll'}(12) = 1/r_{12} - K_{ll} - K_{l'l'} + \langle [ll']_{12}\,|\,(1/r_{12})\,|\,[ll']_{12}\rangle, \tag{3.8}$$

where $V_{ll'}$ is defined only if $l \neq l'$, then, after a bit of algebra which is presented in Appendix B for the convenience of the reader, the third-order (diagonal-hole) energy can be written as

$$E_{\mathrm{dh}}^{(3)} = \sum_{l>l'}\langle [ll']_{12}\,|\,\frac{1}{r_{12}}\,\frac{Q_{12}}{\epsilon_{ll'} - H_0(12)}\,V_{ll'}(12)\,\frac{Q_{12}}{\epsilon_{ll'} - H_0(12)}\,\frac{1}{r_{12}}\,|\,[ll']_{12}\rangle \tag{3.9a}$$

$$= \sum_{l>l'}\langle U_{ll'}^{(1)}(12)\,|\,V_{ll'}(12)\,|\,U_{ll'}^{(1)}(12)\rangle \tag{3.9b}$$

$$= \sum_{l>l'}\langle [ll']_{12}\,|\,\frac{1}{r_{12}}\,|\,U_{ll'}^{(2)}(12)\rangle, \tag{3.9c}$$

where the second-order pairs in (3.9c) are the solutions to the equations

$$[\epsilon_{ll'} - H_0(12)]Q_{12}U_{ll'}^{(2)}(12) - Q_{12}V_{ll'}(12)Q_{12}U_{ll'}^{(1)}(12) = 0, \tag{3.10}$$

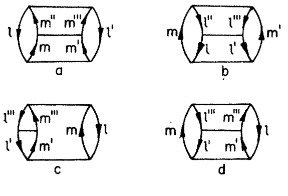


FIG. 2. Some of the third-order "antisymmetrized" energy diagrams.

and could be evaluated variationally in a manner similar to that described for $U_{ll'}^{(1)}$. Equation (3.9b) is a consequence of the "$2n+1$" rule of perturbation theory that knowledge of the wave function to nth order enables one to calculate the energy to the $(2n+1)$st order in perturbation theory.[39] In this case, the $U_{ll'}^{(1)}$ and the ground-state HF spin-orbitals determine the first-order wave function, and these first-order pairs can also be used to evaluate the nondiagonal-hole contributions to the third-order energy.

We should note that the diagonal-hole third-order energy diagrams are constructed from the second-order diagrams by placing a vertex between each pair of lines in the second-order diagram at a time intermediate between the two vertices in Fig. 1. The extra vertex—call it a bar vertex—in Fig. 3, which does not connect any specific pair of lines, is used to denote that this diagram is the sum of all of the distinct "antisymmetrized" diagrams which can be formed by letting this vertex connect any pair of lines that it crosses. Thus, the diagram in Fig. 3 is equivalent to all the third-order energy diagrams, i.e., Fig. 2 including the mirror images of Figs. 2(c) and (d). The restriction to diagonal-hole diagrams is made by placing dh over the bar vertex.

All the possible fourth-order diagonal-hole energy diagrams containing only double excitations can be formed from the third-order diagonal-hole energy diagrams by adding another vertex between each pair of lines (holes diagonal) in each of the third-order diagonal-hole energy diagrams. Figure 4 summarizes the sum of all double excitation fourth-order energy diagrams. Just as the diagonal-hole bar vertex in the third-order energy diagrams introduces the factor $V_{ll'}(12)Q_{12}/[\epsilon_{ll'}-H_0(12)]$ in going from (3.1b) to (3.9a) Fig. 4 has the value

$$E_{2\,\mathrm{dh}}^{(4)}=\sum_{l>l'}\langle[ll']_{12}|\frac{1}{r_{12}}\frac{Q_{12}}{\epsilon_{ll'}-H_0(12)}\left[V_{ll'}(12)\frac{Q_{12}}{\epsilon_{ll'}-H_0(12)}\right]^2\frac{1}{r_{12}}|[ll']_{12}\rangle. \tag{3.11}$$

By induction we can write the sum of all diagonal-hole two-body diagrams as a single diagram as in Fig. 5 with a two-body diagonal-hole infinite-order bar vertex, and the value of this diagram, which contains the diagonal-hole two-body contributions to all orders of perturbation theory, is

$$E_{2\,\mathrm{dh}}=\sum_{n=2}^{\infty}E_{2\,\mathrm{dh}}^{(n)}=\sum_{l>l'}\langle[ll']_{12}|\frac{1}{r_{12}}\frac{Q_{12}}{\epsilon_{ll'}-H_0(12)}\sum_{n=0}^{\infty}\left[V_{ll'}(12)\frac{Q_{12}}{\epsilon_{ll'}-H_0(12)}\right]^n\frac{1}{r_{12}}|[ll']_{12}\rangle. \tag{3.12a}$$

But (3.12a) contains the Born series for the diagonal-hole two-particle propagators[49]

$$G_{ll';\,\mathrm{dh}}^{(2)}=Q_{12}[Q_{12}(\epsilon_{ll'}-H_0(12))-Q_{12}V_{ll'}(12)Q_{12}]^{-1}Q_{12}, \tag{3.13a}$$

and hence (3.12a) can be written as

$$E_{2\,\mathrm{dh}}=\sum_{l>l'}E_{2\,\mathrm{dh};\,ll'}=\sum_{l>l'}\langle[ll']_{12}|\frac{1}{r_{12}}G_{ll';\,\mathrm{dh}}^{(2)}\frac{1}{r_{12}}|[ll']_{12}\rangle. \tag{3.12b}$$

By analogy with (3.1b) and (3.5a), we define the pair functions

$$U_{ll'}(12)=G_{ll';\,\mathrm{dh}}^{(2)}\frac{1}{r_{12}}|[ll']_{12}\rangle, \tag{3.13b}$$

so that

$$E_{2\,\mathrm{dh}}=\sum_{l>l'}\langle[ll']_{12}|\frac{1}{r_{12}}|U_{ll'}(12)\rangle, \tag{3.14}$$

$$Q_{12}[\epsilon_{ll'}-H_0(12)-V_{ll'}(12)Q_{12}]U_{ll'}(12)-Q_{12}(1/r_{12})|[ll']_{12}\rangle=0, \tag{3.15a}$$

and $U_{ll'}(12)$ are the Bethe-Goldstone pair correlation functions (the total BG pairs are $[ll']_{12}+U_{ll'}(12)$).

If we note that $\epsilon_{ll'}-\langle[ll']_{12}|(1/r_{12})|[ll']_{12}\rangle$ is the HF pair energy for electrons in spin-orbitals l and l' (since $\epsilon_l+\epsilon_{l'}$ counts the ll' repulsion twice) and that the K_{ll} and $K_{l'l'}$ in $V_{ll'}(12)$ remove the Coulomb and exchange operators for orbitals l and l' from $H_0(12)$, then it is clear that the BG pair corrections in (3.15a) describe the perturbative correlation corrections for pairs of electrons moving in the field of the remain-

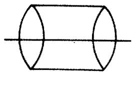


FIG. 3. Sum of all the third-order energy diagrams. Since no hole or particle indices are presented, a sum over all possible hole and particle indices is implied.

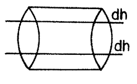


FIG. 4. Sum of all doubly excited diagonal-hole fourth-order energy diagrams represented schematically in terms of bar vertices.

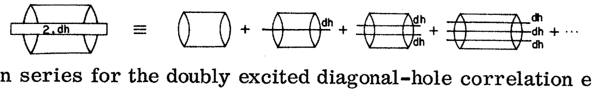


FIG. 5. Diagrammatic Born series for the doubly excited diagonal-hole correlation energy $E_{2\mathrm{dh}}$. The Born series for the propagator $G^{(2)}{}_{ll',\,\mathrm{dh}}$ is obtained by removing the first and last vertices and by labeling the hole lines with l and l', where a sum over all particle indices is still implied.

ing electrons, which are in their ground-state HF spin-orbitals. Thus, provided we introduce some S-type unlinked clusters which can be written in terms of the BG pairs,[41] the MBPT calculations of Kelly[14,15] are equivalent to the physical assumption that the total correlation energy is well approximated by the sum of independent pair correlation energies for each of the pairs which are moving in the field of the remaining electrons. As opposed to the calculation of Kelly, (3.15a) is in a form where the BG pairs can be expanded in an arbitrary basis including correlated functions.[43] Furthermore, these BG pairs can be used in an approximate wave function of the form of (2.10c) in order to calculate properties other than energies. In the following sections, we examine some of the corrections to the physical assumptions embodied in equations (3.14) and (3.15a). However, before discussing what is neglected when BG pairs are used, (3.15a) should be discussed in more detail.

Equations (3.15a) are a set of uncoupled *linear* inhomogeneous integrodifferential equations, as opposed to the eigenvalue equations obtained using the variational-type theories of Sinanoğlu and Nesbet[31] in which they initially solve for the *stationary states* of a pair of electrons which are moving in the field of the remaining electrons, which are in their ground-state HF spin-orbitals. Nesbet's formulation includes orbital excitations in addition to the double excitations of the pair and is written in terms of an orbital expansion of the pair function, while Sinanoğlu neglects the orbital excitations.[4-7] Orbital excitations are discussed in Sec. V. Beyond the form of the pair functions, the theories of Sinanoğlu and Nesbet differ significantly.

The BG pair equations can be solved variationally since the functional

$$F_{ll'}[\tilde{U}_{ll'}]=\langle[ll']_{12}|(1/r_{12})Q_{12}|\tilde{U}_{ll'}(12)\rangle+\langle\tilde{U}_{ll'}(12)|Q_{12}(1/r_{12})|[ll']_{12}\rangle$$
$$+\langle\tilde{U}_{ll'}(12)|Q_{12}[H_0(12)+V_{ll'}(12)Q_{12}-\epsilon_{ll'}]|\tilde{U}_{ll'}(12)\rangle \qquad (3.16a)$$

is stationary with respect to variations about the $U_{ll'}$ which satisfy (3.15a), i.e.,

$$\delta F_{ll'}/\delta\tilde{U}_{ll'}=\delta F_{ll'}/\delta\tilde{U}_{ll'}{}^{*}=0 \qquad (3.16b)$$

yields Eq. (3.15a). The stationary value of the functional in (3.16a) is just the pair correlation energy $E_{2\,\mathrm{dh},\,ll'}$ of (3.12b), and hence, this variational principle corresponds to a variation of each of the pair correlation energies *independently*. The variational principle in Eqs. (3.16a) can be obtained from the approximate cluster wave function in (2.10c) by varying only some of the terms in $\langle\psi_{\mathrm{CL}}|H-E_{\mathrm{HF}}|\psi_{\mathrm{CL}}\rangle$ *without any normalization constraints* except that we have made $\langle\psi_{\mathrm{CL}}|\Phi_0\rangle=1$. (See Sec. IV for a discussion of the omitted terms.) This is the manner in which Sinanoğlu derived the BG pair equations.[5,6] However, here we can enumerate the MBPT diagrams which in effect have been summed in making this approximation.

If $\{\chi_i\}$ denotes a complete set of two-particle antisymmetrized orthonormal functions (containing both space and spin variables) which are strongly orthogonal to the HF ground-state spin-orbitals,[40] then if the $\{U_{ll'}\}$ are expanded in this basis set,

$$U_{ll'}=\sum_i a_i^{ll'}\chi_i, \qquad (3.17a)$$

the variational principle in Eqs. (3.16) is equivalent to

$$a_i^{ll'}=\sum_j\langle\chi_i(12)|1/[\epsilon_{ll'}-H_0(12)-V_{ll'}(12)]|\chi_j(12)\rangle\langle\chi_j(12)|1/r_{12}|[ll']_{12}\rangle, \qquad (3.17b)$$

where $\langle\chi_i(12)|1/[\epsilon_{ll'}-H_0(12)-V_{ll'}(12)]|\chi_j(12)\rangle$ is the inverse of the matrix $\langle\chi_i(12)|\epsilon_{ll'}-H_0(12)-V_{ll'}(12)\times|\chi_j(12)\rangle$. Equations (3.17a) and (3.17b) give the linear variational approximation to the BG pairs for the case in which the basis set $\{\chi_i(12)\}$ is not a complete set.

One simple choice for the basis set $\{\chi\}$ is the set (exact, or approximate in the case of a truncated basis set) which diagonalizes the operator $Q_{12}[H_0(12)+V_{ll'}(12)Q_{12}]$, i.e., $\{\chi_i^{ll'}\}$ such that

$$Q_{12}[H_0(12)+V_{ll'}(12)Q_{12}]\chi_i^{ll'}=\epsilon_i^{ll'}Q_{12}\chi_i^{ll'}. \qquad (3.18a)$$

Then the expansion coefficients in (3.17a) are simple, namely,

$$a_i^{ll'}=\langle\chi_i^{ll'}(12)|1/r_{12}|[ll']_{12}\rangle/(\epsilon_{ll'}-\epsilon_i^{ll'}), \qquad (3.18b)$$

where (3.17a) and (3.18a, b) represent "the spectral expansion" of the BG pairs. For a neutral system the eigenvalues of $Q_{12}H_0(12)$ which correspond to antisymmetric functions are greater than zero (in the "HF continuum"), and the $\langle[ll']_{12}|1/r_{12}|[ll']_{12}\rangle$ in $V_{ll'}(12)$ give another positive contribution to the eigenvalues $\epsilon_i^{ll'}$. The rest of $V_{ll'}(12)$, i.e., $1/r_{12}-K_{ll}-K_{l'l'}$, however, is not necessarily a positive-definite operator. It seems reasonable to expect that this part of $V_{ll'}(12)$ does not appreciably change the spectrum in the sense that the $\epsilon_i^{ll'}$ should be either positive or slightly negative and smaller in magnitude than $\epsilon_{ll'}$. If one of the $\epsilon_i^{ll'}$ were comparable in magnitude to $\epsilon_{ll'}$, the energy denominator in (3.18b) could get very small, and hence the $a_i^{ll'}$ would be large. This situation is contrary to our expectation that for a closed shell HF system the pair corrections should be small in the sense that $\langle U_{ll'}|U_{ll'}\rangle\ll1$. If $\langle U_{ll'}|U_{ll'}\rangle\sim1$, perturbation theory cannot be expected to converge. If (as seems reasonable) $\epsilon_{ll'}-\epsilon_i^{ll'}<0$ for all i, ll', the variational principle in Eqs. (3.16a) has a stable minimum. The presence of a stable minimum can, of course, be checked in a given case.

At this point it is of interest to examine the relationship between Sinanoğlu's "exact pairs"[4-7] and the BG pairs, which are the variational and perturbative analogs of each other. The "exact pairs" $U_{ll'}{}^v$ are the lowest eigenfunctions of the equation

$$Q_{12}[\epsilon_{ll'}-H_0(12)-V_{ll'}(12)Q_{12}]U_{ll'}{}^v(12)-Q_{12}(1/r_{12})\,|[ll']_{12}\rangle=-\epsilon_{ll'}{}^v U_{ll'}{}^v(12), \tag{3.19}$$

where the eigenvalue $\epsilon_{ll'}{}^v=\langle[ll']_{12}\,|1/r_{12}|\,U_{ll'}{}^v(12)\rangle$ is the pair correlation energy. If the eigenvalue $\epsilon_{ll'}{}^v$ is known exactly, then (3.19) can be solved as an inhomogeneous integrodifferential equation. In terms of the basis set of (3.18*a*), the solution is

$$U_{ll'}{}^v(12)=\sum_i \chi_i^{ll'}(12)\langle\chi_i^{ll'}(12)\,|Q_{12}(1/r_{12})\,|[ll']_{12}/(\epsilon_{ll'}-\epsilon_i^{ll'}+\epsilon_{ll'}{}^v). \tag{3.20}$$

However, typically the correlation energy is a small number in the sense that

$$|\epsilon_{ll'}{}^v|\ll|\epsilon_{ll'}-\epsilon_i^{ll'}| \tag{3.21}$$

(otherwise $\langle U_{ll'}|U_{ll'}\rangle$ would not be $\ll 1$), and hence, the $\epsilon_{ll'}{}^v$ represents a small energy denominator shift in (3.20) as opposed to the coefficients in (3.18b). Hence, when $\langle U_{ll'}|U_{ll'}\rangle\ll 1$, $U_{ll'}\approx U_{ll'}{}^v$.[50] This condition is one of the conditions used by Sinanoğlu to justify the variation of part of the energy in the derivation of the equations for the "exact pairs" (the other condition was that certain kinds of exclusion effects, the triangles of Ref. 5, are negligible).[51] Sinanoğlu also noted the similarity between the BG and "exact pairs" when their norm is much less than one.[5]

A slightly better approximation then $U_{ll'}$ to $U_{ll'}{}^v$ would be obtained by taking $\epsilon_{ll'}{}^v$ in the denominator of (3.20) to be $\langle[ll']_{12}\,|(1/r_{12})Q_{12}\,|U_{ll'}(12)\rangle$ (and possibly iterating this result so that in the limit of self-consistency $\epsilon_{ll'}{}^v=\langle[ll']_{12}\,|(1/r_{12})Q_{12}\,|U_{ll'}{}^v(12)\rangle$).

As discussed in this section, the perturbative BG pairs are obtained by summing only some of the diagrams in which two particles are excited at one time. Explicitly, we have neglected the off-diagonal-hole contributions. These off-diagonal-hole terms arise from exclusion effects[5,51] namely, when a pair of electrons is excited from the HF spin-orbitals ll', the Pauli principle no longer prohibits other electrons from occupying the spin-orbitals l and l'. Hence the resulting orbital pair correlation functions become connected,[35] as is shown in the next section, where the concept of "localized pairs" analogous to the idea of localized orbitals[52] is used to discuss the order of magnitude of these exclusion effects. In Sec. IV the relationship between the two-particle density matrix obtained from MBPT[53] and a related cluster-type wave function are used to compare the variational and perturbative approaches to electron correlation in the two-electron approximation (i.e., when we only consider double excitations).

IV. EXCLUSION EFFECTS FOR THE DOUBLE EXCITATIONS

Exclusion effects[51] begin to contribute to the energy in the third order of perturbation theory (for the energy), and are present in all succeeding orders of perturbation theory. In this section the exclusion effect diagrams are considered in which only two electrons are excited at a given time (i.e., these are the contributions from double excitations.) The third-order-energy double-excitation exclusion-effect diagrams are Fig. 2(b) for the pair $ll'\neq l''l'''$ and 2(c) and (d) for $l'\neq l'''$. The nondiagonal-hole diagrams in Figs. 2(c) and (d) are often referred to as three-body diagrams. However, since only two electrons are excited as a given time, it is more appropriate to call these diagrams three-orbital two-body disgrams, since three ground-state HF spin-orbitals are involved. Qualitatively, exclusion-effect terms are expected to be smaller than the corresponding diagonal-hole diagrams when matrix elements of operators like $K_{ll'}$ for $l\neq l'$ are smaller than those of K_{ll} or $K_{l'l'}$. In Be Kelly finds that these nondiagonal-hole diagrams are not of importance.[14] A more thorough discussion of the order of magnitude of exclusion effects is given later in this section.

Before evaluating the doubly-excited nondiagonal-hole diagrams, we can anticipate their contributions to the new pair-correlation correction functions. Each of the BG pair corrections in (3.15a) contains a different (E^0-H)-like operator acting on the $U_{ll'}$ [namely, $(G_{ll'};\mathrm{dh}^{(2)})^{-1}$] and has a different inhomogeneous term. We can collect these different operators into a matrix. Let $\alpha=ll'$ be shorthand for a distinct pair $(l\neq l')$, and define

$$\begin{aligned}\{\alpha\,|(G_0{}^{(2)})^{-1}|\,\beta\}&=(G_{\alpha;\,\mathrm{dh}}{}^{(2)})^{-1}\delta_{\alpha\beta}\\&=Q_{12}[\epsilon_\alpha-H_0(12)-V_\alpha(12)Q_{12}]\delta_{\alpha\beta},\end{aligned} \tag{4.1a}$$

$$\{\alpha\,|V^{(2)}|\,\alpha\}=Q_{12}V_\alpha(12)Q_{12}, \tag{4.1b}$$

$$\{\alpha\,|E-H_0{}^{(2)}|\,\beta\}=\delta_{\alpha\beta}[\epsilon_\alpha-H_0(12)]Q_{12}, \tag{4.1c}$$

where the curly bracket matrix notation is used to denote a quantity which is the component of an operator as distinguished from the *c* number which is the matrix element of an operator. Thus, the BG pair equations can be compactly written as

$$\{\alpha\,|(G_0^{(2)})^{-1}|\,\alpha\}U_\alpha(12)-Q_{12}(1/r_{12})\,|\,\alpha(12)\rangle=0, \tag{3.15b}$$

where $|\alpha(12)\rangle\equiv|[ll']_{12}\rangle$. (4.1d)

In Eq. (3.15b) the $\{U_\alpha\}$ represent independent pair excitations due to correlation. However, the electrons are indistinguishable (the orbitals are not), and the Pauli exclusion principle must therefore connect these pair excitations. Let $\{w_\alpha\}$ denote the pair-correlation correction functions which contain all the doubly excited exclusion terms. It will not be surprising to find the equations for these $\{w_\alpha\}$ to be coupled.[35] Specifically, if

$$\{\alpha\,|(G^{(2)})^{-1}|\,\alpha\}=\{\alpha\,|(G_0^{(2)})^{-1}|\,\alpha\},$$

$$\{\alpha\,|(G^{(2)})^{-1}|\,\beta\}=-\{\alpha\,|V^{(2)}|\,\beta\},\quad\alpha\neq\beta,$$

then

$$\textstyle\sum_\beta\{\alpha\,|(G^{(2)})^{-1}|\,\beta\}w_\beta(12)-Q_{12}(1/r_{12})\,|\,\alpha(12)\rangle=0, \tag{4.2}$$

where the two-body potential of (4.1b) now has off-diagonal components $\{\alpha\,|V^{(2)}|\,\beta\}$ which describe the "driving forces for the exclusion effects."[51] In (4. 2) the column indices of $(G^{(2)})^{-1}$ (and all other matrix operators that are used in Secs. IV and V) must match those of the function upon which it acts. Thus, although the pairs $\beta=ll'$ and $\overline{\beta}=l'l$ (for $l\neq l'$) are not distinct, in (4. 2) we can use $\{\alpha\,|(G^{(2)})^{-1}|ll'\}U_{ll'}$ *or* $\{\alpha\,|(G^{(2)})^{-1}|l'l\}U_{l'l}$ *but not* $\{\alpha\,|(G^{(2)})^{-1}|l'l\}U_{ll'}$ in a summation over $l>l'$. The $\sum_\beta$ in (4. 2) is over distinct pairs.

It now remains for us to compute the form of $\{\alpha\,|V^{(2)}|\,\beta\}$ from the nondiagonal-hole diagrams, where an investigation of these off-diagonal potentials gives insight into the magnitude of the exclusion effects.

There are a number of ways in which we can sum up the doubly-excited exclusion-effect diagrams. Rather than treating successive orders of perturbation theory, the BG pairs can be corrected to 1st, 2nd, ···, *n*th, ···, ∞ order in the exclusion effects. Let $w_\alpha^{(0)}=U_\alpha$ be the BG correction pairs, $w_\alpha^{(n)}$ be the *n*th-order correction for exclusion effects, and finally the w_α in (4.2) are

$$w_\alpha=\sum_{n=0}^{\infty}w_\alpha^{(n)}. \tag{4.3}$$

Figure 6(a) describes the contribution to the correlation energy from double excitations which are first-order in exclusion effects. The bar vertex in this figure with ndh denotes that this is the sum of all of the distinct antisymmetrized diagrams in which a nondiagonal-hole vertex at this time connects all possible pairs of lines that the bar vertex crosses. The sum over all the diagrams containing diagonal-hole interactions is still implied by the infinite-order diagonal-hole bar vertex in Fig. 6. Figure 6(a) has the value [cf. (4.1a) and (3.13b)]

$$\sum_{\alpha\neq\beta}\langle\alpha(12)\,|\frac{1}{r_{12}}\{\alpha\,|G_0^{(2)}|\,\alpha\}\{\alpha\,|V^{(2)}|\,\beta\}\{\beta\,|G_0^{(2)}|\,\beta\}\frac{1}{r_{12}}|\,\beta(12)\rangle \tag{4.4a}$$

$$=\sum_{\alpha\neq\beta}\langle U_\alpha(12)\,|\{\alpha\,|V^{(2)}|\,\beta\}\,|\,U_\beta(12)\rangle \tag{4.4b}$$

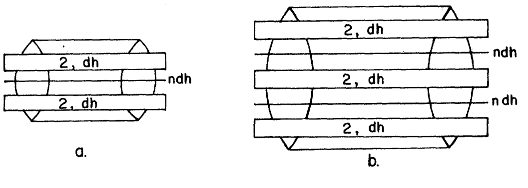
$$=\textstyle\sum_\alpha\langle\alpha(12)\,|1/r_{12}\,|w_\alpha^{(1)}(12)\rangle, \tag{4.4c}$$

where the same index, say α, in Eqs. (4.4) must be ordered in the same way in each term in which it appears, and

$$\{\alpha=ll'|V^{(2)}|\,\beta=l''l'''\}=\langle\beta(12)\,|1/r_{12}\,|\,\alpha(12)\rangle Q_{12},\quad l\text{ or }l'\neq l''\text{ or }l''', \tag{4.4d}$$

$$\{ll'\,|V^{(2)}|\,ll''\}\equiv\{l'l\,|V^{(2)}|\,l''l\}=-Q_{12}K_{l''l'}Q_{12}+Q_{12}\langle[ll'']_{12}\,|1/r_{12}\,|[ll']_{12}\rangle,\quad l'\neq l''. \tag{4.4e}$$

The sums in (4.4a, b) are over all distinct pairs $\alpha\neq\beta$. [The row (column) indices on the right-hand side of (4.4d, e) are the column (row) indices—in the same order—on the left-hand side of (4.4d, e) because "holes travel backwards in time."] The $\langle\beta(12)|1/r_{12}|\,\alpha(12)\rangle$ is just the repulsion energy (Coulomb minus exchange contributions) between the different spin-orbital pairs α and β, while the $K_{l''l'}$ as given by Eq. (3.7) are "hole scattering operators."



a. b.

FIG. 6. (a) The correlation energy to first order in exclusion effects. (b) The correlation energy to second order in exclusion effects. Again a sum over all hole and particle indices is implied.

Equation (4.4b) is a manifestation of the so-called "$2n+1$ rule of perturbation theory,"[39] and here indicates that a knowledge of the pair correction functions to nth order in exclusion effects enables the evaluation of the double-excitation energies to $2n+1$ order in the exclusion effects.

Comparing (4.4a) and (4.4c) using (3.13b) gives the equations for $w_\alpha^{(1)}$ as

$$\{\alpha|(G_0^{(2)})^{-1}|\alpha\}w_\alpha^{(1)}(12)-\sum_{\beta\neq\alpha}\{\alpha|V^{(1)}|\beta\}w_\beta^{(0)}(12)=0, \tag{4.5}$$

which is a set of *linear* inhomogeneous equations which could be solved variationally as in the case of $U_\alpha^{(1)}$ and $U_\alpha=w_\alpha^{(0)}$ in Eqs. (3.6) and (3.16a).

By analogy with the transition from Eqs. (3.9) to (3.11), Fig. 6(b) has the value

$$\sum_{\alpha\neq\beta,\,\beta\neq\gamma}\langle\alpha(12)|\frac{1}{r_{12}}\{\alpha|G_0^{(2)}|\alpha\}\{\alpha|V^{(2)}|\beta\}\{\beta|G_0^{(2)}|\beta\}\{\beta|V^{(2)}|\gamma\}\{\gamma|G_0^{(2)}|\gamma\}\frac{1}{r_{12}}|\gamma(12)\rangle \tag{4.6a}$$

$$=\sum_\alpha\langle\alpha(12)|1/r_{12}|\omega_\alpha^{(2)}(12)\rangle. \tag{4.6b}$$

It is clear that the higher-order terms in exclusion effects represent successive corrections of the form

$$\{\alpha|(G_0^{(2)})^{-1}|\alpha\}w_\alpha^{(n)}(12)-\sum_{\beta\neq\alpha}\{\alpha|V^{(2)}|\beta\}w_\beta^{(n-1)}(12)=0, \tag{4.7}$$

where the contribution to the double-excitation energy, nth order in exclusion effects, is just $\langle\alpha(12)|1/r_{12}|w_\alpha^{(n)}(12)\rangle$.

If we interpret, e.g.,

$$\sum_{\alpha\neq\beta}\{\alpha|V^{(2)}|\beta\}\{\beta|G_0^{(2)}|\beta'\}$$

in (4.4a) and (4.6a) as a matrix multiplication of the components of the operators $V^{(2)}$ and $G_0^{(2)}$ (with column and row indices ordered in the same way and sums run over distinct pairs) then the summation implied in the first line of Fig. 7 is just the diagrammatic Born series expansion of the double-excitation energy

$$E_2=\sum_\alpha E_{2\alpha}=\sum_\alpha\langle\alpha(12)|1/r_{12}|w_\alpha(12)\rangle \tag{4.8a}$$

$$=\sum_{\alpha,\beta}\langle\alpha(12)|(1/r_{12})\{\alpha|G^{(2)}|\beta\}(1/r_{12})|\beta(12)\rangle, \tag{4.8b}$$

which is still the sum of individual pair correlation energies $E_{2\alpha}$. The second line in Fig. 7 indicates the diagrammatic Born series expansion of (4.8b) in orders of ordinary perturbation theory.

Thus the "complete pairs" $w_\alpha(12)$ are defined by the equations

$$\sum_\beta\{\alpha|(G^{(2)})^{-1}|\beta\}w_\beta(12)-Q_{12}(1/r_{12})|\alpha(12)\rangle=0, \tag{4.9a}$$

or equivalently,

$$\sum_\beta\{\alpha|E-H_0^{(2)}-V^{(2)}|\beta\}w_\beta(12)-Q_{12}(1/r_{12})|\alpha(12)\rangle=0. \tag{4.9b}$$

Equations (4.9) are coupled *linear* inhomogeneous equations which can be solved variationally from the functional

$$F_2(\{\tilde{w}_\alpha\})=\sum_\alpha[\langle\alpha(12)|(1/r_{12})Q_{12}|\tilde{w}_\alpha(12)\rangle+\langle\tilde{w}_\alpha(12)|Q_{12}(1/r_{12})|\alpha(12)\rangle$$
$$-\sum_\beta\langle\tilde{w}_\alpha(12)|\{\alpha|(G^{(2)})^{-1}|\beta\}|\tilde{w}_\beta(12)\rangle], \tag{4.10a}$$

since (4.9) imply that

$$\delta F_2/\delta\tilde{w}_\gamma=0,\quad \text{all } \gamma. \tag{4.10b}$$

Equations (4.9) are, of course, equivalent to the $\sum_{n=0}^{\infty}$ of (4.7) where $w_\alpha^{(-1)}\equiv|\alpha(12)\rangle$. It should be noted that the variational principle obtained from (4.10) represents a variation of the total correlation energy, i.e., the stationary value of F_2 is E_2 (including only double excitation contributions) as opposed to (3.16a) in which the individual pair correlation energies are varied independently. This variational principle is also obtained by varying the cluster wave function in (2.10c) in the expression $\langle\psi_{\rm CL}|H-E_{\rm HF}|\psi_{\rm CL}\rangle$ *without any normalization constraints* other than requiring $\langle\psi_{\rm CL}|\Phi_0\rangle=1$. The HF wave function is invariant

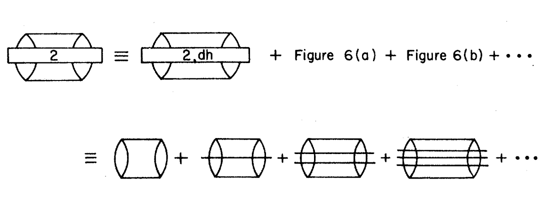


FIG. 7. Diagrammatic Born series for the doubly excited correlation energy E_2 to all orders in exclusion effects. The first line gives the Born series in orders of exclusion effects, while the second line gives the series in orders of ordinary perturbation theory. The series for the propagator $G^{(2)}$ is obtained by removing the first and last vertices.

under a unitary transformation among the HF spin-orbitals of the wave function. Such a transformation induces the transformation on the HF pairs

$$|\bar{\alpha}(12)\rangle = \sum_\alpha \{\bar{\alpha}|T|\alpha\}|\alpha(12)\rangle,$$

where $\{\bar{\alpha}|T|\alpha\}$ is unitary. Applying $\sum_\alpha\{\bar{\alpha}|T|\alpha\}$ to (4.9a) and defining

$$w_{\bar{\alpha}}(12) = \sum_\alpha \{\bar{\alpha}|T|\alpha\} w_\alpha(12), \tag{4.11b}$$

$$\{\bar{\alpha}|(G^{(2)})^{-1}|\bar{\beta}\} = \sum_{\alpha,\beta} \{\alpha|T|\alpha\}\{\alpha|(G^{(2)})^{-1}|\beta\}\{\beta|T^{-1}|\bar{\beta}\} \tag{4.11c}$$

give[54]

$$\sum_\beta \{\bar{\alpha}|(G^{(2)})^{-1}|\bar{\beta}\} w_{\bar{\beta}}(12) - Q_{12}(1/r_{12})|\bar{\alpha}(12)\rangle = 0. \tag{4.11d}$$

[The unitary transformation could likewise be applied in F_2 in (4.10a).] In particular, $\{\alpha|T|\bar{\alpha}\}$ can be chosen such that the $|\bar{\alpha}(12)\rangle$ have definite spin and spatial symmetries.[55] However, a much more interesting transformation might be expected to exist, namely, a unitary transformation which completely decouples (4.11d), i.e., $\{\bar{\alpha}|(G^{(2)})^{-1}|\bar{\beta}\} = \{\bar{\alpha}|(G^{(2)})^{-1}|\bar{\alpha}\}\delta_{\bar{\alpha}\bar{\beta}}$ where $\{\bar{\alpha}|T|\alpha\}$ may in general be an operator. The pairs $|\bar{\alpha}(12)\rangle$ could be termed "localized HF pairs" in this case by analogy with the concept of localized orbitals.[52] From (4.4d) we see that the exclusion effects are qualitatively proportional to the repulsion (Coulomb minus exchange) between the different pairs. The localized pairs would therefore qualitatively correspond to pairs which are noninteracting with each other. Since $(G^{(2)})^{-1}$ contains the operators $K_{l'l'}$, K_{ll}, etc., it would not be advantageous to attempt to diagonalize $(G^{(2)})^{-1}$ as we diagonalize ordinary matrices. However, if we qualitatively expect that both the parts in (4.4d) contribute in the same manner, these localized pairs should be related to the pairs that diagonalize the constant terms in $(G^{(2)})^{-1}$, namely the matrix $\epsilon_\alpha\delta_{\alpha\beta} - \langle\alpha|1/r_{12}|\beta\rangle$.

The diagonalization of $(G^{(2)})^{-1}$ would imply that we can solve variationally for each of the pair functions and energies independently. If exclusion effects are significant only between some pairs (e.g., possibly in delocalized systems), then only blocks of $(G^{(2)})^{-1}$ need be "diagonalized." In order to make a rough estimate of the ratio of exclusion effects to diagonal terms, we assume that the overlap between two pair functions $\langle w_\alpha|w_\beta\rangle$ is appreciable (compared to $\langle w_\alpha|w_\alpha\rangle$ or $\langle w_\beta|w_\beta\rangle$) when the interaction between the HF pairs is also appreciable, i.e., when the HF pairs can get near to each other. Thus, qualitatively,

$$\frac{\text{exclusion energies}}{\text{diagonal energies}} \sim \frac{\langle w_\alpha|\langle\beta|1/r_{12}|\alpha\rangle|w_\beta\rangle}{\langle w_\alpha|\langle\alpha|1/r_{12}|\alpha\rangle|w_\alpha\rangle} \sim \left|\frac{\langle\beta|1/r_{12}|\alpha\rangle}{\langle\alpha|1/r_{12}|\alpha\rangle}\right|^2, \tag{4.11e}$$

where a typical energy is chosen to represent both types of energies. In Be, Kelly found that the diagrams which contribute to the energy to first order in exclusion effects[51] are very small.[14] This is to be expected since Be has the strongly localized $(1s)^2$ and $(2s)^2$ pairs.

So far in Secs. III and IV the correlation energy as calculated by perturbation theory in the double excitation approximation has been discussed. It is of considerable interest to compare these results with those obtainable from related cluster-type wave functions and the variational theories of Sinanoğlu and Nesbet when these later theories are also restricted to the double excitation approximation. These theories are easily compared by using two-electron density matrices.

If we insert the "complete pairs" which are the solutions to (4.9) into the *normalized* double-excitation cluster-type wave function

$$\psi_{\mathrm{CL}}(w) = \nu(w)a[\varphi_0 + 2^{-1/2}\sum_\alpha \varphi_\alpha w_\alpha], \tag{4.12a}$$

where

$$\nu(w)^{-2} = 1 + \sum_\alpha \langle w_\alpha|w_\alpha\rangle, \tag{4.12b}$$

then the two-particle reduced density matrix[1,56-59] for this wave function can be written after some rearrangement in the form

$$\Gamma_{\mathrm{CL}}(12;1'2') = \binom{N}{2}\int\psi_{\mathrm{CL}}(1,2,\cdots,N)\psi_{\mathrm{CL}}{}^*(1',2',3,\cdots,N)d(3,\cdots,N) \tag{4.13a}$$

$$= \Gamma_{\mathrm{HF}} + \nu(w)^2\Gamma_{\mathrm{CORR}}(w), \tag{4.13b}$$

where in operator form

$$\Gamma_{\mathrm{HF}}(12;1'2') = \sum_\alpha |\alpha(12)\rangle\langle\alpha(1'2')|, \tag{4.13c}$$

and Γ_{CORR} is written in terms of the $\{w_\alpha\}$ and the ground-state HF spin-orbitals. From the definition of density matrices,[1,56-59] if

$$H = \sum_i \bar{H}(i) + \sum_{i>j} \bar{H}(ij), \tag{4.14a}$$

then $$\langle\psi_{\mathrm{CL}}|H|\psi_{\mathrm{CL}}\rangle=\mathrm{Tr}(H^{\mathrm{R}}\Gamma_{\mathrm{CL}}), \tag{4.14b}$$

where $$H^{\mathrm{R}}=(N-1)^{-1}[\overline{H}(1)+\overline{H}(2)]+\overline{H}(12) \tag{4.14c}$$

Note that (4.13a) implies that

$$\mathrm{Tr}\,\Gamma_{\mathrm{CL}}=\binom{N}{2}=\frac{N(N-1)}{2}$$

since ψ_{CL} is normalized, and hence $\mathrm{Tr}\,\Gamma_{\mathrm{CORR}}\equiv 0$.

MBPT provides an explicit perturbative expansion for the two-electron reduced density matrix in addition to an expansion for the wave function. The rules for the diagrammatic expansion of the two-electron density matrix will be presented in a future work by Reinhardt,[19,53] but these results are used to investigate this density matrix within the model of one-, two-, and three-particle excitations and to compare this with the form of the cluster-type wave functions as used by Sinanoğlu and others.[4-10]

If we define a two-electron density matrix $\Gamma_{\mathrm{MB}}(w)$[53] such that

$$\mathrm{Tr}[(H^{\mathrm{R}}-E_{\mathrm{HF}})\Gamma_{\mathrm{MB}}(w)]=E_2, \tag{4.15a}$$

where E_2 is the correlation energy of (4.8), then

$$\Gamma_{\mathrm{MB}}(w)=\Gamma_{\mathrm{HF}}+\Gamma_{\mathrm{CORR}}(w), \tag{4.15b}$$

where the Γ_{CORR} in (4.15b) and (4.13b) are identical provided they are constructed with the same sets of pair functions.

Equations (4.13b) and (4.15b) differ only in the presence of the normalization term $\nu(w)^2$, and hence, in the language of the cluster-type wave functions, (4.15b) contains some 4-, 6-, $\cdots$ body effects which are necessary to cancel out the normalization constant $\nu(w)^2$. Since no N-electron wave function is apparent which yields the density matrix Γ_{MB}, this reduced density matrix is not necessarily N-representable, and hence E_2 is neither a rigorous upper or lower bound to the true correlation energy. However, the correlation energy from the wave function $\psi_{\mathrm{CL}}(w)$ in (4.12), $E_2\nu(w)^2$, is an upper bound to the correlation energy of the N-electron system.

As discussed in Appendix A, the exact wave function is composed of S-type unlinked clusters [when we use the many-body normalization which is defined after (2.10)], and once approximations to the exact pair functions such as the "complete" or BG pairs are calculated, some of the contributions from 4-, 6-, $\cdots$ electron excitations can be included in terms of these pair functions.[41] The major effect of these S-type unlinked clusters is probably just to reduce the size of the normalization constant (4.12b) when it appears in the correlation energy for such a cluster-type wave function.[41] Equivalently, some of the 4-, 6-, $\cdots$ body energy diagrams MBPT can be expressed in terms of the pair functions.[18,60,61] Some of these diagrams are the ones that Kelly calls EPV (exclusion principle violating) diagrams, and they arise from the linked-cluster factorization in MBPT.[41]

If exclusion effects are neglected and the BG pairs are used, then $\Gamma_{\mathrm{CORR}}(U)$ can be written as a sum of $\Gamma_{\mathrm{CORR;\,dh}}(U)$ and $\Gamma_{\mathrm{CORR;\,ndh}}(U)$ where

$$\mathrm{Tr}[(H^{\mathrm{R}}-E_{\mathrm{HF}})\Gamma_{\mathrm{CORR;\,dh}}]=E_{2\,\mathrm{dh}}, \tag{4.16}$$

and $E_{2\,\mathrm{dh}}$ is given by (3.14) and (3.12b). However, $E_{2\,\mathrm{dh}}$ is again not necessarily an upper or lower bound to the correlation energy and neither is $E_{2\,\mathrm{dh}}\nu(U)^2$! A rigorous upper bound is obtained from $\mathrm{Tr}[(H^{\mathrm{R}}-E_{\mathrm{HF}})\Gamma_{\mathrm{CORR}}(U)]\nu^2(U)$ which contains energies to first order in exclusion effects.[4-7]

When the complete pairs are small, i.e., $\langle w_\alpha|w_\alpha\rangle\ll 1$, $\Gamma_{\mathrm{CL}}(\{w_\alpha\})$, and $\Gamma_{\mathrm{MB}}[\{w_\alpha\})$ are roughly equivalent. Furthermore, when exclusion effects are also small, the complete pairs, BG pairs, and "exact pairs" are also roughly equivalent. Thus the correlation energies calculated from any of these sets of pairs, with or without the first-order exchusion energies, a normalization term (4.12b), or a smaller normalization due to S-type unlinked clusters, should be roughly the same.[50]

Sections III and IV have dealt with the description of electron correlation in closed-shell atoms and molecules[32] in the double-excitation approximation. Some mention, however, was made of the S-type unlinked clusters which give some information about higher excitations from the HF ground state.[41] The double-excitation approximations have given very good results when applied to small atoms, and it would be a very satisfactory situation if this approximation would suffice for larger systems (possibly including the use of S-type unlinked clusters), since this would mean that all of quantum chemistry could be reduced to a set of one- and two-particle problems for a given state of an atom or molecule. (For a system whose approximate single-determinantal wave function is built up from non-HF spin-orbitals, or for a single-determinantal restricted HF wave function for an open-shell system, we should, of course, expect orbital corrections to be of importance in order to obtain fairly accurate wave functions and correlation energies.[32,33]) If this is in fact the true situation, then we have learned that the singly, triply, $\cdots$, excited functions in (2.10a) and (2.10b) are essentially negligible. If, on the other hand, the double-excitation ap-

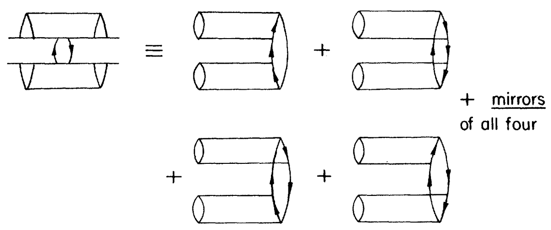


FIG. 8. The contribution to the fourth-order correlation energy containing single excitations summarized in terms of bar vertices.

proximation proves not to be an entirely adequate description of some atoms and molecules (i.e., possibly in delocalized π systems), these single and triple (and possibly higher) excitations would be the next logical candidates to investigate. In the next section, the single and triple (S-type linked) excitations of (2.10a) and (2.10b) are investigated. Our aim is again to obtain some qualitative and physical understanding of the role of these one- and three-particle cluster functions, i.e., their effect on the correlation enegy and the modification they induce on the resulting pair-correlation correction functions.

V. EFFECTS OF SINGLE AND TRIPLE EXCITATIONS

First the effects of including the possibility of single excitations in addition to double excitations is considered. The treatment of both double and triple excitations is analogous to that for single and double excitations and will be shown to have the same kind of physical effect on the correlation energy. Both single and triple excitations first contribute to the energy of a closed-shell HF system in the fourth order of perturbation theory and are present in all higher orders. By single and triple excitations we mean that during some time interval in the MBPT diagrams for the energy one or three electrons, respectively, are excited out of the "HF sea," or equivalently, that singly or triply excited configurations are contributing to the energy. It should also be noted that quadruply excited states contribute to the energy in the fourth order of perturbation theory. However, these terms occur as matrix elements of S-type unlinked clusters, i.e., they can be expressed solely in terms of the first-order pairs defined in (3.5).[18,41,60,61] As discussed in Appendix A there are four-electron diagrams of this nature in all higher orders of perturbation theory (as well as 6-, 8-, 10-, ··· electron diagrams) and these are then expressible in terms of the "complete pairs" of (4.9) or more approximately in terms of the BG pairs of (3.10).

The one-body excitations could be treated in successive orders of perturbation theory. However, it is just as easy to correct the correlation energy of a closed-shell HF system to 1st, 2nd, ···, nth, ··· order in the single excitations. Using this method, the summation to all orders of single excitations is analogous to that in Sec. IV for the exclusion effects. The method of assigning "orders in single excitations" is arbitrary, but is chosen below to correspond to orders in a perturbative expansion of the final equations.

The lowest-order energy diagrams in perturbation theory (fourth order) for a closed-shell HF system containing single excitations are summarized in Fig. 8. The bar vertices on the left-hand side of the equality of Fig. 8 which separate the intervals of single and double excitations denote the sum of all possible distinct antisymmetrized vertices which can change the number of excited electrons between one and two. Both diagonal- and nondiagonal-hole lines are considered, since the exclusion effects can be neglected by dropping some of the coupling terms in the final equations. In order to generalize the diagrams in Fig. 8 to infinite order in perturbation theory, it is convenient to define the one-particle propagator $\{l\,|\,G^{(1)}\,|\,l'\}$ by Fig. 9. The diagrams in Fig. 9 have values (when they appear in an energy diagram) which form the Born series

$$\{l\,|\,G^{(1)}\,|\,l'\}=\frac{Q_1}{\epsilon_l-H_0(1)}\delta_{ll'}+\frac{Q_1}{\epsilon_l-H_0(1)}\{l\,|\,V^{(1)}\,|\,l'\}\frac{Q_1}{\epsilon_{l'}-H_0(1)}$$

$$+\sum_{l''}\frac{Q_1}{\epsilon_l-H_0(1)}\{l\,|\,V^{(1)}\,|\,l''\}\frac{Q_1}{\epsilon_{l''}-H_0(1)}\{l''\,|\,V^{(1)}\,|\,l'\}\frac{Q_1}{\epsilon_{l'}-H_0(1)}+\cdots \tag{5.1}$$

or

$$\{l\,|(G^{(1)})^{-1}\,|\,l'\}=Q_1[\epsilon_l-H_0(1)+K_{ll}(1)Q_1]\delta_{ll'}+Q_1K_{l'l}(1)Q_1(1-\delta_{ll'}) \tag{5.2a}$$

$$=Q_1[\epsilon_l-H_0(1)]\delta_{ll'}-\{l\,|\,V^{(1)}\,|\,l'\}. \tag{5.2b}$$

Note that $H_0(1)-K_{ll}(1)$ in (5.2) describes the Hamiltonian for the motion of a single electron in the field of the remaining electrons which are in their ground-state HF orbitals.

The top bar vertex in Fig. 8 can be shown to give a contribution which is equal to the matrix element of

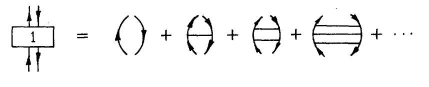


FIG. 9 The diagrammatic series for the one-particle propagator $G^{(1)}$. (Sum over all hole and particle indices.)

the operator (putting in hole indices)

$$\{ll' \,|\, V^{(2,1)} \,|\, l\} = Q_{12}(1/r_{12} - K_{l'l'})2^{-1/2}(1-P_{12})\,|l(2)\rangle Q_1, \tag{5.3a}$$

$$\{ll' \,|\, V^{(2,1)} \,|\, l'\} = Q_{12}(1/r_{12} - K_{ll})2^{-1/2}(1-P_{12})\,|l'(2)\rangle Q_1, \tag{5.3b}$$

$$\{ll' \,|\, V^{(2,1)} \,|\, l''\} = -Q_{12}K_{l''l'}2^{-1/2}(1-P_{12})\,|l(2)\rangle Q_1, \quad l'' \neq l, l', \tag{5.3c}$$

(as well as introducing an extra energy denominator). The bottom bar vertex yields

$$\{l'' \,|\, V^{(1,2)} \,|\, ll'\} = \{ll' \,|\, V^{(2,1)} \,|\, l''\}^{\dagger}. \tag{5.3d}$$

In terms of this one-body propagator and the potential connecting single and double excitations, the energy to first order in single excitations as represented in Fig. 10(a) is

$$\textstyle\sum_{\alpha,\beta}\langle\alpha(12)\,|(1/r_{12})\{\alpha \,|\, G^{(2)}V^{(2,1)}G^{(1)}V^{(1,2)}G^{(2)} \,|\, \beta\}(1/r_{12})\,|\beta(12)\rangle \tag{5.4a}$$

$$= \textstyle\sum_{\alpha,\beta}\langle w_\alpha(12)\,|\{\alpha \,|\, V^{(2,1)}G^{(1)}V^{(1,2)} \,|\, \beta\}w_\beta(12)\rangle \tag{5.4c}$$

$$= \textstyle\sum_{\alpha,l''}\langle w_\alpha(12)\,|\{\alpha \,|\, V^{(2,1)} \,|\, l''\}\,|w_{l''}^{(1)}(1)\rangle, \tag{5.4c}$$

where the indicated matrix multiplication is to be performed between the components of the operators G and V. The first-order single-excitation functions defined by (5.4c), $w_l^{(1)}$, are equivalently the solutions to the linear coupled inhomogeneous equations

$$\textstyle\sum_{l'}\{l \,|\, (G^{(1)})^{-1} \,|\, l'\}w_{l'}^{(1)}(1) - \sum_{\alpha}\{l \,|\, V^{(1,2)} \,|\, \alpha\}w_\alpha(12) = 0. \tag{5.5}$$

If exclusion effects are to be neglected then w_α is to be replaced by the BG pair U_α, and only the diagonal components of $(G^{(1)})^{-1}$ and $V^{(1,2)}$ are to be taken, i.e., the equations become uncoupled. Equation (5.5) can be solved variationally in the same manner as described in (4.10) for w_α or in (3.16) for U_α if exclusion effects are to be neglected.

Define the two-particle "self-energy" operator A_1 which contains a sum over all one-particle states which are orthogonal to the ground-state HF spin-orbitals by

$$\{\alpha \,|\, A_1 \,|\, \beta\} = \{\alpha \,|\, V^{(2,1)}G^{(1)}V^{(1,2)} \,|\, \beta\}. \tag{5.6}$$

The energy to second order in one-electron excitations which is presented in Fig. 10(b) has the value

$$\textstyle\sum_{\alpha,\beta}\langle\alpha(12)\,|(1/r_{12})\{\alpha \,|\, G^{(2)}A_1G^{(2)}A_1G^{(2)} \,|\, \beta\}(1/r_{12})\,|\beta(12)\rangle, \tag{5.7}$$

and could be calculated from knowledge of the $\{w_l^{(1)}\}$ (so can the third-order term) as well as providing a definition of $w_l^{(2)}$. If the diagram in Fig. 10(c) denotes the sum of the energy to all orders in one-electron excitations (including the "zeroth order" energy of Fig. 7 which contains only double excitations), the resulting Born series may be summed to give

$$E_{2\,SE1} = \textstyle\sum_\alpha E_{\alpha,\,2\,SE1} = \sum_\alpha\langle\alpha(12)\,|1/r_{12}\,|y_\alpha(12)\rangle = \sum_{\alpha,\beta}\langle\alpha(12)\,|(1/r_{12})\{\alpha \,|\, G_{SE1}^{(2)} \,|\, \beta\}(1/r_{12})\,|\beta(12)\rangle, \tag{5.8}$$

where $y_\alpha(12) = \sum_\beta\{\alpha \,|\, G_{SE1}^{(2)} \,|\, \beta\}(1/r_{12})\,|\beta(12)\rangle,$ (5.9a)

and $\{\alpha \,|\, (G_{SE1}^{(2)})^{-1} \,|\, \beta\} = \{\alpha \,|\, (G^{(2)})^{-1} - A_1 \,|\, \beta\}.$ (5.9b)

Equation (5.9a) is equivalent to the inhomogeneous integrodifferential equation for the new pair functions y_α

$$\textstyle\sum_\beta\{\alpha \,|\, (G_{SE1}^{(2)})^{-1} \,|\, \beta\}y_\beta(12) - Q_{12}(1/r_{12})\,|\alpha(12)\rangle = 0. \tag{5.10}$$

Again exclusion effects may be neglected by taking only diagonal components of all the operators in $(G_{SE1}^{(2)})^{-1}$. It should also be noted that the total correlation energy can be written as a sum of individual pair-correlation energies. [The exact pair-correlation energies are determined by a knowledge of the pair-correlation functions $U_{\mathrm{exact}}^{\alpha}$ that occur in the exact wave function by $\langle\alpha(12)\,|1/r_{12}\,|U_{\mathrm{exact}}^{\alpha}(12)\rangle$.] As should be obvious, (5.10) could, in principle, be solved variationally in analogy with (4.10) for the w_α.

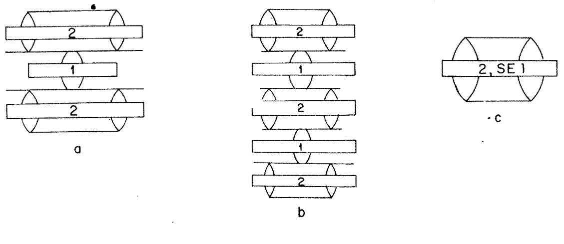


FIG. 10. (a) The correlation energy to first order in single excitations. (b) The correlation energy to second order single excitations. (c) The correlation energy summed to all orders in single excitations.

The only difference between (5.10) and (4.9a) is the presence of the integral operator A_1 in (5.10). This two-body operator is also the only new addition to the expression for the pair-correlation energy in the last term of (5.8). Since A_1 contains a sum over all one-electron states outside of the "HF sea," it represents an effective two-body operator describing the virtual de-excitation of an electron due to the mutual correlation of that electron with another electron. Just as (3.17a) and (3.18a) provide the "spectral expansion" of $\{\alpha|G_0^{(2)}|\alpha\}$, i.e., $\{\alpha|G_0^{(2)}|\alpha\}=\sum_i|\chi_i^\alpha(12)\rangle\langle\chi_i^\alpha(12)|/(\epsilon_\alpha-\epsilon_i^\alpha)$, we could also define a spectral expansion of $\{\alpha|G^{(2)}|\beta\}$ in terms of the eigenfunctions of $(G^{(2)})^{-1}$. The "self-energy" operator A_1 then qualitatively just gives energy shifts in the denominators in the spectral expansion of $\{\alpha|G_{SE1}^{(2)}|\beta\}$ over what they are in $\{\alpha|G^{(2)}|\beta\}$. Provided A_1 is "small" compared with $(G^{(2)})^{-1}$, the single excitations will have a negligible effect on the pair functions, i.e., $y_\alpha\approx w_\alpha$, and the pair correlation energies.

In its present form (5.10) is not easily soluble since A_1 contains a sum over states (or more precisely it contains the operator $G^{(1)}$ for which we cannot easily write a functional form). We can remove this self-energy operator from (5.10) by defining the orbital excitation functions

$$y_l(1)=\sum_{l',\alpha}\{l|G^{(1)}|l'\}\{l'|V^{(1,2)}|\alpha\}y_\alpha(12), \tag{5.11}$$

and we obtain coupled *linear* inhomogeneous equations for the pair and orbital functions

$$\begin{aligned}&\sum_l\{l'|(G^{(1)})^{-1}|l\}y_l(1)-\sum_\alpha\{l'|V^{(1,2)}|\alpha\}y_\alpha(12)=0,\\&\sum_\beta\{\alpha|(G^{(2)})^{-1}|\beta\}y_\beta(12)-\sum_l\{\alpha|V^{(2,1)}|l\}y_l(1)-Q_{12}(1/r_{12})|\alpha(12)\rangle=0.\end{aligned} \tag{5.12}$$

Equations (5.12) no longer contain any self-energy operators and can be solved variationally since the pair of equations

$$\begin{aligned}F_{2\,SE1}[\tilde{y}_l,\tilde{y}_\alpha]=\sum_\alpha[&\langle\tilde{y}_\alpha(12)|Q_{12}(1/r_{12})|\alpha(12)\rangle+\langle\alpha(12)|(1/r_{12})Q_{12}|\tilde{y}_\alpha(12)\rangle\\&+\sum_l(\langle\tilde{y}_\alpha(12)|\{\alpha|V^{(2,1)}|l\}|\tilde{y}_l(1)\rangle+\langle\tilde{y}_l(1)|\{l|V^{(1,2)}|\alpha\}|y_\alpha(12)\rangle)\\&+\sum_\beta\langle\tilde{y}_\alpha(12)|-\{\alpha|(G^{(2)})^{-1}|\beta\}|\tilde{y}_\beta(12)\rangle]+\sum_{l,l'}\langle\tilde{y}_{l'}(1)|-\{l'|(G^{(1)})^{-1}|l\}|\tilde{y}_l(1)\rangle,\end{aligned} \tag{5.13a}$$

$$\delta F_{2\,SE1}/\delta\tilde{y}_l{}^*=\delta F_{2\,SE1}/\delta\tilde{y}_\alpha{}^*=\delta F_{2\,SE1}/\delta\tilde{y}_l=\delta F_{2\,SE1}/\delta\tilde{y}_\alpha=0 \tag{5.13b}$$

are equivalent to (5.12). Equations (5.13a, b) correspond to a variation of $\langle\tilde{\psi}_{\rm CL}|H-E_{\rm HF}|\tilde{\psi}_{\rm CL}\rangle$ where $\tilde{\psi}_{\rm CL}=\mathcal{A}[\varphi_0+\sum_l\varphi_l\tilde{y}_l+(2)^{-1/2}\sum_\alpha\varphi_\alpha\tilde{y}_\alpha]$ and no normalization constraint is imposed other than requiring that $\langle\tilde{\psi}_{\rm CL}|\Phi_0\rangle=1$. The stationary value of $F_{2\,\rm SE1}$ is the total correlation energy of (5.8). However, in varying only part of the energy expression from this cluster-type wave function, we can now enumerate which of the terms in perturbation theory we are actually evaluating. Again the neglect of exclusion effects enables the decoupling of some of the equations in (5.12) and enables the modified variational principle to correspond to a variation of individual pair-correlation energies. The functional $F_{2\,\rm SE1}$ still is very similar in structure to the functional used in ordinary second-order variational-perturbation theory (3.6), and hence is amenable to solution. The couplings can also be handled by using iterative or perturbative techniques, and the pair functions $\{y_\alpha\}$ may be expanded in a correlated basis set if desired.[43] As in the discussion of the BG and "exact" pairs in (3.19) to (3.21), the solutions to the stationary-state equivalent of (5.12) should be very similar to the solutions to (5.12) since pair-correlation energies are small in the sense of (3.21), etc.

The treatment of the three-electron excitations follows in the same manner as the above discussion of the one-electron excitations. Letting $s=ll'l''$, where the indices are distinct ($l\neq l'$, $l''\neq l,l'$) and their order is preserved throughout an equation, we define the three-body propagator $\{s|G^{(3)}|t\}$ by

$$\{s|(G^{(3)})^{-1}|t\}=[\epsilon_s-H_0(123)]Q_{123}\delta_{st}-\{s|V^{(3)}|t\}, \tag{5.14a}$$

where $\epsilon_s=\epsilon_l+\epsilon_{l'}+\epsilon_{l''}$ $(s=ll'l'')$, (5.14b)

$$Q_{123}=Q_1Q_2Q_3, \tag{5.14c}$$

$$\begin{aligned}\{s|V^{(3)}|s\}=Q_{123}\Big[&\langle[ll']_{12}|(1/r_{12})|[ll']_{12}\rangle+\langle[ll'']_{12}|(1/r_{12})|[ll'']_{12}\rangle\\&+\langle[l'l'']_{12}|(1/r_{12})|[l'l'']_{12}\rangle+\sum_{i>j=1}^{3}\frac{1}{r_{ij}}Q_{123}-\sum_{i=1,2,3}\sum_{\bar{l}\in s}K_{\bar{l}\bar{l}}(i)Q_{123}\Big],\end{aligned} \tag{5.14d}$$

$$\{\alpha l|V^{(3)}|\alpha l'\}=Q_{123}\left(\sum_{\bar{l}\in\alpha}\langle[\bar{l}l']_{12}|\frac{1}{r_{12}}|[\bar{l}l']_{12}\rangle-\sum_{i=1}^{3}K_{l'l}(i)Q_{123}\right),\quad l\neq l', \tag{5.14e}$$

$$\{\alpha l|V^{(3)}|\beta l\}=Q_{123}\langle\beta(12)|1/r_{12}|\alpha(12)\rangle,\quad \alpha\cap\beta=0, \tag{5.14f}$$

$$\{s|V^{(3)}|t\}=0,\quad s\cap t=0, \tag{5.14g}$$

and $\{s|V^{(3)}|t\}$ is defined only when s (and t) refer to distinct spin-orbital triplets, e.g., $s\neq ll l'$.

The bar vertex which couples two particles to three particles introduces the operator $V^{(3,2)}$ where

$$\{ll'l''\,|\,V^{(3,2)}\,|\,ll'\}=Q_{123}\left[\sum_{i>j}^{3}\frac{1}{r_{ij}}-\sum_{i=1}^{3}\sum_{\bar{l}=l,l'}K_{\bar{l}\bar{l}}(i)\right]\frac{(1-P_{13}-P_{23})}{\sqrt{3}}\,|\,l''(3)\rangle Q_{12}\,, \tag{5.15a}$$

$$\{ll'l''\,|\,V^{(3,2)}\,|\,ll'''\}=-Q_{123}\sum_{i=1}^{3}K_{l'''l'}(i)\,\frac{(1-P_{13}-P_{23})}{\sqrt{3}}\,|\,l''(3)\rangle Q_{12},\quad l'''\neq l,l',l'', \tag{5.15b}$$

$$\{ll'l''\,|\,V^{(3,2)}\,|\,l'''l^{iv}\}=0,\quad l''',l^{iv}\neq l,\ l',\ \text{or}\ l''. \tag{5.15c}$$

The correlation energy to all orders in the triple excitations (including the "zeroth-order" energy of Fig. 7 which contains only double excitations) is again obtained by summing a Born series and is

$$\begin{aligned}E_{2\,\mathrm{SE3}}&=\textstyle\sum_\alpha E_{\alpha,\,2\,\mathrm{SE3}}=\sum_\alpha\langle\alpha(12)\,|\,1/r_{12}\,|\,z_\alpha(12)\rangle\\&=\sum_{\alpha,\beta}\langle\alpha(12)\,|\,(1/r_{12})\{\alpha\,|\,G_{\mathrm{SE3}}{}^{(2)}\,|\,\beta\}(1/r_{12})\,|\,\beta(12)\rangle,\end{aligned} \tag{5.16}$$

where $\{\alpha\,|\,(G_{\mathrm{SE3}}{}^{(2)})^{-1}\,|\,\beta\}=\{\alpha\,|\,(G^{(2)})^{-1}-A_3\,|\,\beta\}$, (5.17a)

$$\{\alpha\,|A_3\,|\,\beta\}=\{\alpha\,|\,V^{(2,3)}G^{(3)}V^{(3,2)}\,|\,\beta\}. \tag{5.17b}$$

The new pair correlation correction functions $\{z_\alpha\}$ are the solutions to the equations

$$\textstyle\sum_\beta\{\alpha\,|\,(G_{\mathrm{SE3}}{}^{(2)})^{-1}\,|\,\beta\}z_\beta(12)-Q_{12}(1/r_{12})\,|\,\alpha(12)\rangle=0. \tag{5.18}$$

Equations (5.18) contain the self-energy operator A_3 which contains a sum over three-electron states outside of the HF sea, and represents an effective two-body potential due to virtual excitations of a third electron as a result of its interaction with the pair of correlating electrons. A_3 is thus a polarization potential for the correlating pair of electrons.

In order to "solve" (5.18), we must introduce the three-electron-correlation correction functions $z_s(123)$ by

$$z_s(123)=\textstyle\sum_{t,\beta}\{s\,|\,G^{(3)}\,|\,t\}\{t\,|\,V^{(3,2)}\,|\,\beta\}z_\beta(12), \tag{5.19}$$

giving the coupled linear equations

$$\begin{aligned}&\textstyle\sum_\beta\{\alpha\,|\,(G^{(2)})^{-1}\,|\,\beta\}z_\beta(12)-\sum_s\{\alpha\,|\,V^{(2,3)}|\,s\}z_s(123)-Q_{12}(1/r_{12})\,|\,\alpha(12)\rangle=0,\\&\textstyle\sum_t\{s\,|\,(G^{(3)})^{-1}\,|\,t\}z_t(123)-\sum_\alpha\{s\,|\,V^{(3,2)}|\,\alpha\}z_\alpha(12)=0;\end{aligned} \tag{5.20}$$

and the discussion following (5.12) as to neglect of exclusion effects, variational principle, etc., is also applicable to (5.20). Again, it should be noted that $\{s\,|\,(G^{(3)})^{-1}\,|\,s\}$ is just the $(E^0-H)_{\mathrm{eff}}$ for three particles moving in the field of the remaining electrons, which are in their ground-state HF spin-orbitals.

Since A_3 contains sums over triply excited states (with corresponding energy denominators) while A_1 contains sums over singly excited states, we should qualitatively expect that $|A_3|\lesssim|A_1|$ in terms of their effect on the spectral resolution of $G_{\mathrm{SE}}{}^{(2)}$. The single and triple excitations can both easily be incorporated together with the double excitations (neglecting interactions between the single and triple excitations) by taking

$$E_{\alpha,\,2\,\mathrm{SE}1+3}=\textstyle\sum_\beta\langle\alpha(12)\,|\,(1/r_{12})\{\alpha\,|\,G_{\mathrm{SE}1+3}{}^{(2)}\,|\,\beta\}(1/r_{12})\,|\,\beta(12)\rangle, \tag{5.21a}$$

where $\{\alpha\,|\,(G_{\mathrm{SE}1+3}{}^{(2)})^{-1}\,|\,\beta\}=\{\alpha\,|\,(G^{(2)})^{-1}-A_1-A_3\,|\,\beta\}$. (5.21b)

If we define the corresponding pair functions, they have the two-body self-energy potentials due to virtual excitations and de-excitations of an electron. Introduction of one- and three-particle functions as in (5.11) and (5.19) leads to a set of coupled linear inhomogeneous equations for the one-, two-, and three-particle functions which can be solved variationally in the same manner as the simpler approximations. The pair correlation energies in (5.21a) calculated from the solutions to these equations contain all contributions to the energy through fifth order in ordinary perturbation theory (as well as what we physically expect to be the most important terms in all higher orders of perturbation theory), provided we include the four-electron S-type unlinked cluster contributions to the energy.[41,60,61]

The process of summation of the MBPT diagrams could be continued to give the exact equations for the cluster functions.[34] Although the equations defining the exact pair functions (i.e., the pair functions that appear in the exact ground-state wave function) are not presented here, there is one aspect of these equations which can be anticipated from the discussion already given: these equations must be of the form

$$\textstyle\sum_\beta\{\alpha\,|\,(G^{(2)})^{-1}-A_{\mathrm{exact}}\,|\,\beta\}u_{\mathrm{exact}}{}^{\beta}(12)-Q_{12}(1/r_{12})\,|\,\beta(12)\rangle=0, \tag{5.22}$$

where A_{exact} is a self-energy operator which describes all of the excitations of the system out of the HF sea. Knowledge of the operator A_{exact} implies a knowledge of the exact wave function for the system. However, since a calculation of the true pair-correlation energies requires us only to have the $\{U_{\text{exact}}{}^{\beta}\}$, a reasonable semi-empirical form for A_{exact} would enable the evaluation of the correlation energy from two-electron equations only. Any pair functions obtained with a semiempirical self-energy operator could be put into a cluster-type wave function with S-type unlinked clusters and possibly some extra variational parameters as discussed in Ref. 42 to obtain a rigorous upper bound to the correlation energy for the purpose of comparison. It is hoped that the highly accurate calculations that are now being made on small systems will help to establish the structure of A_{exact} in a manner that would be helpful for semiempirical work. The formal structure of A_{exact} can be obtained from the results of another paper,[33] where the generalization of this work to the case in which the zeroth order wave function is a single determinant of *arbitrary* orthonormal spin-orbitals is also given.

VI. CONCLUSIONS

In using perturbation theory to approach the problem of the description of electron correlation in atoms and molecules, (if we start from a closed-shell HF wave function as the simplest example[32]) contributions to the energy, wave function, and density matrix can be classified according to the order of perturbation theory in which they appear and according to the type of terms they represent. Thus, terms in the perturbation expansion can be separated into contributions from singly, double, triply, $\cdots$ excited configurations, those which do or do not contain exclusion effects,[51] those which do or do not contribute to S-type unlinked clusters, etc. It is hoped that for a particular class of terms the contributions from successive orders of perturbation theory are monotonically decreasing beyond the first or second orders in which they first occur. However, contributions from different classes in the same order of perturbation theory may differ greatly in numerical orders of magnitude.[14] Therefore, in order to bring perturbation theory in line with orders of magnitudes, we could assign order parameters to each of the classes of terms, and take the products of the order of the class with the order of ordinary perturbation theory to arrive at an order parameter for an "order-of-magnitude-oriented form of perturbation theory." In practice, however, it is much more physical to order classes of terms and sum terms of a given class to all orders of ordinary Rayleigh-Schrödinger perturbation theory This type of summation thus is equivalent to a physical model.

MBPT is a convenient tool to use in the investigation of different models. Because of their pictorial nature, diagrams are easily classified, and terms in a particular class are easily found to all orders of perturbation theory. In calculating the correlation energy of Be and the oxygen atom, Kelly found that certain classes of terms were dominant and approximated these terms to all orders of perturbation theory.[14-16] Diagrams in MBPT are evaluated as sums over states using a complete set of HF spin-orbitals as a basis set. In this form it is difficult to compare models in MBPT (i.e., summation of certain classes of terms to all orders of perturbation theory) with models which are expressed in terms of a certain kind of wave function or an approximate Schrödinger equation. However, sums over states can always be related to the solution of differential equations, and the models discussed in this work are those which, within the framework of MBPT, most closely resemble the theories of Kelly, Sinanoğlu, and Nesbet; thereby enabling a comparison between these methods and providing insight into some of the corrections to their models.

A generalized form of perturbation theory in which some of the models presented (e.g., the BG pairs) *naturally form the first approximations* is presented in another paper.[33] In this work the contributions to the correlation energy, wave function, and density matrix of an N-electron wave function, which is initially approximated by a closed-shell HF wave function, are examined in the double-excitation approximation as well as in approximations in which single and triple excitations are also present.

A subset of all the diagrams contributing to the correlation energy are summed to all orders in perturbation theory. This result is shown to be equivalent to that which can be obtained from knowledge of the Bethe-Goldstone (BG) pairs as defined by Sinanoğlu. These BG pairs, which are the solutions to uncoupled *linear* inhomogeneous integrodifferential equations, describe the correlation of a pair of electrons in the field of the remaining electrons which are in their ground-state HF spin-orbitals. Since these BG pairs along with approximate pair correlation energies can be obtained by varying part of the energy of a simple cluster-type wave function, such a variation of part of the energy is equivalent to the summation of certain classes of diagrams in MBPT. When these BG pairs are small, as Sinanoğlu has also noted, they are very similar to Sinanoğlu's "exact pairs" which are the eigenvalue equivalents of the BG pairs. The pairs that Nesbet calls BG pairs are identical to Sinanoğlu's "exact pairs" when the latter are expanded in an orbital basis set and orbital excitations are omitted from the former. Knowledge of the BG pairs would enable the evaluation of the majority of the diagrams calculated by Kelly, including some of the higher-order EPV diagrams which are parts of S-type unlinked clusters.

The mathematical discussion of the coupling between the pairs and between the triple and single excitations leads very naturally to the physical concepts of localized orbitals and "self-energy" or "polarization energy" contributions.

While the equations derived here (as well as the higher-order approximations which are presented in another work[33,34]) could be solved by expansion in a correlated basis set, some workers in the field believe that orbital expansions are more convenient at present. It is obvious that it is impossible to do a complete CI calculation (i.e., exactly solve Nesbet's N-body Bethe-Goldstone equation).

In fact, Nesbet has used secular determinants on the order of 2000 by 2000 in order to calculate what he calls BG pairs. It would be more advantageous to solve a number of smaller problems than to attempt to approach a complete CI calculation (e.g., rather than adding triply excited configurations to those used in Nesbet's BG pairs, we could attempt to solve a smaller problem within the space of the triply excited configurations alone), and then we could correct these simpler problems by some iterative technique. Thus, for instance, we could solve for the "complete pairs" of (4.9a) by first obtaining the simpler BG pairs of (3.15a) and then iterating these results in (4.9a). The matrix that must be inverted to solve (4.9a) directly is roughly $N(N-1)/2$ times the size of the matrix necessary to obtain the BG pairs for a given size of basis set. The single, triple, $\cdots$, excitations can also be approached by iterative techniques.

VII. ADDENDUM

After this work was completed, an interesting article by L. Szasz and J. Byrne[62] appeared and deserves comment with regards to the discussion presented in this paper. Their calculation is for the Be atom where they formulate what we call generalized configuration interaction in Ref. 33. As discussed in Sec. II, the pair functions used by Szasz are orthogonalized to the ground-state HF spin-orbitals in such a manner as to include the single excitation functions in the pairs. They considered only the $(1s)^2$ and $(2s)^2$ pairs in this case. First Szasz and Byrne (SB) varied the energy from each of the pairs independently. With this choice of orthogonalization to the HF ground-state orbitals, the resulting pairs are identical to Nesbet's BG pairs,[37] except that a correlated basis set was chosen by SB. It is interesting to note that SB's results for the correlation energies are identical to those of Nesbet to within 0.001 a.u.; however, SB used only 10 parameters for the $(1s)^2$ correlation energy and 16 parameters for the $(2s)^2$ correlation energy, while Nesbet used on the order of 1000 configurations for each.

What is equally interesting is that, again to 0.001 a.u., the results of Nesbet[31] and SB are identical to those of Geller, Taylor, and Levine (GTL)[11] who calculated the same pair functions, but omitted the orbital excitations (i.e., Sinanoğlu's "exact pairs"). When SB recalculated the correlation energies obtained from the wave functions of GTL with and without the single excitations, the difference in the correlation energy was on the order of 1% of the correlation energy, or on the order of 0.001 a.u. which is in line with Sinanoğlu's discussion of the single excitations for Be.[4] SB point out, however, that their choice of orthogonalization of the pair functions requires the evaluation of fewer integrals.

When SB calculated the total correlation energy (a rigorous upper bound) from a wave function which contained *both* $(1s)^2$ *and* $(2s)^2$ pairs, i.e., when $(1s)^2$-$(2s)^2$ exclusion effects were included, the total correlation energy was *decreased in absolute magnitude* by 0.003 a.u. This is not in conflict with the qualitative expectation in Sec. IV that such exclusion effects should be small for Be.

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APPENDIX A: *S*-TYPE UNLINKED CLUSTERS

There has been some confusion in the literature concerning the properties of *S*-type unlinked clusters[36] (e.g., their contribution to the linked cluster energy of MBPT[36]): Much of this difficulty is due to the semantic problem already discussed.[36] In this appendix we give a brief discussion and criticism of the literature on this subject, and also present a few examples which are sufficient to illustrate the properties of *S*-type unlinked clusters referred to in the main body of the text.

It should be noted, first of all, that the MBPT expansion for the wave function (2.16) can naturally be separated into the *S*-type cluster expansion since the right-hand side of this equation contains some diagrams which are unconnected, but the unconnected parts each have at least two (one particle and one hole) external lines. Since there are diagrams in which these disconnected parts occur with all relative time orderings, the time integrations [cf (2.14) and (2.15)] for each of these unconnected parts can be performed independently. These diagrams therefore contribute to *S*-type unlinked-cluster orbital correlation functions.[18,36] One simple example of this property is the already well-known result[60,61] that the second-order quadruply excited cluster functions can be expressed entirely in terms of first-order pair functions. This result can *immediately* be seen by writing down the wave function diagram for the quadruply excited part of the second-order wave function: This diagram is simply an unconnected diagram containing the vertex in Goldstone's[20] Fig. 10 twice. (The two vertices are at different times and contain no hole or particle indices in common if antisymmetrized vertices are used.[46]) Since this diagram occurs with the two vertices in both relative time orderings, the time integrations factor, and we obtain the above stated results.

Yaris and Musher[63] have had the semantic difficulties discussed in Footnote 36. They essentially show that *S*-type unlinked clusters do contribute to the energy in ordinary Rayleigh-Schrödinger perturbation theory (independent of any form in which this perturbation theory may be expressed), and furthermore they demonstrate what is probably the dominant contribution. For instance, the pair energies $\tilde{\varepsilon}_{kl}$ which appear in Eq. (18) of their paper and are defined in their Eq. (19) contain the denominator $1+\langle ukl|ukl\rangle$. Since we can imagine calculating these pair functions by perturbation theory, Eq. (19) is the ratio of two power series in the perturbation to the HF Hamiltonian. The linked-cluster energy of MBPT written in any of its forms[20,38] is a single power series in the perturbation. Thus, only two possibilities exist, namely, either the denominator in (19) is an *exact factor* of the numerator, or terms of the form $\epsilon_{kl}(-1)^n\langle u_{kl}|u_{kl}\rangle^n$, $n=1, 2, \cdots\infty$, must contribute to the energy, since the denominator must in the latter case be expanded to obtain a single power series in the perturbation. As discussed below, such terms do contribute to the energy in perturbation theory. The case of $n = 1$ above has been verified, and it is reasonable to expect to find that the higher members of this series occur with coefficients $(-1)^n$. This denominator correction is probably the major correction due to S-type unlinked clusters. Provided what we call exclusion effects[51] and the terms in Eqs. (44-48) of Ref. 4 are negligible, Sinanoglu's many-electron theory shows that (because of this energy denominator in the $\mathcal{E}_{kl}$ discussed above) a sum of independent "exact pair" energies is a justifiable approximation which is a better approximation to the true correlation energy than this sum of pair energies divided by some normalization factor (which is always greater than unity).

The existence of S-type unlinked clusters in the fourth- and fifth-order energies of ordinary perturbation theory (or MBPT) follows directly from the $2n+1$ rule of perturbation theory [knowledge of the wave function through nth order enables a calculation of the energy through $(2n+1)$st order] and the above-stated fact that the second-order quadruply-excited cluster functions can be expressed entirely in terms of the first-order pair functions.[60,61] As can easily be seen by writing down the diagrams for the third-order quadruply-excited parts of the wave function (and then invoking the $2n+1$ rule again), four-electron S-type linked clusters begin to contribute to the sixth-order energy where there are also a large number of S-type unlinked clusters. As illustrated below, these S-type unlinked clusters are necessary in order that the four-electron diagrams of the same class as those in the fourth- and fifth-order energies can be summed to infinite order to replace the first-order pairs in the fourth- and fifth-order energy expressions by BG (or better) perturbative correction pairs. Thus, it is not too surprising that in variationally determined wave functions (i.e., those determined on the basis of energetics) for closed-shell systems, Sinanoğlu found primarily S-type unlinked clusters like $u_{ij}u_{kl}$ as opposed to the linked terms.

We should note that the higher-order EPV diagrams of Kelly[14] represent contributions of S-type unlinked clusters. The two EPV diagrams $Y1$ and $Y2$ of Ref. 14, which have the values given by Eqs. (3.6) and (3.8) of that reference, *when added together* have the value (in Kelly's notation)

$$
\begin{aligned}
Y1+Y2 &= \sum_{kk'k''k'''} \frac{1}{D(k,k')}\langle pq|v|kk'\rangle \\
&\quad\times\langle k''k'''|v|pq\rangle\langle kk'|v|pq\rangle/D^2(k'',k''') \\
&= E_2(p,q)\sum_{k'',k'''}\langle k''k'''|v|pq\rangle/D^2(k'',k''').
\end{aligned}
$$

Although these terms give contributions from S-type unlinked clusters, it is important to note that both diagrams $Y1$ and $Y2$ are each connected diagrams [when obtained from the contractions of our Eq. (2.17)], i.e., they give contributions to the MBPT linked-cluster energy.[36] The S-type unlinked contributions which result from the sum of $Y1$ and $Y2$ cannot be written as a single unconnected diagram.

Brenig used wave-function arguments to derive the same results for the nuclear many-body problem as obtained by diagram summations.[29] Brenig's principle assumption is the use of S-type unlinked clusters to decompose the three- and four-particle orbital-correlation functions. The need for such an assumption should not be too surprising when it is realized that the diagrams which represent energy contributions from S-type unlinked clusters are just those diagrams which in nuclear many-body theory are necessary in order that the reaction matrix be evaluated on the energy shell. After completion of this work, the review article by Day[64] appeared, and the discussion in this review is now used to illustrate this connection. In Day's Fig. 27, for the sake of greater generality, let the upper m (later time) be l' and the lower m (earlier time) be n' in 27(a), while in 27(b) let the upper m be n' and the lower be l'. In the notation of Sec. III of this paper, *the sum* of Day's Fig. 27(a) and Fig. 27(b) (with the above relabeling and antisymmetrized vertices[46]) has the value

$$
\begin{aligned}
&-\sum_{ll'nn'}\langle U_{ll'}{}^{(1)}|U_{ln'}{}^{(1)}\rangle \\
&\qquad\times\langle U_{nn'}{}^{(1)}(12)|1/r_{12}|[nl']_{12}\rangle
\end{aligned}
$$

when we sum over all particle indices. Thus, this represents a fourth-order energy contribution from quadruple excitations which is solely expressible in terms of first-order pairs. These diagrams can be generalized to infinite order to replace the first-order pairs $U_{ll'}{}^{(1)}$ by BG pairs $U_{ll'}$ (or even better pairs) by introducing infinite-order bar vertices into Day's relabeled Fig. 27 in the following manner:

Let t_1 denote the time of the earliest vertex (lowest one) in Day's Fig. 27(a), and t_2, t_3, t_4 label the other three vertices such that $t_4>t_3>t_2>t_1$. In this figure place an infinite-order bar vertex between the lines $ln'ab$ at a time between t_2 and t_1; the second infinite-order bar vertex is placed across $nn'cd$ between t_3 and t_2; the third bar vertex crosses the lines $ll'ab$ between t_3 and t_2, but is understood to be comprised of diagrams which have their vertices in all possible time orderings with respect to those of the second infinite-order bar vertex; and the last bar vertex is placed across $ll'ab$ between t_4 and t_3. In Day's Fig. 27(b) we again denote the vertices by times $t_4>t_3>t_2>t_1$, and between t_2 and t_1 place an infinite-order bar vertex across $nn'cd$; between t_3 and t_2 place two, one across $ll'ab$ and another across $nn'cd$, with all relative time orderings; and the last infinite-order bar vertex between t_4 and t_3 across $ln'ab$. If we sum over all intermediate particle indices and take all the vertices to be antisymmetrized,[46] the above stated results follow simply.

Day's Fig. 32(b), if interpreted in terms of antisymmetrized vertices, along with the diagram obtained from this one by interchanging the times of the first and second vertices, when added together give

$$\sum_{m>l,k>n} \langle U_{ml}{}^{(1)} | 1/r_{12} | [kn]_{12} \rangle \times \langle U_{kn}{}^{(1)} | U_{ml}{}^{(1)} \rangle$$

when summed over particle indices.

This result can be similarly generalized to infinite order by the use of bar vertices to replace the first-order pairs by BG (or better) pairs.

These two sets of diagrams, when restricted to the case of only two excited holes, sum to give the coefficient stated above for the $n=1$ term in the expansion of the denominator of $\mathcal{E}_{kl}$ of Yaris and Musher.

Similarly, it is not difficult to draw diagrams in which there are 6, 8, $\cdots$, $2n$, where $n\to\infty$, excited electrons (remember that the final diagrams correspond to a field in which the number of particles is arbitrary) that modify the pair correlation energies by the addition of terms

$$\sum_{n=3}^{\infty} C_n \langle \alpha | 1/r_{12} | w_\alpha \rangle \langle w_\alpha | w_\alpha \rangle^{n-1},$$

where the C_n are integers $(0, \pm 1, \cdots)$. As discussed above, it is reasonable to guess that these terms sum (along with the diagrams in which two and four electrons are excited) to give a total pair-correlation energy of

$$\langle \alpha | 1/r_{12} | w_\alpha \rangle / [1 + \langle w_\alpha | w_\alpha \rangle].$$

There is also a set of exchange S-type unlinked terms (obtained from diagrams analogous to Day's Figs. 27 and 32(b) if hole and particle are interchanged) which have values of the form

$$C_n{}' \langle \alpha(12) w_\alpha(34) | 1/r_{12} | w_\alpha(13) w_\alpha(24) \rangle \times \langle w_\alpha | w_\alpha \rangle^n,$$

where $n = 0, 1, \cdots, \infty$ and the $C_n{}'$ are also integers. These two types of S-type unlinked clusters demonstrate that perturbation theory is meaningless unless $\langle w_\alpha | w_\alpha \rangle \ll 1$. In that case, $\nu[w]^{-2}$ in (4.12b) is ≈ 1 and evaluating the correlation energies by $\langle \alpha | 1/r_{12} | w_\alpha \rangle$ divided by 1, $\nu[w]^{-2}$ or $1 + \langle w_\alpha | w_\alpha \rangle$ etc. makes little real difference (see Sec. VII). In the above equations w_α could be taken to be first-order, BG, "complete," etc. pairs.

APPENDIX B

Figure 2(a) contains an extra particle-particle interaction and has the value

$$E(2a) = (-1)^{2+2} \sum_{l>l', m>m', m''>m'''} \frac{\langle ll' | (1-P_{12})/r_{12} | m''m''' \rangle \langle m''m''' | (1-P_{12})/r_{12} | mm' \rangle}{(\epsilon_{ll'} - \epsilon_{m''m'''})(\epsilon_{ll'} - \epsilon_{mm'})} \times \langle mm' | (1-P_{12})/r_{12} | ll' \rangle, \tag{B.1}$$

where $|ll'\rangle \equiv |l(1)l'(2)\rangle$, etc. Since, as in (3.2) and (3.3a), when antisymmetry is included,

$$\sum_{m>m'} \frac{|mm'\rangle\langle mm'|}{\epsilon_{ll'} - \epsilon_{mm'}} = \tfrac{1}{2} \frac{Q_{12}}{\epsilon_{ll'} - H_0(12)}, \tag{B.2}$$

using $\mathcal{A}_{12} = (1-P_{12})/2$ (B.1) becomes

$$2 \sum_{l>l'} \langle ll' | \frac{1}{r_{12}} \mathcal{A}_{12} \frac{Q_{12}}{[\epsilon_{ll'} - H_0(12)]} \frac{1}{r_{12}} \mathcal{A}_{12} \frac{Q_{12}}{[\epsilon_{ll'} - H_0(12)]} \frac{1}{r_{12}} \mathcal{A}_{12} | ll' \rangle. \tag{B.3}$$

Since $\mathcal{A}_{12}{}^2 = \mathcal{A}_{12}$; $\mathcal{A}_{12}(1/r_{12}) = (1/r_{12})\mathcal{A}_{12}$, $\mathcal{A}_{12} Q_{12} = Q_{12} \mathcal{A}_{12}$,

$$\sqrt{2} \langle ll' | \mathcal{A}_{12} = \langle [ll']_{12} |, \tag{B.4}$$

$$E(2a) = \sum_{l>l'} \langle [ll']_{12} | \frac{1}{r_{12}} \frac{Q_{12}}{[\epsilon_{ll'} - H_0(12)]} \frac{1}{r_{12}} \frac{Q_{12}}{[\epsilon_{ll'} - H_0(12)]} \frac{1}{r_{12}} | [ll']_{12} \rangle. \tag{B.5}$$

The diagonal-hole diagram of the form of Fig. 2(b) has the value

$$\begin{aligned} E(2b)_{\mathrm{dh}} &= (-1)^{4+2} \sum_{l>l', m>m'} \frac{\langle ll' | (1-P_{12})/r_{12} | mm' \rangle \langle ll' | (1-P_{12})/r_{12} | ll' \rangle \langle mm' | (1-P_{12})/r_{12} | ll' \rangle}{(\epsilon_{ll'} - \epsilon_{mm'})^2} \\ &= 2 \sum_{l>l'} \langle ll' | \frac{1-P_{12}}{r_{12}} | ll' \rangle \langle ll' | \frac{1}{r_{12}} \mathcal{A}_{12} \frac{Q_{12}}{[\epsilon_{ll'} - H_0(12)]^2} \frac{1}{r_{12}} \mathcal{A}_{12} | ll' \rangle \\ &= \sum_{l>l'} \langle [ll']_{12} | \frac{1}{r_{12}} \frac{Q_{12}}{[\epsilon_{ll'} - H_0(12)]} \langle [ll']_{12} | 1/r_{12} | [ll']_{12} \rangle \frac{Q_{12}}{[\epsilon_{ll'} - H_0(12)]} \frac{1}{r_{12}} | [ll']_{12} \rangle \end{aligned} \tag{B.6}$$

by just repeating the steps used in going from (B.1) to (B.5).

The diagonal-hole forms of Figs. 2(c) and (d) and the mirror-image diagrams of both of these add to give

$$E(2c,d)_{\rm dh} = (-1)^{3+2} \sum_{l \neq l';\, m \neq m',\, m'''} \frac{\langle ll' \,|\, (1-P_{12})/r_{12} \,|\, mm''' \rangle \langle l'm''' \,|\, (1-P_{12})/r_{12} \,|\, l'm' \rangle}{(\epsilon_{ll'} - \epsilon_{mm'''})(\epsilon_{ll'} - \epsilon_{mm'})} \times \langle mm' \,|\, (1-P_{12})/r_{12} \,|\, ll' \rangle. \tag{B.7}$$

Since the terms for which $m = m'$ or m''' vanish because the Coulomb and exchange integrals are identical, using the definition of $K_{l'l'}(2)$ in (3.7) and a sum rule like (B.2), the right-hand side of (B.7) becomes

$$-\sum_{l \neq l'} \langle ll' \,|\, \frac{(1-P_{12})}{r_{12}} \, \frac{Q_{12}}{[\epsilon_{ll'} - H_0(12)]} K_{l'l'}(2) \frac{Q_{12}}{[\epsilon_{ll'} - H_0(12)]} \, \frac{(1-P_{12})}{r_{12}} \,|\, ll' \rangle. \tag{B.8}$$

Taking $\frac{1}{2}$ of the sum of (B.8) and the equation obtained from (B.8) by interchanging the dummy variables 1 and 2, breaking up the summation into parts for which $l > l'$ and $l' > l$, and using the properties of $\mathcal{Q}_{12}$, we have finally

$$E(2c,d)_{\rm dh} = \sum_{l > l'} \langle [ll']_{12} \,|\, \frac{1}{r_{12}} \, \frac{Q_{12}}{[\epsilon_{ll'} - H_0(12)]} \times (-K_{ll} - K_{l'l'}) \{ Q_{12} / [\epsilon_{ll'} - H_0(12)] \} (1/r_{12}) \,|\, [ll']_{12} \rangle. \tag{B.9}$$

Comparing the sum of (B.5), (B.6), and (B.9) with (3.9a) gives the definition of $V_{ll'}(12)$ in (3.8). The potential $\{\alpha \,|\, V^{(2)} \,|\, \beta\}$ for $\alpha \neq \beta$ as given in (4.4d) can be found from the nondiagonal-hole third-order energy diagrams in an analogous fashion.

We could have also identified the $V_{ll'}(12)$ in (3.8) from the diagonal-hole part of the third-order energy written in the conventional form of Rayleigh-Schrödinger perturbation theory

$$E_{\rm dh}^{(3)} = \sum_{l > l',\, m > m',\, m'' > m'''} \frac{\langle \Phi_0 \,|\, H_1 \,|\, \Phi_{ll';\, m''m'''} \rangle \langle \Phi_{ll';\, m''m'''} \,|\, H_1 \,|\, \Phi_{ll';\, mm'} \rangle}{(\epsilon_{ll'} - \epsilon_{m''m'''})(\epsilon_{ll'} - \epsilon_{mm'})} \langle \Phi_{ll';\, mm'} \,|\, H_1 \,|\, \Phi_0 \rangle - \sum_{l > l',\, m > m'} \frac{|\langle \Phi_0 \,|\, H_1 \,|\, \Phi_{ll';\, mm'} \rangle|^2}{(\epsilon_{ll'} - \epsilon_{mm'})^2} \langle \Phi_0 \,|\, H_1 \,|\, \Phi_0 \rangle, \tag{B.10}$$

where Φ_0, $\Phi_{ll';\, mm'}$, and H_1 are defined in (2.7), (2.11b), and (2.5) respectively. The terms in (B.10) must be rearranged considerably to demonstrate their equality with the diagrammatic results since the second term in (B.10) cancels out part of the first term and only the EPV part of this second term remains.[14]

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[29] There exists an extensive body of literature on the application of MBPT to the nuclear many-body problem (NMBP). Many of the relevant references are quoted by Kelly (Refs 14-18) and need not be repeated here. Because of the singular nature of the short-range nucleon-nucleon interaction as opposed to the soft, long-range Coulombic interaction between electrons in atoms and because of the loss of the symmetries of an infinite system (in the NMBP) when dealing with electrons in finite systems, the methods for treating the NMBP (notably the use of reaction matrices) differ considerably and may be of no use in the techniques used in the electron correlation problem (see Ref. 35). However, W. Brenig, Nucl. Phys. 4, 363 (1957) attacks the NMBP in a form which

appears to resemble theories of electron correlation: Brenig first shows that the cluster-type wave functions for the NMBP satisfy an infinite hierarchy of equations in much the same manner as one obtains the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy in statistical mechanics. Kelly has discussed the *analogous* hierarchy for atomic systems (Refs. 17 and 18) where the cluster functions are expanded in a complete set of orbitals. In order to truncate these equations, Brenig approximates the higher (three- and four-particle) clusters in terms of what Sinanoğlu (Refs. 4 and 5) has called "unlinked clusters" (Ref. 36). (See Appendix A.) [Kelly makes a similar approximation (Ref. 18).] After a few more approximations, which are often used in the NMBP, Brenig obtains the same BG equations of nuclear theory that are obtained by a diagrammatic analysis.

The hierarchy (finite) of equations appropriate for atomic systems is presented in another work. *In this paper we derive approximations to this atomic hierarchy by using MBPT in order that approximations made with the cluster-type wave functions (i.e., from the hierarchy) can be directly related to approximations made in terms of diagrams.*

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[37] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

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[42] Since the $\{\tilde{U}_{ll'}\}$ obtained from a variation of part of the energy expression using ψ_{CL} of (2.10c) are not the pair functions which necessarily minimize the energy, the further approximation in (2.19c) can only be improved by introducing free variational parameters $\{a_{ll'}, a_{ll'l''l'''}, \cdots\}$ as constant multipliers of $\{\tilde{U}_{ll'}, \tilde{U}_{ll'l''l'''}, \cdots\}$ in (2.10b), where $\{a_l \cdots\}$ are to be determined from the variational principle. They should be close to unity (as Sinanoğlu showed they are in approximate CI calculations for Be and LiH[4]) when, for localized electrons, the $\{\tilde{U}_{ll'}\}$ are close to optimum values and terms like (2.19c) are the (energetically) dominant contributions to the wave functions (Ref. 41).

[43] Provided the evaluation of integrals can be done more efficiently. See Ref. 11 for a comment on this matter.

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[46] The use of antisymmetrized vertices is equivalent to replacing the first term in (2.13b) by $\sum_{r>s,\, m>n} [\langle rs|v|mn\rangle - \langle rs|v|nm\rangle] \eta_r^\dagger \eta_s^\dagger \eta_n \eta_m$. (2.13c) This replacement greatly reduces the number of different diagrams, provided the excited spin-orbitals are considered ordered in some manner. Contractions and diagrams are then formed in the usual manner. Many of these contractions will now be zero, and the nonzero diagrams obtained may be exchanges of each other. However, because of the antisymmetry of the matrix elements, the exchanges may all be "transformed" to the form chosen as the "direct diagram." The use of (2.13c) simplifies the counting problem when dealing with the four-, six-, $\cdots$ body S-type unlinked clusters.

[47] For the sake of mathematical rigor, the operator in (3.1b) should be written as $Q_{12}\{\alpha(1-Q_{12}) + Q_{12}[\epsilon_{ll'} - H_0(12)]\}^{-1} Q_{12}$, where $\alpha \neq 0$. This is unnecessary if we consider all two-particle operators and their inverses containing Q_{12} to be defined within the space spanned by Q_{12} and to be zero elsewhere.

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[49] No discussion of convergence of the Born series is presented. We could have written the electron repulsion as λ / r_{12} where λ is a complex variable which finally is given the value unity. Then (3.12a) and (3.13a) are equivalent by analytic continuation. Actually, as is shown in Ref. 33, the use of (3.13a) corresponds to beginning perturbation theory from a new starting point.

[50] In the light of this relationship, the similarity of the results of Kelly (Refs. 14 and 15) with those obtained by Geller *et al/* (Ref. 11) [a calculation of the $(1s)^2$ and $(2s)^2$ "exact pairs" for Be] is not too surprising.

[51] The term "exclusion effects" is used in many contexts in Refs. 4-7, including the strong orthogonality of the cluster functions to the ground-state HF spin-orbitals. Here we use the term exclusion effects only to denote the effect of the Pauli exclusion principle on the space left behind by electrons which have been excited from the "HF sea" due to correlation.

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Generalized Perturbation Theory and its Application to the Problem of the Description of Electron Correlation in Atoms and Molecules*

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For the case in which the zeroth-order wave function is a single Slater determinant of arbitrary orthonormal spin-orbitals, the exact wave function can be expressed in terms of a cluster-type expansion. If perturbation theory is applied in the standard (and systematic) fashion to the Schrödinger equation for the cluster functions, a generalized form of Rayleigh-Schrödinger perturbation theory (GPT) is obtained. Although GPT is quite flexible, the form presented in this work is chosen so that the terms initially calculated in GPT correspond as closely as possible to the starting points in the theories of Sinanoğlu, Kelly, Conkie, Nesbet, and others.

The first-order corrections to the wave function in GPT are written in terms of one- and two-electron functions which respectively describe the perturbative corrections for the motion of one and two electrons in the field of the remaining electrons which are in their ground-state orbitals (i.e., perturbative Bethe-Goldstone-like equations). This is a more physical starting point than the first-order wave function of ordinary Rayleigh-Schrödinger perturbation theory (OPT), and GPT should be much more rapidly convergent than OPT.

By analogy with OPT, GPT also has a $2n+1$ rule, a variational principle for the nth-order energy and the 2^nth-order wave function, and interchange theorems of double-perturbation theory. As in OPT, the equations of GPT can be solved by the use of correlated functions; however, in GPT, H_0 is not required, and the zeroth-order spin-orbitals need not all be eigenfunctions of the same one-electron Hamiltonian.

I. INTRODUCTION

The theories for the description of electron correlation in atoms and molecules of Sinanoğlu, Szász, Nesbet, and others begin with approximate Schrödinger equations (in different forms) describing the stationary states of a pair of electrons which are moving in the field of the remaining electrons which are in their ground-state orbitals.[1-10] Although the results presented in this work are valid for the case in which the zeroth-order wave function is a single Slater determinant of arbitrary orthonormal spin-orbitals, the discussion in the first three sections is limited to the simplest case of a closed-shell Hartree-Fock (HF) zeroth-order wave function.

When approaching the problem of electron correlation by ordinary Rayleigh-Schrödinger perturbation theory, the first-order corrections to the wave function are written in terms of first-order pairs. If $\{l_i \mid i=1,\cdots,N\}$ denote the occupied spin-orbitals in the zeroth-order HF wave function,[11]

$$Q_1=\hat{1}(1)-\textstyle\sum_{l\text{occpd}}\lvert(1)\rangle\langle l(1)\rvert, \tag{1.1a}$$

$$Q_{12}=Q_1Q_2=Q_2Q_1, \tag{1.1b}$$

$$\lvert[ll']_{12}\rangle=2^{-1/2}(1-P_{12})\lvert l(1)l'(2)\rangle, \tag{1.1c}$$

where P_{12} is the operator which permutes the space and spin variables of particles one and two, then the first-order pairs $u_{ll'}{}^{(1)}(12)$ are the solutions to the uncoupled *linear* inhomogeneous integrodifferential equations,

$$Q_{12}[\epsilon_{ll'}-H_0(12)]u_{ll'}{}^{(1)}(12) \\ -Q_{12}(1/r_{12})\lvert[ll']_{12}\rangle=0, \tag{1.2}$$

where $H_0(i)$ is the HF Hamiltonian for particle i, $H_0(12)=H_0(1)+H_0(2)$, $\epsilon_{ll'}=\epsilon_l+\epsilon_{l'}$ is a sum of HF orbital energies via

$$H_0(i)l_k(i)=\epsilon_k l_k(i), \tag{1.3a}$$

and Q_{12} is a projection operator which makes any pair function strongly orthogonal to the HF orbitals which are occupied in the zeroth-order wave function, i.e.,

$$\int d(1)l_k(1)Q_{12}f(12)=0 \tag{1.3b}$$

for all $k\leqslant N$ and $f(12)$ arbitrary.

From the homogeneous part of Eq. (1.2), we see that the pairs see the full HF Hamiltonian, and the inhomogeneity (or "forcing" term) is the product of the perturbation to the HF Hamiltonian and zeroth-order occupied spin-orbitals. This Eq. is, howev-