

# Many-Electron Theory of Nonclosed-Shell Atoms and Molecules. I. Orbital Wavefunction and Perturbation Theory\*

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A theory of electron correlation in nonclosed-shell states, such as excited states of atoms and molecules, triplet states, free radicals, and transient species, is developed. A general (multiconfiguration) restricted Hartree-Fock (GRHF) wavefunction is taken as the starting point. When near degeneracies are not strong enough to cause large orbital and charge deformations, Roothaan-type restricted Hartree-Fock (RHF) open-shell orbital theories are used. The first-order Schrödinger equation with RHF as the zeroth-order wavefunction is solved. Various correlation processes (near-degeneracy-type internal correlations, semi-internal pair correlations in which only one electron is ejected out of the Hartree-Fock sea, external pair correlations as in closed shells, and spin and symmetry orbital average polarization effects) are obtained in a form separated from one another. The second-order energy also includes "cross-pair correlation effects," an open-shell phenomenon that need be taken into account in the evaluation of electronic spectral levels and stability of open-shell systems. The first-order solution yields the main open-shell correlation processes, which are generalized to the variational theory in II with means for evaluation of the separate effects.

## I. INTRODUCTION

A PREVIOUS series of papers<sup>1-6</sup> was concerned with the calculation of the many-electron wavefunction and energy of an atom or molecule, including correlation effects, to within chemical accuracy ( $\sim 0.1$  eV). The theory was developed primarily for closed-shell states, i.e., states for which the orbital approximation is a single (normalized) Slater determinant  $\phi_0$  not degenerate with any other. The closed-shell many-electron theory can be applied to a few nonclosed-shell states as well,<sup>5</sup> namely single determinantal ones (<sup>3</sup>P-C, <sup>4</sup>S-N, etc.), if certain "orbital average polarization" effects are neglected.

The treatment of electronic spectra, of interatomic potential-energy curves and surfaces, and of the properties of radicals, triplets, and transient species requires a theory applicable to a general open-shell state. (The terms "open shell" and "nonclosed shell" are used here synonymously.)

The closed-shell theory cannot be applied to open-shell states without modification for two reasons: (1) There are important correlation effects in open-shell states not present in closed-shell states, and (2) difficulties arise as to which orbitals the correlation functions must be orthogonal to, when the orbitals are only partially occupied in the open-shell orbital approximation  $\phi_0$ . In the present two papers (I and II)

we give a many-electron theory<sup>7</sup> applicable to a general open-shell state.

The approach used allows—as in the closed-shell case—the separate evaluation of parts of an atom or molecule providing the "environmental" effects of other electrons on a given part.<sup>4-6</sup> It is also suitable for semiempiricism. Nonempirically, the parts may be calculated by various methods including two-electron ones like the use of " $r_{12}$  coordinates."<sup>4,5</sup>

In Paper I, taking a suitably selected open-shell-orbital wavefunction as zeroth order, we derive the wavefunction (wf) to first order of perturbation theory. This solution indicates and separates the physically important correlation effects in the wavefunction and energy of the open-shell many-electron system. In Paper II, the results are extended to make the first-order (wf) processes "exact to all orders," to include unlinked clusters, and to obtain the complete form of the energy as an upper bound. New features of correlation that arise in open shells absent in closed shells, nonempirical evaluations, semiempirical implications of the form of the energy and some examples (e.g., <sup>2</sup>S-Li, <sup>1</sup>S-C and C<sub>2</sub>H<sub>4</sub><sup>+</sup>) are also discussed in Paper II.

## II. MATHEMATICAL FORM OF THE EXACT WAVEFUNCTION

The first step in calculating an  $N$ -electron wavefunction  $\psi$  is to determine an orbital approximation  $\phi_0$ . For open-shell states, the general  $\phi_0$  is a linear combination of (normalized)  $N$ -electron Slater determinants  $\Delta_K$ :

$$\Delta_K = \alpha [k_1(\mathbf{x}_1) k_2(\mathbf{x}_2) \cdots k_N(\mathbf{x}_N)] \quad (1)$$

$$\equiv \alpha (k_1 k_2 \cdots k_N). \quad (2)$$

<sup>7</sup> H. J. Silverstone and O. Sinanoğlu, "Many-Electron Theory of Nonclosed-Shell Atoms and Molecules. II. Variational Theory," *J. Chem. Phys.* (to be published); for a qualitative description, see H. J. Silverstone and O. Sinanoğlu, in *Modern Quantum Chemistry—Istanbul Lectures* (Academic Press Inc., New York, to be published).

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<sup>1</sup> O. Sinanoğlu, *J. Chem. Phys.* **36**, 706 (1962).

<sup>2</sup> O. Sinanoğlu, *J. Chem. Phys.* **36**, 3198 (1962).

<sup>3</sup> O. Sinanoğlu and D. F. Tuan, *J. Chem. Phys.* **38**, 1740 (1963).

<sup>4</sup> D. F. Tuan and O. Sinanoğlu, *J. Chem. Phys.* **41**, 2677 (1964).

<sup>5</sup> V. McKoy and O. Sinanoğlu, *J. Chem. Phys.* **41**, 2689 (1964).

<sup>6</sup> O. Sinanoğlu, *Advan. Chem. Phys.* **6**, 315 (1964).

$\mathcal{A}$  is the antisymmetrization operator,

$$\mathcal{A} = \sum_P (-1)^P P.$$

The  $N$  spin orbitals in  $\Delta_K$ ,  $[k_1, k_2, \dots, k_N]$  are chosen from a set of  $M$  spin orbitals  $[1(\mathbf{x}), 2(\mathbf{x}), \dots, M(\mathbf{x})]$ , so that there are in general  $\binom{M}{N}$  Slater determinants which may contribute to  $\phi_0$  (although in actuality, many of the coefficients  $C_K$  are zero for reasons of symmetry);

$$\phi_0 = \sum_{K=1}^{\binom{M}{N}} C_K \Delta_K. \quad (3)$$

The question of how the spin orbitals should be chosen [e.g., Hartree-Fock (HF) or Slater-type orbitals, etc.] is taken up in the next section; in this section they may be regarded as chosen in a completely arbitrary manner.

The difference  $\chi$  between the exact wavefunction and the orbital approximation  $\phi_0$  is called the correlation part of the wavefunction.  $\chi$  is unambiguously defined by

$$\chi = \psi - \phi_0, \quad (4)$$

$$\langle \phi_0, \phi_0 \rangle = 1, \quad (5)$$

$$\langle \phi_0, \chi \rangle = 0. \quad (6)$$

It is convenient to separate  $\chi$  into two parts,  $\chi_{\text{int}}$  and  $\chi_{\text{ext}}$ :

$$\chi = \chi_{\text{int}} + \chi_{\text{ext}}, \quad (7)$$

where

$$\langle \chi_{\text{int}}, \chi_{\text{ext}} \rangle = 0. \quad (8)$$

The internal correlation part of  $\chi$ ,  $\chi_{\text{int}}$ , is that part of  $\chi$  which can be expressed as a linear combination of the  $\binom{M}{N}$  Slater determinants  $\Delta_K$ ;

$$\chi_{\text{int}} = \sum_{K=1}^{\binom{M}{N}} d_K \Delta_K. \quad (9)$$

$\chi_{\text{int}}$  is orthogonal to  $\phi_0$ ;

$$\langle \phi_0, \chi_{\text{int}} \rangle = 0 \quad (10)$$

$$= \sum_{K=1}^{\binom{M}{N}} C_K^* d_K. \quad (11)$$

The external correlation  $\chi_{\text{ext}}$ , is the rest of  $\chi$ . In configuration-interaction (CI) language, the configurations which contribute to  $\chi_{\text{ext}}$  (by definition) are those which involve one or more spin orbitals outside of (external to) the set of  $M$  spin orbitals.

The exact  $\chi_{\text{ext}}$  can be written (see Appendix A; cf. Ref. 8) as a sum of terms, each of which has a certain number of electrons,  $N-n$ , in  $N-n$  of the  $M$  spin orbitals  $[k_1, k_2, \dots, k_{N-n}]$  and  $n$  electrons in a correlation function  $\hat{U}'_{(n)K_{N-n}}$ ;

$$\chi_{\text{ext}} = \sum_{n=1}^N \left\{ \sum_{K_{N-n}=1}^{\binom{M}{N-n}} \mathcal{A}[k_1(\mathbf{x}_1)k_2(\mathbf{x}_2)\dots k_{N-n}(\mathbf{x}_{N-n}) (n!)^{-\frac{1}{2}} \hat{U}'_{(n)K_{N-n}}(\mathbf{x}_{N-n+1}, \dots, \mathbf{x}_N)] \right\} \quad (12)$$

$$= \sum_{n=1}^N \left\{ \sum_{K_{N-n}=1}^{\binom{M}{N-n}} \mathcal{A}[k_1k_2\dots k_{N-n}(n!)^{-\frac{1}{2}} \hat{U}'_{(n)K_{N-n}}] \right\}. \quad (13)$$

The  $n$ -electron correlation functions  $\hat{U}'_{(n)K_{N-n}}$  are completely antisymmetric and they are one-electron orthogonal to all  $M$  spin orbitals in the set associated with  $\phi_0$ ;

$$U'_{(n)K_{N-n}}(\mathbf{x}_{N-n+1}, \mathbf{x}_{N-n+2}, \dots) = -\hat{U}'_{(n)K_{N-n}}(\mathbf{x}_{N-n+2}, \mathbf{x}_{N-n+1}, \dots), \text{ etc.}, \quad (14)$$

$$\langle l, \hat{U}'_{(n)K_{N-n}} \rangle = \int l^*(\mathbf{x}_a) U'_{(n)K_{N-n}} dV_{\mathbf{x}_a} = 0$$

$$(l=1, 2, \dots, M; a=N-n+1, N-n+2, \dots, N). \quad (15)$$

In CI language, Eq. (15) is the statement that  $U'_{(n)}$  is made up of  $n$ -electron configurations in which none of the spin orbitals are in the set  $M$ . ("Set  $M$ "  $\equiv$  the spin orbitals  $1, 2, \dots, M$ .) The  $(n!)^{-\frac{1}{2}}$  in Eqs. (12) and (13) is a normalization convention, the subscript  $(n)$  indicates the number of electrons of which  $U'_{(n)K_{N-n}}$  is a function, the caret ( $\wedge$ ) denotes the one-electron orthogonality [Eq. (15)], and the prime ( $'$ ) relates to unlinked clusters,<sup>6</sup> which will be discussed in Paper II. In Eqs. (1), (2), (12), and (13) the spin orbitals

(denoted by  $K_{N-n}$ ) appear in strictly ascending order:  $k_1 < k_2 < \dots < k_{N-n}$ . [There are  $\binom{M}{N-n}$  different combinations of  $N-n$  spin orbitals.]

Equations (7), (9), and (13) combined, give the exact  $\chi$  in orbital-correlation-function language:

$$\chi = \sum_{K=1}^{\binom{M}{N}} d_K \Delta_K + \sum_{n=1}^N \sum_{K_{N-n}=1}^{\binom{M}{N-n}} \mathcal{A}\{k_1k_2\dots k_{N-n} \hat{U}'_{(n)K_{N-n}}\}. \quad (16)$$

<sup>6</sup> O. Sinanoğlu, Rev. Mod. Phys. **35**, 517 (1963).

Equation (16) is an identity. Once the set  $M$  and  $\phi_0$  are specified, the decomposition (16) is unique. If one had the exact wavefunction  $\psi$ , the coefficients  $d_K$  and the correlation functions  $\hat{U}'_{(n)K_{N-n}}$  could be determined by the method of successive partial orthogonalizations, as in the closed-shell theory.<sup>6,8</sup> (This is shown in Appendix A.) On the other hand, if  $\chi$  is not known, we may calculate  $\chi$  (exactly or approximately) by calculating  $d_K$ ,  $\hat{U}'_{(1)K_{N-1}}$ ,  $\hat{U}'_{(2)K_{N-2}}$ , etc. (e.g., by perturbation theory, the variation-perturbation method,<sup>6</sup> etc., see Sec. IV).

Compare now  $\chi$ , Eq. (16), with the exact  $\chi$  of the closed-shell theory [Ref. 1, Eq. (23)]. Since the closed shell  $\phi_0$  is a single determinant [ $M=N$  for closed-shell states, and  $(\frac{M}{N})=1$ ], there is no internal correlation. Hence  $\chi_{\text{int}}$  has no closed-shell counterpart. If one calls the collection of spin orbitals  $\{l | l=1, 2, \dots, M\}$  the "spin-orbital sea," then  $\chi_{\text{int}}$  has no electrons outside of the sea. The closed-shell sea is filled, but the open-shell sea is only partially filled. The closed-shell  $n$ -electron correlation functions<sup>1</sup>  $\hat{U}'_{i_1, i_2, \dots, i_n}$  represent "collisions" (correlations) of the  $n$  electrons originally in spin orbitals  $i_1, i_2, \dots, i_n$ . By analogy,  $n$ -electron open-shell correlation functions  $\hat{U}'_{(n)K_{N-n}}$  can represent correlations of  $n$  electrons. However, there may be more than one determinant in  $\phi_0$  in which the  $(N-n)$  spin orbitals  $K_{N-n}$  occur, so that  $\hat{U}'_{(n)K_{N-n}}$  cannot (in general) be associated with a single set of  $n$  spin orbitals occupied in  $\phi_0$ . Thus the  $\hat{U}'_{(n)K_{N-n}}$  must be composite correlation functions.

In the closed-shell case, the exact  $\chi$  leads to the detailed variational form of the exact  $E$ . Then by the variation-perturbation approach<sup>6</sup> large portions of this are minimized to get the approximate  $\chi'_s$  and  $E'_s$  of the many-electron theory. For open shells the form of the exact  $\chi$  obtained above is not sufficiently detailed into physically meaningful processes and therefore does not indicate the parts to be made stationary according to the variation-perturbation method. We therefore turn to the alternative derivation. We solve the first-order Schrödinger equation which gives the more detailed form of  $\chi$  to first order ( $\chi^{(1)}$ ). Then  $\chi^{(1)}$  is generalized in Paper II to make the resulting effects exact to "all orders" and to include unlinked clusters to yield the open-shell many-electron theory.

Before obtaining  $\chi$  to first order, it is necessary to discuss the nature and choice of the zeroth-order wavefunction  $\phi_0$ .

### III. ORBITAL APPROXIMATION

The choice of  $\phi_0$ , the orbital approximation, is crucial in the many-electron theory. The closed shell  $\phi_0$  was chosen as the Hartree-Fock (HF) determinant for quantitative reasons.<sup>1,3,6</sup> For open-shell states, there is not one, but several self-consistent-field (SCF) Hartree-Fock procedures, and a choice most suitable for a correlation theory is required.

### $\phi_0$ Chosen for the Open-Shell Many-Electron Theory

Several considerations enter into the choice of  $\phi_0$  most appropriate for an open-shell many-electron theory:

- (1)  $\phi_0$  must have the same symmetry properties as  $\chi$  so that  $\chi$  does not have "correlation effects" which merely correct the symmetry properties of  $\phi_0$ .
- (2)  $\phi_0$  must have the lowest energy of all functions of the same form, otherwise  $\chi$  would contain terms which turn the orbitals in  $\phi_0$  into the orbitals of a "better"  $\phi_0$ .
- (3)  $\phi_0$  should have a sufficiently general form if one is to be able to include especially the strong near-degeneracy resonances.
- (4) To be practical, the orbitals should be symmetry orbitals.

A fifth consideration concerns the nature of unlinked clusters in  $\chi$  and will be discussed more appropriately in Sec. II of Paper II.

The  $\phi_0$  which meets all of these requirements is the most general multiconfigurational wavefunction that can be made from the set of  $M$  spin orbitals, the general restricted Hartree-Fock (GRHF) wavefunction.<sup>9</sup> Both the coefficients  $C_K$  [Eq. (3)] and the  $M$  spin orbitals are chosen to minimize  $\langle \phi_0, H\phi_0 \rangle / \langle \phi_0, \phi_0 \rangle$ . The spin orbitals are restricted to be symmetry orbitals and to be orthogonal. [For example, in each of the atoms, B, N, C, O, F, and Ne, the spin-orbital sea for the ground state consists of 10 spin orbitals ( $1s\alpha, 1s\beta, 2s\alpha, 2s\beta, 2p_{+\alpha}, 2p_{+\beta}, 2p_{0\alpha}, 2p_{0\beta}, 2p_{-\alpha}, 2p_{-\beta}$ ); but for each atomic state three radial functions completely specify the sea.] The  $C_K$  are restricted so that  $\phi_0$  has the same symmetry properties as  $\psi$ .

For a discussion of other types of open-shell HF methods which satisfy some of the requirements above, the reader is referred to the literature.<sup>10</sup>

### Computation of $\phi_{\text{GRHF}}$

Computer programs that can calculate  $\phi_{\text{GRHF}}$  for atoms exist<sup>11</sup> and are in preparation.<sup>12</sup> Nevertheless, computational methods for the single configurational restricted Hartree-Fock (RHF) wavefunction have

<sup>9</sup> Variants of the GRHF method select a few of the excited configurations to mix with the ground configuration. See (a) D. R. Hartree, W. Hartree, and B. Swirles, *Phil. Trans. Roy. Soc. A238*, 229 (1939); (b) A. P. Yutsis, *Zh. Eksperim. i Teor. Fiz.* **23**, 129 (1952); (c) A. P. Yutsis, V. V. Kibartas, and I. I. Glembotskiy, *ibid.* **27**, 425 (1954); (d) V. V. Kibartas, V. I. Kavetskiy, and A. P. Yutsis, *Soviet Phys.—JETP* **2**, 481 (1956) [*Zh. Eksperim. i Teor. Fiz.* **29**, 623 (1955)]; (e) R. E. Watson, *Ann. Phys. (N.Y.)* **13**, 250 (1961); (f) T. L. Gilbert (preprint).

<sup>10</sup> For a discussion of other HF methods as starting points for a correlation theory, see Ref. 6, p. 363, and (a) O. Sinanoğlu, *J. Phys. Chem.* **66**, 2283 (1962); (b) O. Sinanoğlu and D. F. Tuan, *Ann. Rev. Phys. Chem.* **15**, 251 (1964), Sec. II-A 1b.

<sup>11</sup> H. W. Joy (private communication).

<sup>12</sup> C. C. J. Roothaan (private communication from P. E. Cade).

been extensively developed by Roothaan and others.<sup>13-18</sup> A simplified approach is to use the RHF spin orbitals and  $\phi_{\text{RHF}}$  to estimate  $\phi_{\text{GRHF}}$  through

$$\phi_{\text{GRHF}} \approx (\phi_{\text{RHF}} + \chi_{\text{int}}^{\text{RHF}}) / (1 + \langle \chi_{\text{int}}^{\text{RHF}}, \chi_{\text{int}}^{\text{RHF}} \rangle)^{1/2}, \quad (17)$$

where  $\chi_{\text{int}}^{\text{RHF}}$  [i.e., the coefficients  $d_K$  in Eq. (9)] is calculated by near-degeneracy-type CI. The less the internal correlation (relative to  $\phi_{\text{RHF}}$ ) affects the spin orbitals—i.e., the closer the RHF spin orbitals approximate the GRHF spin orbitals—the more accurate is Eq. (17). We expect Eq. (17) to be a valid approximation for first-row atoms.<sup>19</sup>

#### Internal and Nondynamical Correlation

For some systems  $\phi_{\text{RHF}}$  and  $\phi_{\text{GRHF}}$  are identical (e.g., lithium ground state), while for others (e.g., carbon  $^3P$  state) they are different;

$$\phi_{\text{RHF}}(\text{Li}) = \phi_{\text{GRHF}}(\text{Li}) = \mathcal{G}\{(1s\alpha)(1s\beta)(2s\alpha)\}, \quad (18)$$

$$\phi_{\text{RHF}}(\text{C-}^3P) = \mathcal{G}\{(1s\alpha)(1s\beta)(2s\alpha)(2s\beta)(2p_{+\alpha})(2p_{0\alpha})\}, \quad (19)$$

$$\begin{aligned} \phi_{\text{GRHF}}(\text{C-}^3P) = & \mathcal{G}\{C_1(1s\alpha)(1s\beta)(2s\alpha)(2s\beta)(2p_{+\alpha})(p_{0\alpha}) \\ & + C_2(1s\alpha)(1s\beta)(2p_{-\alpha})(2p_{+\beta})(2p_{+\alpha})(2p_{0\alpha}) \\ & + C_3(2p_{-\alpha})(2p_{+\beta})(2s\alpha)(2s\beta)(2p_{+\alpha})(2p_{0\alpha}) \\ & + C_4[(1s\alpha)(2s\beta) + (2s\alpha)(1s\beta)]/\sqrt{2}\} \\ & \times (2p_{-\alpha})(2p_{+\beta})(2p_{+\alpha})(2p_{0\alpha})\}. \quad (20) \end{aligned}$$

The major difference of physical importance between  $\phi_{\text{GRHF}}$  and  $\phi_{\text{RHF}}$  here is that  $\phi_{\text{GRHF}}$  includes the nondynamical<sup>2-5</sup> (near-degeneracy) correlations but  $\phi_{\text{RHF}}$  does not. The  $(1s)^2(2p)^4$  term ( $C_2$ ) in  $\phi_{\text{GRHF}}$  represents the nondynamical  $(2s)^2$  correlation.<sup>5</sup> The  $(1s2s)(2p)^4$  and  $(2s)^2(2p)^4$  terms represent contributions to  $\phi_{\text{GRHF}}$  formally similar to the nondynamical  $(2s)^2$  correlation, but not important in magnitude ( $|C_1| > |C_2| \gg |C_4| > |C_3|$ ). In this example where the closed-shell type of theory can be applied,<sup>5</sup> they would be part of the  $(1s2s)$  and  $1s^2$  dynamical correlations. Thus  $\chi_{\text{int}}^{\text{RHF}}$

<sup>13</sup> C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 179 (1960).

<sup>14</sup> C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. 2.

<sup>15</sup> S. Huzinaga, *Phys. Rev.* **122**, 131 (1961).

<sup>16</sup> F. W. Birss and S. Fraga, *J. Chem. Phys.* **38**, 2552 (1963).

<sup>17</sup> R. Lefebvre, *J. Chim. Phys.* **54**, 168 (1957).

<sup>18</sup> L. Goodman and J. R. Hoyland, *J. Chem. Phys.* **39**, 1068 (1963).

<sup>19</sup> Another simplified starting point for solving the correlation equations is obtained by an HF based on the average energy of the configuration, but with some symmetry and equivalence restrictions. (See Ref. 10.) A theory based on this HF would be suitable formally, but new estimates show that the remaining HF type  $f_i$ 's are not always small. Though these  $f_i$ 's could be added on by perturbation theory, it appears simpler to base the correlation theory on the Roothaan HF method, as we discuss in this paper. Another reason for this choice would be a pragmatic one; many Roothaan HF calculations by this method on atoms and molecules are now available. [See references in Part II-A2 of Ref. 10(b).]

represents a generalization of nondynamical correlation, which is then incorporated into  $\phi_{\text{GRHF}}$  in a self-consistent manner.

Note that energy matrix elements of  $\phi_{\text{GRHF}}$  with other (orthogonal) linear combinations of the  $\Delta_K$  vanish. Thus it is to be expected that further internal correlation (relative to  $\phi_{\text{GRHF}}$ ) should be small;

$$\chi_{\text{int}}^{\text{GRHF}} \approx 0. \quad (21)$$

#### IV. PERTURBATION-THEORY RESULTS

We now investigate the correlation effects in  $\chi$  by first<sup>20</sup> solving the first-order Schrödinger equation based on  $\phi_{\text{RHF}}$  as zeroth order. In a later section we indicate how the form of  $\chi^{(1)}$  would change as one goes from  $\phi_{\text{RHF}}$  to  $\phi_{\text{GRHF}}$ . When Roothaan's HF method is applicable,<sup>13,14</sup> the RHF orbitals are eigenfunctions of a one-electron Hamiltonian  $F$ , and  $\phi_{\text{RHF}}$  is an eigenfunction of

$$\sum_{i=1}^N F(i).$$

#### Perturbation Solution for the Wavefunction to First Order Based on Roothaan's SCF Method

Consider a nonclosed-shell state containing only one open subshell. Number the determinants arising from the single configuration to which  $\phi_{\text{RHF}}$  belongs from  $K=1$  to  $\kappa$ ;

$$\phi_{\text{RHF}} = \sum_{K=1}^{\kappa} C_K \Delta_K. \quad (22)$$

Suppose that no other linear combination of the  $\kappa - \Delta_K$  has the same symmetry as  $\phi_{\text{RHF}}$ , so that the  $C_K$  are determined by symmetry. The (spin-independent) one-electron Hamiltonian  $F$  of which the RHF spin orbitals are eigenfunctions is defined by Eq. (36) of Ref. 13.  $F$  has the form

$$F = h_0 + V_R, \quad (23)$$

where  $h_0$  is the bare-nuclei one-electron Hamiltonian, and  $V_R$  is an effective self-consistent-field potential. For the spin orbital  $i$ ,

$$F|i\rangle = \epsilon_i|i\rangle. \quad (24)$$

Each  $\Delta_K$  ( $K \leq \kappa$ ) and  $\phi_{\text{RHF}}$  itself are eigenfunctions of  $H_0$  with the same eigenvalue  $E_0$ ;

$$H_0 = \sum_{i=1}^N F(i), \quad (25)$$

$$H_0 \Delta_K = E_0 \Delta_K \quad (K=1, 2, \dots, \kappa), \quad (26)$$

$$E_0 = \sum_{\alpha=1}^N \epsilon_{\alpha}, \quad (27)$$

$$H_0 \phi_{\text{RHF}} = E_0 \phi_{\text{RHF}}. \quad (28)$$

<sup>20</sup> We wish to thank B. Schneider for preliminary work on open-shell perturbation theory.

The first-order wavefunction  $\chi^{(1)}$  satisfies the equation Eqs. (A.1) and (29) as

$$(H_0 - E_0)\chi^{(1)} = -(1 - |\phi_{\text{RHF}}\rangle\langle\phi_{\text{RHF}}|)H_1\phi_{\text{RHF}}, \quad (29)$$

$$H_1 = \sum_{i < j}^N g_{ij} - \sum_i^N V_R(i), \quad (30)$$

$$g_{ij} = 1/r_{ij}. \quad (31)$$

The right-hand side of Eq. (29) is automatically orthogonal to all  $\Delta_K$  ( $K=1, 2, \dots, \kappa$ ) with the energy  $E_0$ , because (a) it is orthogonal to  $\phi_{\text{RHF}}$ , and (b) there is no other linear combination of the  $\Delta_K$  ( $K \leq \kappa$ ) with the same symmetry as  $\phi_{\text{RHF}}$ . Therefore Eq. (29) has a solution.<sup>21</sup>

The determinants  $K = \kappa + 1, \dots, \binom{M}{N}$  often constitute a significant portion of  $\chi$  since they include the nondynamical correlations as discussed above. This part of  $\chi$ , involving only the unfilled portions of the RHF sea, is  $\chi_{\text{int}}^{\text{RHF}}$ . It is obtained to first order from

$$\chi_{\text{int}}^{(1)} = \sum_{K=\kappa+1}^{\binom{M}{N}} \Delta_K \frac{\langle \Delta_K, H_1 \phi_{\text{RHF}} \rangle}{E_0 - E_K}, \quad (32)$$

where

$$E_K = \sum_{a=1}^N \epsilon_{k_a}. \quad (33)$$

The  $\epsilon_{k_a}$  are spin-orbital energies of  $k_a$  appearing in  $\Delta_K$ , Eq. (1).

The remaining part of  $\chi^{(1)}$  is  $\chi_{\text{ext}}^{(1)}$  [cf. Eqs. (7) and (8)] and satisfies

$$(H_0 - E_0)\chi_{\text{ext}}^{(1)} = -(1 - \sum_{K=1}^{\binom{M}{N}} |\Delta_K\rangle\langle\Delta_K|)H_1\phi_{\text{RHF}}. \quad (34)$$

This equation gives the remaining correlations, which are external to the sea and quite similar in nature to those in closed shells. Equation (34) can be solved formally by a straightforward application of the method of successive partial orthogonalizations (Appendix A). The result is:

$$\chi^{(1)}_{\text{ext}} = \sum_{K=1}^{\kappa} C_K \chi^{(1)}_K \quad (35)$$

$$= \sum_{K=1}^{\kappa} C_K \mathcal{G} \left\{ (k_1 k_2 \dots k_N) \left[ \sum_{a=1}^N \frac{\hat{f}^{(1)}_{k_a}(K)}{(k_a)} + \sum_{1 \leq a < b}^N \sum_{l=1}^M \frac{l f^{(1)}_{k_a k_b; l}}{(k_a k_b)} + 2^{-\frac{1}{2}} \sum_{1 \leq a < b}^N \frac{\hat{u}^{(1)}_{k_a k_b}}{(k_a k_b)} \right] \right\}, \quad (36)$$

$[l \neq k_1, k_2, \dots, k_N],$

where

$$\hat{f}^{(1)}_{k_a(K)} = (\epsilon_{k_a} - F)^{-1} Q_1 \left( \sum_{b=1}^N \bar{S}_{k_b} - V_R \right) | k_a \rangle, \quad (37)$$

$$\hat{f}^{(1)}_{k_a k_b; l} = (\epsilon_{k_a} + \epsilon_{k_b} - \epsilon_l - F)^{-1} Q_1 [ \langle l, g_{12} k_a \rangle k_b - \langle l, g_{12} k_b \rangle k_a ], \quad (38)$$

$$\hat{u}^{(1)}_{k_a k_b} = [ \epsilon_{k_a} + \epsilon_{k_b} - F(1) - F(2) ]^{-1} Q_2 g_{12} | B(k_a k_b) \rangle. \quad (39)$$

$\bar{S}_{k_a}$  is the Coulomb minus exchange operator for spin orbital  $k_a$ . The projection operators  $Q_1$  and  $Q_2$  ensure that the  $\hat{f}$ 's and  $\hat{u}$ 's are one-electron orthogonal to all the spin orbitals in the sea.

$$Q_1 \equiv 1 - \sum_{i=1}^M | i \rangle \langle i |, \quad (40)$$

$$Q_2 \equiv 1 - \sum_{i=1}^M \{ | i(\mathbf{x}_1) \rangle \langle i(\mathbf{x}_1) | + | i(\mathbf{x}_2) \rangle \langle i(\mathbf{x}_2) | \} + \sum_{i < j}^M | B(ij) \rangle \langle B(ij) |, \quad (41)$$

$$\langle m, \hat{f}^{(1)}_{k_a(K)} \rangle = \langle m, \hat{f}^{(1)}_{k_a k_b; l} \rangle = \langle m, \hat{u}^{(1)}_{k_a k_b} \rangle = 0 \quad (m = 1, 2, \dots, M). \quad (42)$$

$B$  is the two-electron antisymmetrizer:  $B = 2^{-\frac{1}{2}}(1 - P_{12})$ .

At an intermediate stage of the derivation of Eq. (36) one obtains the  $n$ -electron correlation functions  $U'_{(n)K_{N-n}}$  [Eq. (13)] to first order.

$$\hat{u}^{(1)}_{(1)I_{N-1}} = \sum_{\substack{K \\ (K=I_{N-1}k)}} (-1)^{\sigma_K} C_K \hat{f}^{(1)}_{k(K)} + \sum_{\substack{K \\ [K=I_{N-1}(k_a/i)k_b]}} (-1)^{\sigma_K} C_K \hat{f}^{(1)}_{k_a k_b; K i} \quad (43)$$

$$\hat{u}^{(1)}_{(2)I_{N-2}} = \sum_{\substack{K \\ (K=I_{N-2}k_a k_b)}} (-1)^{\sigma_K} C_K \hat{u}^{(1)}_{k_a k_b} \quad (44)$$

$$\hat{u}^{(1)}_{(n)I_{N-n}} = 0 \quad (n \geq 3). \quad (45)$$

<sup>21</sup> O. Sinanoğlu, Proc. Roy. Soc. (London) **A260**, 379 (1961).

These equations clearly show the composite nature of the  $\hat{U}_{(1)}$  and  $\hat{U}_{(2)}$ .

### Notation

$I_{N-1}k$  stands for the determinant  $\Delta_K$  whose spin orbitals are  $i_1, i_2, \dots, i_{N-1}, k$ . The  $(-1)^{\sigma_K}$  is  $\pm 1$  depending whether  $i_1, i_2, \dots, i_{N-1}, k$  is an even or odd permutation of the strictly ascending order. For exact correlation functions [Eq. (13)] we use capital  $U$ 's; for approximate, lower case  $u$ 's.

### Types of Correlation

Equations (32) and (35)–(39) suggest the following picture of nonclosed-shell correlation:

(1) Internal correlation: electrons in  $\phi_{\text{RHF}}(K \leq \kappa)$  may be "scattered" into unfilled regions of the RHF sea  $\Delta_K(K > \kappa)$ .

(2) Semi-internal correlation: in each  $\Delta_K$  of  $\phi_{\text{RHF}}$  a pair of electrons ( $k_a k_b$ ) may "collide," "scattering" one outside the sea into  $\hat{f}_{k_a k_b; l}^{(1)}$ , the other into a spin orbital  $l$  (which must not be occupied at that moment).

(3) External pair correlations: pair correlations similar to those in closed shells;  $k_a$  and  $k_b$  "collide," "scattering" both outside the sea into  $\hat{u}_{k_a k_b}^{(1)}$ .

(4) Spin- and symmetry-orbital average polarizations:  $\hat{f}_{k(K)}^{(1)}$ .

The interpretation of the  $\hat{f}_{k(K)}^{(1)}$  requires some comment. The open-shell restricted HF  $\phi_0$  is not truly a self-consistent-field wavefunction. In particular, for  $S \neq 0$  the different exchange fields for  $\alpha$  and  $\beta$  electrons lead to first-order spin-polarizing corrections to doubly occupied orbitals.<sup>22,23</sup> The asymmetry of the Coulomb and exchange fields leads to first-order changes in the symmetry of the orbitals. (An example in Paper II shows the  $d$ -symmetry correction to a  $2s$  orbital in  $^1S$  carbon.) The potential which gives rise to the first-order spin and/or symmetry polarizations is the difference between the sum of the Coulomb and exchange potentials acting on Orbital  $k$  in the determinant  $\Delta_K$ , and the average (symmetric) potential  $V_R$ .

$$\Delta V_{k(K)} = \sum_{\alpha=1}^N \bar{S}_{k\alpha} - V_R. \quad (46)$$

Since  $\Delta V_{k(K)}$  depends explicitly on the spin orbitals in  $\Delta_K$ ,  $\hat{f}_{k(K)}^{(1)}$  depends not only on  $k$ , but also on the determinant that  $k$  is in.

Comparing the open-shell perturbation-theory results with those for closed shells,<sup>1,2,21</sup> one notes that the closed shell  $\chi^{(1)}$  [Eq. (19) of Ref. 1] contains no  $\hat{f}_{ij;k}^{(1)}$  or  $\hat{f}_{ij;k}^{(1)}$ . To have  $\hat{f}_{ij;k}^{(1)}$  there must be at least two possible Slater determinants and an available unoccupied spin orbital  $k$ . The  $\hat{f}_{ij;k}^{(1)}$  does not enter the closed shell  $\chi^{(1)}$  as a consequence of the Brillouin theorem. [ $\Delta V_{k(K)}$ , Eq. (46), vanishes in the closed-shell case.] Thus the nonclosed-shell "orbital average polarizations"  $\hat{f}_{k(K)}^{(1)}$  are of a fundamentally different origin than the closed shell  $\hat{f}_k$ , which arise from the higher-order effect of correlation on orbitals, and which are usually negligible.<sup>3</sup>

Although Eq. (39) for  $\hat{u}_{k_a k_b}^{(1)}$  and Eq. (44) of Ref. 2 are formally identical, note that the projection operator in the closed-shell case makes  $g_{ij} | B(ij) \rangle$  one electron orthogonal to the occupied  $N$  closed-shell HF spin orbitals, whereas  $Q_2$  in the open-shell case makes  $g_{ij} | B(ij) \rangle$  one-electron orthogonal to all  $M$  spin orbitals in the RHF sea, occupied or unoccupied.

### Second-Order Energy

From the first-order wavefunction obtained above, the form of the energy may be determined. The second-order energy is given by

$$\begin{aligned} E^{(2)} &= \langle \phi_{\text{RHF}}, H_1 \chi^{(1)}_{\text{int}} \rangle + \langle \phi_{\text{RHF}}, H_1 \chi^{(1)}_{\text{ext}} \rangle \\ &= E^{(2)}_{\text{int}} + E^{(2)}_{\text{ext}}. \end{aligned} \quad (47)$$

In the second-order energy, the internal and external correlation energies are uncoupled.

If  $\phi_{\text{RHF}}$  is a single determinantal nonclosed-shell state,  $\chi^{(1)}_{\text{int}}$  may easily be written in terms of internal correlations arising from various spin orbitals in the  $\phi_{\text{RHF}}$ . This is in fact done where the closed-shell-type theory is still applicable.<sup>5</sup> In general,  $\chi_{\text{int}}$  (to all orders) also includes collective and longer-range-type correlations that may give rise to over-all charge deformation. For such a general nonclosed-shell state it is best to treat the  $E_{\text{int}}$  in totality. Since  $\chi_{\text{int}}$  and  $E_{\text{int}}$  are essentially the near-degeneracy-type CI effects, their total calculation is easy.

The more difficult part is the  $E_{\text{ext}}$  similar to the closed-shell dynamical effects involving shorter-range but strong correlations. From Eqs. (35) and (30),  $E^{(2)}_{\text{ext}}$  is obtained as

$$E^{(2)}_{\text{ext}} = \sum_{K=1}^{\kappa} |C_K|^2 \langle \Delta_K, H_1 \chi^{(1)} \rangle + \sum_{L \neq K} C_L^* C_K \langle \Delta_L, H_1 \chi^{(1)} \rangle. \quad (48)$$

<sup>22</sup> O. Sinanoğlu, J. Chem. Phys. **33**, 1212 (1960).

<sup>23</sup> A. D. McLachlan, Mol. Phys. **3**, 233 (1960).

The first term contains the diagonal second-order correlations of each  $\Delta_K$  in  $\phi_{\text{RHF}}$ :

$$\langle \Delta_K, H_1 \chi^{(1)}_K \rangle = \sum_{a=1}^N \langle k_a, (\sum_{b=1}^N \bar{S}_{k_b} - V_R) \hat{f}^{(1)}_{k_a(K)} \rangle + \sum_{1 \leq a < b}^N \sum_{l \neq (K)}^M \langle B(k_a k_b), g_{12} B(l \hat{f}^{(1)}_{k_a k_b; l}) \rangle + \sum_{1 \leq a < b}^N \langle B(k_a k_b), g_{12} \hat{u}^{(1)}_{k_a k_b} \rangle \quad (49)$$

$$= \sum_a^N \bar{\epsilon}^{(2)}_{k_a(K)} + \sum_{a < b}^N \sum_{l \neq (K)}^M \bar{\epsilon}^{(2)}_{k_a k_b; l(K)} + \sum_{a < b}^N \bar{\epsilon}^{(2)}_{k_a k_b(K)}. \quad (50)$$

Thus the diagonal terms yield simply the "orbital average polarization" energies, the semi-internal correlation energies, and the pair correlation energies of the various spin orbitals in each determinant.

The multideterminant nonclosed shell also contains however some new off-diagonal effects. For example, if  $L$  and  $K$  differ by only one spin-orbital,  $L = K(l/k_a)$ , then

$$\begin{aligned} \langle \Delta_L, H_1 \chi^{(1)}_K \rangle &= (-1)^{\sigma_{LK}} \{ \langle l, (\sum_{b=1}^N \bar{S}_{k_b} - V_R) \hat{f}^{(1)}_{k_a(K)} \rangle + \sum_{c=1, (c \neq a)}^N \langle B(k_c l), g_{12} B(\hat{f}^{(1)}_{k_c(K)} k_a) \rangle \\ &+ \sum_{c=1, (c \neq a)}^N \langle k_c, (\sum_{b=1, (b \neq a, c)}^N \bar{S}_{k_b} + \bar{S}_l - V_R) \hat{f}^{(1)}_{k_a k_c; l} \rangle + \sum_{c=1, (c \neq a)}^N \sum_{m, (m \neq k_1, k_2, \dots, k_N, l)} \langle B(l k_c), g_{12} B(m \hat{f}^{(1)}_{k_a k_c; m}) \rangle \\ &- \sum_{b < a, (b, c \neq a)}^N \langle B(k_b k_c), g_{12} B(k_a \hat{f}^{(1)}_{k_b k_c; l}) \rangle + \sum_{b=1, (b \neq a)}^N \langle B(l k_b), g_{12} \hat{u}^{(1)}_{k_a k_b} \rangle \}. \quad (51) \end{aligned}$$

Other off-diagonal terms are given in Appendix B. Equations (51), (B.1), and (B.2) show that even in the second-order energy, a general nonclosed-shell state contains new "cross-correlation" terms. These are very much a part of the nature of the nonclosed shell. They need to be taken into account.

### Coupling and Uncoupling

$\chi^{(1)}$  may be calculated by minimizing  $\bar{E}^{(2)}$ :

$$E^{(2)} \leq \bar{E}^{(2)} = 2 \langle \phi_{\text{RHF}}, H_1 \tilde{\chi}^{(1)} \rangle + \langle \tilde{\chi}^{(1)}, (H_0 - E_0) \tilde{\chi}^{(1)} \rangle. \quad (52)$$

In  $E^{(2)}$  the correlation functions are coupled, but they come out uncoupled in Eqs. (37)–(39). We illustrate the nature of this uncoupling with the  $(2p)^2$  pairs in  $^1S$  carbon.

The  $\phi_0$  is

$$\phi_{\text{RHF}}(^1S\text{-carbon}) = \alpha ((1s)^2 (2s)^2 \{ [(2p_x)^2 + (2p_y)^2 + (2p_z)^2] / 3^{\frac{1}{2}} \}). \quad (53)$$

The  $(2p)^2$  contribution to  $E^{(2)}$  is

$$E^{(2)}(2p^2) = \frac{1}{3} \{ \bar{\epsilon}^{(2)}_{2p_x^2} + \bar{\epsilon}^{(2)}_{2p_y^2} + \bar{\epsilon}^{(2)}_{2p_z^2} + \bar{\epsilon}^{(2)}(2p_x^2; 2p_y^2) + \bar{\epsilon}^{(2)}(2p_x^2; 2p_z^2) + \bar{\epsilon}^{(2)}(2p_y^2; 2p_z^2) \}, \quad (54)$$

where

$$\bar{\epsilon}^{(2)}_{2p_x^2} = 2 \langle B(2p_x^2), g_{12} \hat{u}^{(1)}_{2p_x^2} \rangle + \langle \hat{u}^{(1)}_{2p_x^2}, [F(1) + F(2) - 2\epsilon_{2p}] \hat{u}^{(1)}_{2p_x^2} \rangle \quad (55)$$

and

$$\bar{\epsilon}^{(2)}(2p_x^2; 2p_y^2) = 2 \langle B(2p_x^2), g_{12} \hat{u}^{(1)}_{2p_y^2} \rangle + 2 \langle B(2p_y^2), g_{12} \hat{u}^{(1)}_{2p_x^2} \rangle + 2 \langle \hat{u}^{(1)}_{2p_x^2}, [F(1) + F(2) - 2\epsilon_{2p}] \hat{u}^{(1)}_{2p_y^2} \rangle. \quad (56)$$

Similar expressions define the pair and "cross-pair" energies for other combinations of orbitals. If  $\hat{u}^{(1)}_{2p_x^2}$  is varied to minimize the diagonal term  $\bar{\epsilon}^{(2)}_{2p_x^2}$ , subject to the orthogonality requirement [Eq. (42)], the following equation is obtained for  $\hat{u}^{(1)}_{2p_x^2}$ :

$$[F(1) + F(2) - 2\epsilon_{2p}] \hat{u}^{(1)}_{2p_x^2} + Q_2 g_{12} B(2p_x^2) = 0. \quad (57)$$

On the other hand,  $E^{(2)}(2p^2)$  is a minimum when

$$\begin{aligned} [F(1) + F(2) - 2\epsilon_{2p}] [\hat{u}^{(1)}_{2p_x^2} + \hat{u}^{(1)}_{2p_y^2} + \hat{u}^{(1)}_{2p_z^2}] \\ + Q_2 g_{12} [B(2p_x^2) + B(2p_y^2) + B(2p_z^2)] = 0. \quad (58) \end{aligned}$$

Clearly, the solution of the coupled equation (58) is just the sum of the solutions of the uncoupled equations (57).

The second-order energy represents the major portion of the correlation effects in the energy. These effects, arising from the "first-order processes" in the wf, will be made "exact to all orders" in Paper II to make them quantitatively more accurate.

### Perturbation Theory Based on $\phi_{\text{GRHF}}$

As a practical matter, the perturbation solution above with  $\phi_0 = \phi_{\text{RHF}}$  would be sufficient where the

remaining near degeneracies ( $\chi_{\text{int}}$ ) are not strong enough to have sizable effects on the RHF orbitals and the charge distribution. Where the (CI) coefficients appearing in  $\chi_{\text{int}}$  are comparable to those in  $\phi_{\text{RHF}}$ , it is necessary to go over to the more general  $\phi_0 = \phi_{\text{GRHF}}$  as discussed in Sec. III. Molecular orbital (+correlation) treatment of interatomic potential-energy curves and surfaces (especially as the  $R \rightarrow \infty$ ) in general requires<sup>3</sup> the  $\phi_{\text{GRHF}}$ .

The solution of the first-order Schrödinger equation starting with  $\phi_0 = \phi_{\text{GRHF}}$  is complicated by the difficulty of defining an  $H_0$ . Nevertheless, how  $\chi^{(1)}$  would be modified for  $\phi_{\text{GRHF}}$  may be seen in the following manner.

The  $\phi_{\text{RHF}}$  included only determinants ( $K=1, \dots, \kappa$ ) arising from the same configuration, and  $\chi^{(1)}_{\text{int}}$  following it contained  $\Delta_K$ 's corresponding to virtually excited configurations.  $\phi_{\text{GRHF}}$  includes all  $\Delta_K$ 's of the spin-orbital "sea,"

$$\phi_0 = \phi_{\text{GRHF}} = \sum_{K=1}^{\binom{M}{N}} C_K \Delta_K, \quad (59)$$

and incorporates the main internal correlations (by CI rather than first order). Therefore,  $\chi^{(1)}$  based on GRHF should no longer contain any significant explicit  $\chi_{\text{int}}$  [cf. Eq. (21)]:

$$\chi^{(1)\text{GRHF}} \cong \chi^{(1)\text{GRHF}}_{\text{ext}}. \quad (60)$$

The  $\phi_{\text{GRHF}}$  in Eq. (59) includes some  $\Delta_K$ 's which are degenerate, some that are not. The latter are responsible for the difficulty of defining the  $H_0$ . Were the near degeneracies viewed however as actual degeneracies (as, e.g.,  $\Delta_K$ 's out of  $1s^2 2s^2 2p^2$  and  $1s^2 2p^4$  would be in the  $Z \rightarrow \infty$  limit), the solution for the GRHF  $\chi^{(1)}$  would become like that for the RHF  $\chi^{(1)}$ , but now the sums in Eq. (36) would run from  $K=1$  to  $\binom{M}{N}$  rather than 1 to  $\kappa$  as in the respective  $\phi_0$ 's.

One other change in going over to  $\phi_{\text{GRHF}}$  is expected. In the RHF case, only the  $\hat{f}^{(1)}_{k_a(K)}$  depended on the parent determinant  $\Delta_K$  in which  $k_a$  was found [see especially Eq. (46)]; the  $\hat{f}^{(1)}_{k_a k_b; l}$  and  $\hat{u}^{(1)}_{k_a k_b}$  did not. In the GRHF case, the  $\hat{f}^{(1)}_{k_a k_b; l}$  and  $\hat{u}^{(1)}_{k_a k_b}$ , too, may depend on parentage [ $\hat{f}^{(1)}_{k_a k_b; l(K)}$  and  $\hat{u}^{(1)}_{k_a k_b(K)}$ ].

With these considerations the expected form of  $\chi^{(1)}$  now becomes

$$\phi_0 + \chi^{(1)} = \phi_{\text{GRHF}} + \chi^{(1)\text{GRHF}} \quad (61)$$

$$\cong \phi_{\text{GRHF}} + \chi^{(1)\text{GRHF}}_{\text{ext}} \quad (62)$$

$$\cong \sum_{K=1}^{\binom{M}{N}} C_K (\Delta_K + \chi^{(1)K}), \quad (63)$$

where

$$\chi^{(1)K} = G \left\{ (k_1 k_2 \dots k_N) \left[ \sum_{a=1}^N \frac{\hat{f}^{(1)}_{k_a(K)}}{(k_a)} + \sum_{a < b} \sum_{l \neq (K)}^M \frac{l \hat{f}^{(1)}_{k_a k_b; l(K)}}{k_a k_b} + \sum_{a < b} \frac{\hat{u}^{(1)}_{k_a k_b(K)}}{\sqrt{2} (k_a k_b)} \right] \right\}. \quad (64)$$

Note especially that compared to Eqs. (35) and (36) for RHF, here

$$\sum_{K=1}^{\kappa} \rightarrow \sum_{K=1}^{\binom{M}{N}};$$

also the above correlation functions are unambiguously defined only if an  $H_0$  is specified.

With  $\phi_{\text{RHF}}$ ,  $\chi^{(1)}_{\text{int}}$  and  $\chi^{(1)}_{\text{ext}}$  represented first-order processes which took out some of the electrons from filled portions of the sea into unfilled portions and to outside regions. In the RHF case, further scattering from electrons caught in the originally unfilled regions becomes a higher-order process not appearing in  $\chi^{(1)}$ . In the GRHF case, the "boundary" between the filled and unfilled portions is self-consistent, and scattering into unfilled regions is a higher-order process. The GRHF  $\chi^{(1)}$  includes external correlations from all the  $\Delta_K$ 's, so that some previously higher-order processes (wrt  $\phi_{\text{RHF}}$ ) now become first-order processes (wrt  $\phi_{\text{GRHF}}$ ).

Though Eqs. (61) to (64) above give the expected form of  $\chi^{(1)\text{GRHF}}$ , it would be worthwhile if formal and rigorous solutions could be obtained to the corresponding first-order Schrödinger equation. The solution obtained for RHF and its generalization above will be sufficient nevertheless for obtaining a variational theory in Paper II containing the processes of practical importance.

## V. SUMMARY

For the treatment of correlation, the multiconfigurational general restricted Hartree-Fock (GRHF) wavefunction forms a general starting point for various types of nonclosed-shell states. For systems where near-degeneracy resonances are not strong enough to upset the charge distribution, a simplified starting point, the Roothaan-type restricted Hartree-Fock (RHF) wavefunction, is convenient.

The first-order Schrödinger equation for  $\phi_0 = \phi_{\text{RHF}}$  was solved and showed the main correlation effects in nonclosed-shell states. These include the general form of the nondynamical (near-degeneracy) correlations (internal correlation), semi-internal correlations, i.e., pair correlations expelling only one of the electrons out of the HF sea, and "external" pair correlations similar to those in closed-shell states, in addition to the "orbital average" symmetry and spin polarizations. The form of the second-order energy is also evaluated and contains in addition to the energies of the above one- and two-electron effects, new "cross correlations" which are a basic feature of nonclosed-shell state energies. Correlation effects in the energy involving one and two spin orbitals out of a determinant  $\Delta_K$  of  $\phi_0$  are weighted by the fractional occupancy  $|C_K|^2$  of that determinant [see Eqs. (48) and (50)]. The generalization of these first-order processes to  $\phi_{\text{GRHF}}$  is also indicated.



In the next paper (II) these results will be extended into a variational many-electron theory by making the first-order processes exact "to all orders" and by including the unlinked clusters. The variational determination of each one- and two-electron correlation function, symmetry effects, and total energy as an upper limit will also be discussed there.

### APPENDIX A: FORM OF $\chi$ BY THE METHOD OF SUCCESSIVE PARTIAL ORTHOGONALIZATIONS

$\chi$  is defined by Eqs. (4) to (6) in the text.  $\chi_{\text{int}}$  is that part of  $\chi$  in which no electrons are removed from the sea.  $\chi_{\text{ext}}$  is the rest of  $\chi$ ;

$$\chi_{\text{int}} = \sum_{K=1}^{\binom{M}{N}} \Delta_K \langle \Delta_K, \chi \rangle; \quad (\text{A.1})$$

$$\chi_{\text{ext}} = \chi - \chi_{\text{int}} \quad (\text{A.2})$$

$$= \left[ 1 - \sum_{K=1}^{\binom{M}{N}} | \Delta_K \rangle \langle \Delta_K | \right] \chi. \quad (\text{A.3})$$

The one-electron correlation function  $\hat{U}_{(1)K_{N-1}}$  is obtained from  $\chi_{\text{ext}}$  by partial orthogonalization to the simple product:  $(N!)^{\frac{1}{2}} [k_1(\mathbf{x}_1) k_2(\mathbf{x}_2) \dots k_{N-1}(\mathbf{x}_{N-1})]$ ;

$$\hat{U}_{(1)K_{N-1}}(\mathbf{x}_N) = (N!)^{-\frac{1}{2}} \langle k_1 k_2 \dots k_{N-1}, \chi_{\text{ext}} \rangle. \quad (\text{A.4})$$

In (A.4), the integration is over the space- and spin-volume elements of the  $N-1$  electrons in  $k_1 k_2 \dots k_{N-1}$ . Once the  $\hat{U}_{(1)K_{N-1}}$  have been determined  $\chi_{\text{ext}}$  can be orthogonalized to all  $K_{N-1}$ ;

$$\chi' = \chi_{\text{ext}} - \sum_{K_{N-1}=1}^{\binom{M}{N-1}} \mathcal{Q} \{ (k_1 k_2 \dots k_{N-1}) \hat{U}_{(1)K_{N-1}} \} \quad (\text{A.5})$$

$$= \chi_{\text{ext}} - \mathcal{Q} \left\{ \sum_{K_{N-1}=1}^{\binom{M}{N-1}} | k_1 k_2 \dots k_{N-1} \rangle (N!)^{\frac{1}{2}} \langle k_1 k_2 \dots k_{N-1}, \chi_{\text{ext}} \rangle \right\}. \quad (\text{A.6})$$

The two-electron correlation functions  $\hat{U}'_{(2)K_{N-2}}$  are obtained from  $\chi'$  by partial orthogonalization to  $(N!/2!)^{\frac{1}{2}} [k_1(\mathbf{x}_1) k_2(\mathbf{x}_2) \dots k_{N-2}(\mathbf{x}_{N-2})]$ ,

$$\hat{U}'_{(2)K_{N-2}}(\mathbf{x}_{N-1}, \mathbf{x}_N) = (N!/2!)^{\frac{1}{2}} \langle k_1 k_2 \dots k_{N-2}, \chi' \rangle. \quad (\text{A.7})$$

Similarly,  $\chi'$  can be orthogonalized to all  $K_{N-2}$ ,

$$\chi'' = \chi' - 2^{-\frac{1}{2}} \sum_{K_{N-2}=1}^{\binom{M}{N-2}} \mathcal{Q} \{ (k_1 k_2 \dots k_{N-2}) \hat{U}'_{(2)K_{N-2}} \} \quad (\text{A.8})$$

$$= \chi' - 2^{-\frac{1}{2}} \mathcal{Q} \left\{ \sum_{K_{N-2}=1}^{\binom{M}{N-2}} | k_1 k_2 \dots k_{N-2} \rangle (N!/2!)^{\frac{1}{2}} \langle k_1 k_2 \dots k_{N-2}, \chi' \rangle \right\}. \quad (\text{A.9})$$

Continuing in this manner, if we denote the remainder after orthogonalizing to the  $K_{N-n}$ , by  $\chi^{(n)}$ , the  $(n+1)$ -electron correlation functions are given by

$$\hat{U}'_{(n+1)K_{N-n-1}} = [N!/(n+1)!]^{\frac{1}{2}} \langle k_1 k_2 \dots k_{N-n-1}, \chi^{(n)} \rangle. \quad (\text{A.10})$$

### APPENDIX B: ADDITIONAL OFF-DIAGONAL TERMS IN $E^{(2)}$

If  $L$  and  $K$  differ by two spin orbitals,  $L = (K/k_a k_b) l_d$ , then

$$\begin{aligned} \langle \Delta_L, H_1 \chi^{(1)K} \rangle &= (-1)^{\sigma_{LK}} \{ \langle B(l_d l_d), g_{12} B(\hat{f}^{(1)}_{k_a(K) k_b}) \rangle + \langle B(l_d l_d), g_{12} B(k_a \hat{f}^{(1)}_{k_b(K)}) \rangle \\ &+ \sum_{m, (m \neq k_1 k_2 \dots k_{N-1} l_d)} \langle B(l_d l_d), g_{12} B(m \hat{f}^{(1)}_{k_a k_b; m}) \rangle + \langle l_d, (\sum_{e=1}^N \bar{S}_e - V_R) \hat{f}^{(1)}_{k_a k_b; l_e} \rangle - \langle l_c, (\sum_{e=1}^N \bar{S}_e - V_R) \hat{f}^{(1)}_{k_a k_b; l_d} \rangle \\ &+ \sum_{e=1, (e \neq a, b)}^N [ \langle B(l_d k_e), g_{12} B(k_b \hat{f}^{(1)}_{k_a k_b; l_e}) \rangle - \langle B(l_c k_e), g_{12} B(k_b \hat{f}^{(1)}_{k_a k_b; l_d}) \rangle \\ &- \langle B(l_d k_e), g_{12} B(k_a \hat{f}^{(1)}_{k_b k_a; l_e}) \rangle + \langle B(l_c k_e), g_{12} B(k_a \hat{f}^{(1)}_{k_b k_a; l_d}) \rangle ] + \langle B(l_d l_d), g_{12} \mathcal{Q}^{(1)}_{k_a k_b} \rangle \}. \quad (\text{B.1}) \end{aligned}$$

If  $K$  and  $L$  differ by three electrons,  $L = (K/k_a k_b k_c) l_a' l_b' l_c'$ , then

$$\langle \Delta_L, H_1 \chi^{(1)K} \rangle = (-1)^{\sigma_{KL}} \{ \langle B(l_b' l_c'), g_{12} B(\hat{f}^{(1)}_{k_a k_b; l_a' l_c'}) \rangle + \dots + \langle B(l_a' l_b'), g_{12} B(\hat{f}^{(1)}_{k_b k_c; l_a' l_c'}) \rangle \}. \quad (\text{B.2})$$

If  $K$  and  $L$  differ by more than three electrons, then  $\langle \Delta_L, H_1 \chi^{(1)K} \rangle$  vanishes.