

Many-Electron Theory of Nonclosed-Shell Atoms and Molecules. II. Variational Theory*

HARRIS J. SILVERSTONE† AND OKTAY SINANOĞLU‡

Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut

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The theory developed in I is generalized into a variational many-electron theory by making the first-order correlation processes in the wavefunction "exact to all orders" and by including the effects of unlinked clusters. Equations for obtaining the significant correlation effects are derived by the variation-perturbation approach. Symmetry properties of the correlation functions and a semiempirical theory based on the form of the variational energy are also discussed. The examples of lithium, ¹S-carbon, and C₂H₄⁺ illustrate some aspects of the theory.

I. INTRODUCTION

THIS series of two papers develops a theory of electron correlation for nonclosed-shell systems such as excited states of atoms and molecules, triplet states, free radicals, and transient species. Paper I¹ discussed the nonclosed-shell orbital wavefunction starting point. The first-order Schrödinger equation was solved and gave the significant "first-order processes." In this paper we make the first-order correlation processes "exact to all orders," include unlinked clusters, and obtain the variational total energy as an upper bound. We then apply the variational-perturbation approach to derive equations for evaluation of individual correlation functions. These results turn the first-order theory

of I into a variational nonclosed-shell many-electron theory which should be sufficiently accurate for calculations. Symmetry properties of the correlation functions and how a semiempirical correlation theory can be based on the form of the energy are also discussed.

II. WAVEFUNCTION ADOPTED IN THE NONCLOSED-SHELL MANY-ELECTRON THEORY

One can obtain a better approximate wavefunction than first order by keeping the same *form* for the wavefunction as in first order, but by calculating the correlation functions from the variational principle (thus obtaining the correlation functions "to all orders"). Equations (63) and (64) of I lead (in this manner) to the approximate wavefunction, $\phi_{\text{GRHF}} + \chi_d$:

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

$$\Delta_K = \mathcal{G}\{(k_1 k_2 \cdots k_N)\}, \quad (2)$$

$$\chi_K = \mathcal{G}\{(k_1 k_2 \cdots k_N) \left[\sum_{a=1}^N \frac{\hat{f}_{k_a}^{(P)K}}{(k_a)} + \sum_{\substack{1 \leq a < b \leq N \\ (l \neq k_1, k_2, \dots, k_N)}} \sum_{l=1}^M \frac{l \hat{f}_{k_a k_b, l}^{(P)K}}{(k_a k_b)} + \sum_{1 \leq a < b \leq N} \frac{\hat{u}_{k_a k_b}^K}{\sqrt{2} (k_a k_b)} \right]\}. \quad (3)$$

Note that our normalization convention [Eqs. (4)–(6) of I] is

$$\langle \phi_{\text{GRHF}}, \phi_{\text{GRHF}} \rangle = 1; \quad \langle \phi_{\text{GRHF}}, \chi_d \rangle = 0. \quad (4)$$

The "best" χ_d would be found by minimizing E_d

$$E_d = \frac{\langle \phi_{\text{GRHF}} + \chi_d, H(\phi_{\text{GRHF}} + \chi_d) \rangle}{\langle \phi_{\text{GRHF}} + \chi_d, \phi_{\text{GRHF}} + \chi_d \rangle} \quad (5)$$

with respect to variations of the \hat{f} 's and \hat{u} 's, subject only to symmetry restrictions (see Sec. IV) and the

one-electron orthogonality conditions [cf. Eq. (15) of I]:

$$\langle m, \hat{f}_{k_a}^{(P)K} \rangle = \langle m, \hat{f}_{k_a k_b, l}^{(P)K} \rangle = \langle m, \hat{u}_{k_a k_b}^K \rangle = 0, \quad (m=1, 2, \dots, M). \quad (6)$$

The important correlation effects in χ_d are: (1) external pair correlations $\hat{u}_{k_a k_b}^K$ representing a "collision" between electrons in spin orbitals k_a and k_b which scatters both electrons outside of the GRHF sea; (2) semi-internal correlations $\hat{f}_{k_a k_b, l}^{(P)K}$ representing a collision of two electrons in k_a and k_b , in which one electron ends up outside the sea in $\hat{f}_{k_a k_b, l}^{(P)K}$, the second in spin orbital l ; and (3) $\hat{f}_{k_a}^{(P)K}$, polarizations of spin orbital k_a . The polarizations $\hat{f}_{k_a}^{(P)K}$ are spin polarizations (which make orbitals of α and β spin different), symmetry polarizations (which, e.g., add d character to an s orbital), and/or configuration polarizations

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† National Science Foundation Postdoctoral Fellow. Present address: Department of Chemistry, The Johns Hopkins University, Baltimore, Md. 21218.

‡ Alfred P. Sloan Fellow.

¹H. J. Silverstone and O. Sinanoğlu, J. Chem. Phys. **44**, 1899 (1966) referred to as I (first paper in the series).

(which tend to make k_a in one configuration in ϕ_{GRHF} different from k_a in another). They are not the higher-order effects of correlation on orbitals which are probably small in open-shell states, as they usually are in closed-shell states.² Note that the K denoting parentage dependence (determinant Δ_K) is written here as a superscript; in the first-order functions K was a subscript.

χ_d will approximate the exact χ closely when:

(1) Internal correlation with respect to ϕ_{GRHF} is negligible. [cf. Eqs. (7)–(9), and (60) of I].

(2) The $\hat{U}_{(1)K_{N-1}}$ and $\hat{U}_{(2)K_{N-2}}$ [Eq. (13) of I] have the physically meaningful internal structures (in terms of the $\hat{f}_{k_a}^{(P)K}$, $\hat{f}_{k_a k_b; l}^K$, and $\hat{u}_{k_a k_b}^K$) implied by Eqs. (43) and (44) of I.

(3) The $\hat{U}_{(n)K_{N-n}}$ [cf. Eq. (13) of I] are negligible for $n > 2$.

The first two conditions are quite reasonable. The third condition can be improved upon. Though true (linked cluster) $n > 2$ correlations may be quite small (at least in some nonclosed-shell states) (see below), the $\hat{U}_{(n)K_{N-n}}$ contain unlinked clusters of the \hat{f} 's and \hat{u} 's, which may be significant. The unlinked clusters are easily included (and should be) in the theory (see below).

Unlinked clusters represent two or more electron correlation effects occurring in separate groups of electrons at the same time. In closed-shell states (usually)

only pair correlations \hat{u}_{ij} are important.²⁻⁵ The simultaneous correlations of two pairs, for example (ij) and (kl) , are represented³⁻⁵ by $\hat{u}_{ij}\hat{u}_{kl}$. The χ of the closed-shell many-electron theory, χ'_d , contains all pair correlations and their unlinked clusters [Eq. (27) of Ref. (3)]. The open-shell χ contains unlinked clusters of not only the \hat{u}_{ij} 's, but also of nonnegligible open-shell-type \hat{f} 's and of such \hat{f} 's and \hat{u} 's.

The unlinked clusters involving two or more \hat{f} 's greatly complicate the open-shell formalism. When there are only one or two open shells localized in one region of space, only those few spin orbitals located near the open shells should have significant \hat{f} 's. [Note that $\Delta V_{k(K)}$, Eq. (46) of I, which gives rise to $\hat{f}_{k(K)}^{(1)}$, involves mainly the Coulomb and exchange operators of the open-shell electrons.] The unlinked clusters affect the energy mainly by cancelling the normalization denominator (see Sec. III). We do not expect the few significant \hat{f} 's to contribute largely to the denominator or to the cancellation, and so for simplicity we do not include unlinked clusters involving two or more \hat{f} 's in the approximate χ . [For systems in which $\hat{f}\times\hat{f}$ unlinked clusters would be significant, e.g., a diradical, two lithium atoms far apart, etc., the important clusters can be easily put in (e.g., $i\rightarrow i+\hat{f}_i$, etc.)⁵]

The generalization of χ_d , which is the basic correlation wavefunction of the nonclosed-shell many-electron theory, and which contains all unlinked clusters of the $\hat{u}_{k_a k_b}^K$ and all unlinked clusters having at most one $\hat{f}_{k_a}^{(P)K}$ or $\hat{f}_{k_a k_b; m}^K$, is χ'_d

$$\chi'_d = \sum_{K=1}^{(M)} C_K \chi'_K, \tag{7}$$

$$\begin{aligned} \chi'_K = \alpha \left\{ (k_1 k_2 \dots k_N) \left[\sum_{a=1}^N \frac{\hat{f}_{k_a}^{(P)K}}{(k_a)} \left(1 + 2^{-1} \sum_{\substack{1 \leq b < c \leq N \\ (b,c \neq a)}} \frac{\hat{u}_{k_b k_c}^K}{(k_b k_c)} + 2^{-1} \sum_{\substack{b < c \\ d < e \\ (b < d, b, c \neq d, e; b, c, d, e \neq a)}} \frac{\hat{u}_{k_b k_c}^K \hat{u}_{k_d k_e}^K}{(k_b k_c k_d k_e)} + \dots \right) \right. \right. \\ + \sum_{\substack{1 \leq a < b \leq N \\ (m \neq k_1, k_2, \dots, k_N)}} \sum_{m=1}^M \frac{m \hat{f}_{k_a k_b; m}^K}{(k_a k_b)} \left(1 + 2^{-1} \sum_{\substack{i < j \\ (i, j = k_1, k_2, \dots, k_N, m; \text{ but } \neq k_a, k_b)}} \frac{\hat{u}_{ij}^K}{(ij)} + 2^{-1} \sum_{\substack{i < j \\ l < p \\ (i < l; i, j \neq l, p; i, j, l, p = k_1, k_2, \dots, k_N, m; \text{ but } \neq k_a k_b)}} \frac{\hat{u}_{ij}^K \hat{u}_{lp}^K}{(ijlp)} + \dots \right) \\ \left. \left. + 2^{-1} \sum_{1 \leq a < b \leq N} \frac{\hat{u}_{k_a k_b}^K}{(k_a k_b)} + 2^{-1} \sum_{\substack{a < b \\ c < d \\ (a < c; a, b \neq c, d)}} \frac{\hat{u}_{k_a k_b}^K \hat{u}_{k_c k_d}^K}{(k_a k_b k_c k_d)} + \dots \right] \right\}. \tag{8} \end{aligned}$$

Parentage

Correlation functions for the same process in different (parent) determinants may differ ($d \rightarrow$ different), as discussed in Sec. IV of Paper I. If the pair (ij) occurs in n different determinants, there can be n different \hat{u}_{ij}^K functions. A reasonable computational simplification would be to make all n of the \hat{u}_{ij}^K functions the same. Accordingly, we define the "anonymous parentage" approximation χ'_d in which all corre-

lation functions are independent of parentage,

$$\begin{aligned} (\hat{u}_{ij}^K = \hat{u}_{ij}^L = \hat{u}_{ij}, \hat{f}_{k_a}^{(P)K} = \hat{f}_{k_a}^{(P)L} = \hat{f}_{k_a}^{(P)}, \\ \hat{f}_{k_a k_b; m}^K = \hat{f}_{k_a k_b; m}^L = \hat{f}_{k_a k_b; m}, \text{ etc.}). \end{aligned}$$

² (a) O. Sinanoğlu and D. F. Tuan, J. Chem. Phys. **38**, 1740 (1963); (b) V. McKoy and O. Sinanoğlu, *ibid.* **41**, 2689 (1964).
³ O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962).
⁴ O. Sinanoğlu, J. Chem. Phys. **36**, 3198 (1962).
⁵ O. Sinanoğlu, Advan. Chem. Phys. **6**, 315 (1964).

Symbolically,

$$\chi'_{s} = \chi'_{a} \text{ (no parentage subscripts)}. \quad (9)$$

There are cases, however, where $f_k^{(P)K}$ and $\hat{f}_k^{(P)L}$ must differ because of symmetry, even when K and L belong to the same configuration. [see Eqs. (67)–(69) for an illustration.] (For \hat{u}_{ij} 's, the anonymous parentage approximation seems consistent with symmetry requirements. See Sec. IV.) Clearly, one may then define a "hybrid" χ in which some correlation functions depend on parentage while others do not.

ϕ_{GRHF} vs ϕ_{RHF} as the Starting Point

As discussed in I, the restricted Hartree–Fock (RHF) orbital wavefunction is a good approximation for many problems (e.g., first-row atoms).^{2b} Then $\chi_{\text{int}}^{\text{RHF}}$ can be obtained by near-degeneracy-type configuration interaction, and Eq. (17) of I is valid. But if ϕ_{GRHF} can be obtained directly from ϕ_{RHF} , can the many-electron χ be obtained by direct generalization of the RHF-perturbation results?

The $\phi_{\text{RHF}} + \chi^{(1)\text{RHF}}$ is given by Eqs. (32) and (36) of I

$$\phi_{\text{RHF}} + \chi^{(1)\text{RHF}} = \sum_{K=1}^{\kappa} C_K (\Delta_K + \chi_K^{(1)}) + \sum_{K=\kappa+1}^{\binom{M}{N}} C_K^{(1)} \Delta_K. \quad (10)$$

By removing the first-order restriction on $\chi_K^{(1)}$ and $C_K^{(1)}$ one could obtain an approximation χ_a^{RHF} analogous to χ_a [Eqs. (1)–(3)]. The $\phi_{\text{RHF}} + \chi_a^{\text{RHF}}$ would be the same as $\phi_{\text{GRHF}} + \chi_a$ except for the external correlations in χ_a arising from the Δ_K , $K > \kappa$, and for normalization. In the next step, i.e., the insertion of higher-order correlation effects (including unlinked clusters), the following questions arise:

(i) When each Δ_K ($K > \kappa$) is expanded to include correlation effects, $\Delta_K \rightarrow \Delta_K + \chi_K$, should χ_K contain only external correlation effects or additional internal correlation effects (which might be called the effects of correlation on coefficients)?

(ii) Should internal correlation effects enter unlinked clusters in χ_K , ($K \leq \kappa$)?

(iii) Will the \hat{f}_i which enter χ_K , ($K > \kappa$), be large corrections (which would try to turn the RHF orbitals into the GRHF orbitals)?

These questions are avoided by including the RHF internal correlation in ϕ (i.e., going over into ϕ_{GRHF}) in a self-consistent way.

Although a complete and *direct* generalization of $\phi_{\text{RHF}} + \chi^{(1)\text{RHF}}$ to a variational many-electron wavefunction is difficult, when ϕ_{RHF} is a good orbital wavefunction the χ'_a [Eqs. (7) and (8)] may still be regarded as based on ϕ_{RHF} in the numerical sense of Eq. (17) of I. The χ'_K for $\binom{M}{N} \geq K > \kappa$ includes dynamical correlations between electrons spending a small fraction of time in the unfilled portion of the RHF sea, i.e., in $\chi_{\text{int}}^{\text{RHF}}$. Since these are like correlations on top of correlations, they ought to be small where $\chi_{\text{int}}^{\text{RHF}}$ is already small, i.e., where ϕ_{RHF} is a good approximation.

III. VARIATIONAL ENERGY

Above we developed an approximate $\chi[\chi'_a$, Eqs. (7) and (8)] which accounts for the physically important correlation effects in the exact wavefunction. In this section we discuss the variational energy from the viewpoints of a nonempirical calculation, a semiempirical theory, and comparison of correlation energies of similar systems. First we discuss the variational energy with χ_a , E_a [Eq. (5)], then with $\chi'_a(E'_a)$. The E'_a is essentially E_a modified by unlinked clusters.

Energy with χ_a

From Eqs. (1) and (4), E_a is

$$E_a = E_{\text{GRHF}} + \frac{2\langle \phi_{\text{GRHF}}, H\chi_a \rangle + \langle \chi_a, (H - E_{\text{GRHF}})\chi_a \rangle}{1 + \langle \chi_a, \chi_a \rangle} \quad (11)$$

$$= E_{\text{GRHF}} + D^{-1} \left\{ \sum_K^{\binom{M}{N}} \sum_L^{\binom{M}{N}} C_K C_L [2\langle \Delta_K, H\chi_L \rangle + \langle \chi_K, (H - E_{\text{GRHF}})\chi_L \rangle] \right\}, \quad (12)$$

where

$$E_{\text{GRHF}} = \langle \phi_{\text{GRHF}}, H\phi_{\text{GRHF}} \rangle, \quad (13)$$

$$D = 1 + \langle \chi_a, \chi_a \rangle. \quad (14)$$

For simplicity we have taken ϕ_{GRHF} and χ_a to be real. The matrix elements in Eq. (12), expanded in $\hat{f}-\hat{u}$ notation, are extremely complex. The various terms may be classified as diagonal correlation energies, "diagonal" terms arising from two determinants, significant "cross-correlation" energies, and remainder terms including more than two electrons correlating at a time.

$$E_a = E_{\text{GRHF}} + D^{-1} \sum_K |C_K|^2 \left\{ \sum_{\alpha=1}^N \tilde{\epsilon}_{k_a}^{(P)K} + \sum_{1 \leq a < b \leq N} \sum_{m=1}^M \tilde{\epsilon}_{k_a k_b; m}^K + \sum_{1 \leq a < b \leq N} \tilde{\epsilon}_{k_a k_b}^K \right\}$$

$$(m \neq k_1, k_2, \dots, k_N)$$

$$+ (\text{"diagonal" two-determinant terms}) + (\text{significant "cross correlations"}) + (R/D), \quad (15)$$

$$\tilde{\epsilon}_{k_a}^{(P)K} = 2 \langle k_a, (h^0 + \sum_{b=1}^N \tilde{S}_{k_b}) f_{k_a}^{(P)K} \rangle + \langle f_{k_a}^{(P)K}, (h^0 + \sum_{b=1}^N \tilde{S}_{k_b} - \eta_{k_a}^K) \hat{f}_{k_a}^{(P)K} \rangle, \tag{16}$$

$$\eta_{k_a}^K = E_{\text{GRHF}} - \sum_{b=1}^N \langle k_b, h^0 k_b \rangle - \sum_{b < c}^N (J_{k_b k_c} - K''_{k_b k_c}), \tag{17}$$

$$\tilde{\epsilon}_{k_a k_b; l}^K = 2 \langle B(k_a k_b), g_{12} B(l \hat{f}_{k_a k_b; l}) \rangle + \langle \hat{f}_{k_a k_b; l}^K, (h^0 + \sum_{c=1}^N \tilde{S}_{k_c} + \tilde{S}_l - \eta_{k_a k_b; l}^K) \hat{f}_{k_a k_b; l}^K \rangle, \tag{18}$$

$$\eta_{k_a k_b; l}^K = E_{\text{GRHF}} - \sum_{c=1}^N \langle k_c, h^0 k_c \rangle - \sum_{c < d}^N (J_{k_c k_d} - K''_{k_c k_d}) - \langle l, (h^0 + \sum_{c=1}^N \tilde{S}_{k_c}) l \rangle, \tag{19}$$

$$\tilde{\epsilon}_{k_a k_b}^K = 2 \langle B(k_a k_b), g_{12} \hat{u}_{k_a k_b}^K \rangle + \langle \hat{u}_{k_a k_b}, \{h^0(1) + h^0(2) + g_{12} + \sum_{c=1}^N [\tilde{S}_{k_c}(1) + \tilde{S}_{k_c}(2)] - \eta_{k_a k_b}^K\} \hat{u}_{k_a k_b}^K \rangle, \tag{20}$$

$$\eta_{k_a k_b}^K = E_{\text{GRHF}} - \sum_{c=1}^N \langle k_c, h^0 k_c \rangle - \sum_{c < d}^N (J_{k_c k_d} - K''_{k_c k_d}), \tag{21}$$

where B is the two-electron antisymmetrizer, h^0 the bare nuclei Hamiltonian, $g_{12} = r_{12}^{-1}$, J_{ij} and K''_{ij} are the Coulomb and exchange integrals, and \tilde{S}_i is the Coulomb minus exchange operator for Spin Orbital i . The η 's are constants.

R consists of three- and four-electron terms, as in the closed-shell case, and two- and three-electron integrals involving \hat{f} 's and \hat{f} 's and \hat{u} 's. (We omit here the long, tedious, explicit expression for R .) Are all the effects appearing in R , especially the three-electron terms, negligible for a general nonclosed-shell state? This is uncertain. For any given case, the magnitudes of these effects can be checked by the variation-perturbation procedure.

Apart from the denominator D , $\tilde{\epsilon}_{k_a}^{(P)K}$ may be inter-

preted as the polarization energy of Spin Orbital k_a in determinant K , $\tilde{\epsilon}_{k_a k_b}^K$ the (external) pair correlation energy for (k_a, k_b) in Δ_K , and $\tilde{\epsilon}_{k_a k_b; m}^K$ the semi-internal correlation energy for $(k_a, k_b; m)$ in Δ_K . The contribution⁶ of each $\tilde{\epsilon}^K$ to the correlation energy is weighted by the square of the coefficient of Δ_K .

In any specific problem, the nature of the significant "diagonal" two-determinant terms and cross-correlation terms depends so strongly on the atomic or molecular state that it is not worthwhile to write down general expressions for all the possible terms.

An example⁷ of a "diagonal" term arising from two different determinants is provided by 1S carbon. Consider only the $(1s)^2(2s)^2(2p)^2$ configuration. Then \hat{u}_{2s^2} will be involved in the contribution:

$$\frac{2}{3} \langle \hat{u}_{(2s)^2}, \hat{u}_{(2s)^2} \rangle [\langle B(2p_x)^2, g_{12} B(2p_y)^2 \rangle + \langle B(2p_x)^2, g_{12} B(2p_z)^2 \rangle + \langle B(2p_y)^2, g_{12} B(2p_z)^2 \rangle]. \tag{22}$$

This same configuration provides a clear example of a significant $(ij; kl)$ —"cross-correlation" term:

$$\begin{aligned} \tilde{\epsilon} [(2p_x)^2; (2p_y)^2] = & 2 \langle B(2p_x)^2, g_{12} \hat{u}_{(2p_y)^2} \rangle + 2 \langle B(2p_y)^2, g_{12} \hat{u}_{(2p_x)^2} \rangle \\ & + 2 \langle \hat{u}_{(2p_x)^2}, \{h^0(1) + h^0(2) + g_{12} + \sum_k [\tilde{S}_k(1) + \tilde{S}_k(2)] - \eta_{(2p_x)^2} \} \hat{u}_{(2p_x)^2} \rangle. \end{aligned} \tag{23}$$

$(k = 1s\alpha, 1s\beta, 2s\alpha, 2s\beta)$

Significant $[\hat{f} \times \hat{f}]$ cross-correlation terms for lithium are included in Eq. (64).

⁶ When ϕ_{GRHF} is approximated by Eq. (17) of I, some simplification of Eqs. (16)–(21) occurs because the orbitals are eigenfunctions of a one-electron Hamiltonian.

⁷ Clearly, the term (22) could and should be included in $\tilde{\epsilon}_{(2s)^2}$ (by changing the definition of $\eta_{(2s)^2}$). All the "diagonal" two-determinant terms could be included in diagonal energies. But since we have not written out all these terms in complete generality to help ensure that they will not be overlooked we have indicated ("diagonal" two-determinant terms) separately.

Energy with χ'_d

The unlinked clusters affect the energy in two ways: Each term in E_d is multiplied by a factor which partially cancels the normalization denominator, and new integrals involving h^0 and g_{ij} , not present in E_d , appear in the numerator. These new integrals are presumably small and are not discussed here. (For a discussion of these integrals in the closed-shell case, see Ref. 3.) With χ'_d , the variational energy becomes [cf. Eq. (15)]

$$E'_d = E_{\text{GRHF}} + (D')^{-1} \sum_K \sum_L C_K C_L \{ 2 \langle \Delta_K, H \chi'_L \rangle + \langle \chi'_K, (H - E_{\text{GRHF}}) \chi'_L \rangle \} \quad (24)$$

$$= E_{\text{GRHF}} + \sum_K |C_K|^2 \left\{ \sum_{a=1}^N \bar{\epsilon}_{k_a}^{(P)K} D_{k_a}^K / D' + \sum_{1 \leq a < b \leq N} \sum_{\substack{m=1 \\ (m \neq (K))}}^M \bar{\epsilon}_{k_a k_b; m}^K D_{k_a k_b; m}^K / D' + \sum_{1 \leq a < b \leq N} \bar{\epsilon}_{k_a k_b}^K D_{k_a k_b}^K / D' \right\} \\ + (\text{"diagonal"} \text{ two-determinant terms}) + (\text{significant "cross-correlation"} \text{ terms}) + (R'/D'), \quad (25)$$

where

$$D' = 1 + \langle \chi'_d, \chi'_d \rangle, \quad (26)$$

$$D_{k_a}^K = 1 + \sum_{\substack{1 \leq b < c \leq N \\ (b, c \neq a)}} \langle \hat{u}_{k_b k_c}^K, \hat{u}_{k_b k_c}^K \rangle + 0(\langle \hat{u}_{ij}, \hat{u}_{ij} \rangle^2), \quad (27)$$

$$D_{k_a k_b; m}^K = 1 + \sum_{\substack{1 \leq c < d \leq N \\ (c, d \neq a, b)}} \langle \hat{u}_{k_c k_d}^K, \hat{u}_{k_c k_d}^K \rangle + \sum_{c=1}^N \langle \hat{u}_{k_c m}^K, \hat{u}_{k_c m}^K \rangle + 0(\langle \hat{u}_{ij}, \hat{u}_{ij} \rangle^2), \quad (28)$$

$$D_{k_a k_b}^K = 1 + \sum_{c=1}^N \langle \hat{f}_{k_c}^{(P)K}, \hat{f}_{k_c}^{(P)K} \rangle + \sum_{\substack{1 \leq c < d \leq N \\ (c, d \neq a, b)}} \sum_{m=1}^M \langle \hat{f}_{k_c k_d; m}^K, \hat{f}_{k_c k_d; m}^K \rangle + \sum_{\substack{1 \leq c < d \leq N \\ (c, d \neq a, b)}} \langle \hat{u}_{k_c k_d}^K, \hat{u}_{k_c k_d}^K \rangle \\ + 0[(\text{correlation functions})^4]. \quad (29)$$

Note that for a given correlation process D^K may be $\neq D^L$, so that in addition to the renormalization effects, the $\bar{\epsilon}^K$ and $\bar{\epsilon}^L$ are given unequal weights.

Average Correlation Energies

Average correlation energies defined below are useful for physical interpretations, a semiempirical theory, and comparison of correlation effects from one system to the next. Denote the fractional occupancy of Spin Orbital k by ρ_k , of the pair (kl) by ρ_{kl} , and of the [pair (kl) + hole m] by $\rho_{kl; m}$

$$\rho_k = \sum_K |C_K|^2, \quad (k \text{ in } K) \quad (30)$$

$$\rho_{kl; m} = \sum_K |C_K|^2, \quad (k, l \text{ in } K; m \text{ not in } K) \quad (31)$$

$$\rho_{kl} = \sum_K |C_K|^2, \quad (k, l \text{ in } K) \quad (32)$$

Then the average correlation energies are defined by

$$[\bar{\epsilon}_k^{(P)}]' = \rho_k^{-1} \sum_K |C_K|^2 \bar{\epsilon}_k^{(P)K} D_k^K / D', \quad (k \text{ in } K) \quad (33)$$

$$[\bar{\epsilon}_{kl; m}]' = \rho_{kl; m}^{-1} \sum_K |C_K|^2 \bar{\epsilon}_{kl; m}^K D_{kl; m}^K / D', \quad (k, l \text{ in } K; m \text{ not in } K) \quad (34)$$

$$[\bar{\epsilon}_{kl}]' = \rho_{kl}^{-1} \sum_K |C_K|^2 \bar{\epsilon}_{kl}^K D_{kl}^K / D', \quad (k, l \text{ in } K) \quad (35)$$

Thus each correlation process contributes to E'_d an average energy weighted by the fractional occupation of its spin orbitals in ϕ_{GRHF} :

$$E'_d = E_{\text{GRHF}} + \sum_{k=1}^M \rho_k [\bar{\epsilon}_k^{(P)}]' \\ + \sum_{\substack{1 \leq k < l \leq M \\ (m \neq k, l)}} \sum_{m=1}^M \rho_{kl; m} [\bar{\epsilon}_{kl; m}]' + \sum_{1 \leq k < l \leq M} \rho_{kl} [\bar{\epsilon}_{kl}]' \\ + (\text{"diagonal"} \text{ two-determinant terms}) \\ + (\text{significant "cross-correlation"} \text{ terms}) \\ + R'/D'. \quad (36)$$

 E'_d in the Closed-Shell Limit

For a closed-shell state, ϕ_{GRHF} is just the single determinantal ϕ_{HF} , $E_{\text{GRHF}} = E_{\text{HF}}$, the \hat{f}_k^P and $\hat{f}_{kl; m}$ vanish, there are no significant cross-correlation or two-determinant terms, $\rho_{kl} = 1$, and E'_d will become

$$E'_d = E_{\text{HF}} + \sum_{k < l} \bar{\epsilon}_{kl} D_{kl} / D' + R'/D'. \quad (37)$$

This equation has the same form as the analogous E'_s of the closed-shell theory, [Eq. (49) of Ref. 3]. Finally, it is easy to verify that Eq. (20) for $\bar{\epsilon}_{kl}$ becomes identical with the closed shell $\bar{\epsilon}_{kl}$ [Eq. (39b) of Ref. 3].

IV. SYMMETRY CONSIDERATIONS

For the approximate correlation wavefunction χ'_d to have the same symmetry properties (specified in atoms

by parity and the angular-momentum quantum numbers, in molecules by spin and the irreducible representation of the spatial symmetry group) as the exact wavefunction ψ , certain symmetry relationships among the correlation functions must be satisfied. Symmetry relationships for closed-shell correlation functions have been discussed briefly.^{4,5,8,9} To discuss symmetry properties in detail will require a separate paper,¹⁰ so here we only state a few of the results.

A symmetry operation R takes Spin Orbital j into a linear combination of spin orbitals of the same subshell. Denote by λ the direct product of the spin irreducible representation with the spatial irreducible representation of the appropriate symmetry groups, which corresponds to the subshell of j . Denote by $D^{(\lambda)}(R)$ the matrices of the representation. Then

$$R |j\rangle = \sum_i^{(\lambda)} D^{(\lambda)}(R)_{ij} |i\rangle \quad (38)$$

(i runs over all spin orbitals in the λ subshell).

The symmetry properties of the $\hat{f}_k^{(P)K}$ and $\hat{f}_{k_a k_b; m}^{K}$ are independent of the \hat{u}_{ij} , and they are found in a straightforward manner by the usual vector-coupling methods. In general, $\hat{f}_k^{(P)K}$ and $\hat{f}_l^{(P)L}$ are related when K and L correspond to the same configuration, and k and l to the same subshell. The $\hat{f}_k^{(P)K}$ and $\hat{f}_{k_a k_b; m}^{K}$ may also be related to each other (see Sec. VII for examples). It does not seem possible to state the symmetry relations among the \hat{f} 's directly in terms of the (k) and ($k_a k_b; m$).

The pair functions arising from the same configuration in ϕ_{GRHF} and the same pair of subshells transform according to the same law as the (antisymmetrized) pairs of spin orbitals they replace. Let λ denote the subshell of j , μ the subshell of k , and let l run over the λ subshell, m the μ subshell. Let the parentage superscript K denote the configuration (rather than the determinant). Then

$$R \hat{u}_{jk}^K = \sum_l^{(\lambda)} \sum_m^{(\mu)} D^{(\lambda)}(R)_{lj} D^{(\mu)}(R)_{mk} \hat{u}_{lm}^K, \quad (\text{for } \lambda \neq \mu), \quad (39)$$

$$R \hat{u}_{jk}^K = \sum_l^{(\lambda)} \sum_m^{(\mu)} \{ D^{(\lambda)}(R)_{lj} D^{(\mu)}(R)_{mk} - D^{(\lambda)}(R)_{mj} D^{(\mu)}(R)_{lk} \} \hat{u}_{lm}^K, \quad (\text{for } \lambda = \mu). \quad (40)$$

For χ'_a , Eqs. (39) and (40) hold without the parentage superscript K .

Under the above conditions, χ'_a (or χ'_s) has the same symmetry properties as the exact ψ .¹⁰

V. EQUATIONS FOR CALCULATING THE ONE- AND TWO-ELECTRON CORRELATION FUNCTIONS

In this section we discuss how to calculate χ'_a and E'_a variationally. The direct variational principle approach—to make the entire E'_a [Eq. (25)] stationary with respect to variations of the $\hat{f}_k^{(P)K}$, $\hat{f}_{kl; m}^{K}$, and \hat{u}_{kl}^K —is too difficult to apply because of the large number of small, difficult integrals coupling the various correlation functions. We use the variation-perturbation approach,⁵ where one first minimizes a large portion of E'_a , chosen to eliminate the negligible coupling terms (but not necessarily all the coupling terms).

If all the coupling terms in E'_a were negligible, then each correlation function could be determined independently. Coupling terms are usually quite small for closed-shell states, but for open shells, cross-correlation coupling terms are significant [e.g., Eqs. (23) and (64)]. The unlinked cluster quotients, D^K/D' [Eqs. (25)–(29)], also couple the correlation functions.

The D_{ij}^K/D' coupling can be avoided by approximating D_{ij}^K/D' with a function depending only on $\langle \hat{u}_{ij}^K, \hat{u}_{ij}^K \rangle$. A general form for this “unlinked cluster cancellation” is

$$D_{ij}^K/D' \approx [A_{ij}^K + B_{ij}^K \langle \hat{u}_{ij}^K, \hat{u}_{ij}^K \rangle]^{-1}. \quad (41)$$

The constants A_{ij}^K and B_{ij}^K should be chosen so that (41) represents both the numerical value of D_{ij}^K/D' and its functional dependence on $\langle \hat{u}_{ij}^K, \hat{u}_{ij}^K \rangle$. Similarly, for D_k^K/D' and $D_{kl; m}^K/D'$, we write:

$$D_k^K/D' \approx [A_k^K + B_k^K \langle \hat{f}_k^{(P)K}, \hat{f}_k^{(P)K} \rangle]^{-1} \quad (42)$$

$$D_{kl; m}^K/D' \approx [A_{kl; m}^K + B_{kl; m}^K \langle \hat{f}_{kl; m}^{K}, \hat{f}_{kl; m}^{K} \rangle]^{-1}. \quad (43)$$

For closed-shell states,^{4,5} $A_{ij} \approx B_{ij} = 1$. For open-shell states, we make the following general approximations:

$$A_{ij}^K \approx A_k^K \approx A_{kl; m}^K \approx 1; B_{ij}^K \approx \rho_{ij}; B_k^K \approx \rho_k; B_{kl; m}^K \approx \rho_{kl; m},$$

$$D_k^K/D' \approx [1 + \rho_k \langle \hat{f}_k^{(P)K}, \hat{f}_k^{(P)K} \rangle]^{-1}, \quad (44)$$

$$D_{kl; m}^K/D' \approx [1 + \rho_{kl; m} \langle \hat{f}_{kl; m}^{K}, \hat{f}_{kl; m}^{K} \rangle]^{-1}, \quad (45)$$

$$D_{ij}^K/D' \approx [1 + \rho_{ij} \langle \hat{u}_{ij}^K, \hat{u}_{ij}^K \rangle]^{-1}. \quad (46)$$

The errors in the approximate A 's are of the order of correlation function lengths squared. In specific applications one might wish to obtain more accurate estimates of the A 's and B 's either numerically or by using symmetry. [See Eq. (63) for an example.]

The correlation functions, when calculated variationally, do not automatically satisfy the symmetry relationships [e.g., Eqs. (39) and (40)] (except in the case of perturbation theory).^{1,5} That out of $N(N-1)/2$ pairs, there are only about N distinct, independent ones, many differing from each other only by M_L , M_S or by orientation was discussed previously.^{3,4,8} Thus, the symmetry-related correlation

⁸ O. Sinanoğlu, Proc. Roy. Soc. (London) **A260**, 379 (1961).

⁹ H. B. Levine, M. Geller, and H. S. Taylor, J. Chem. Phys. **40**, 595 (1964).

¹⁰ H. J. Silverstone and O. Sinanoğlu (to be published).

functions must naturally be set equal throughout variations or be varied simultaneously.

To leave in the portion of E'_d to be minimized, the significant "cross correlations" (a nonclosed-shell phenomenon) which couple correlation functions already related by symmetry, clearly does not add much computational difficulty. In the first-order case (I) variation of pairs with or without cross terms gives the same result. Thus, one may obtain separate variational

equations for sets of symmetry-related correlation functions by using the approximations (44)–(46) and neglecting cross terms of symmetry-unrelated functions at first. From the functions obtained, one can then calculate the remaining cross-term matrix elements to see if they are really small. If not, variation of the larger portion, involving these terms too, will be needed.

The variational equations for the separate sets of symmetry-related functions are

$$\delta_{\text{sym}} \left\{ \sum_K \sum_k |C_K|^2 \tilde{\epsilon}_k^{(P)K} (1 + \rho_k \langle \hat{f}_k^{(P)K}, \hat{f}_k^{(P)K} \rangle)^{-1} + \sum_K \sum_{k < l} \sum_m |C_K|^2 \tilde{\epsilon}_{kl;m}^{K} (1 + \rho_{kl;m} \langle \hat{f}_{kl;m}^K, \hat{f}_{kl;m}^K \rangle)^{-1} + \sum_{K < L} C_K C_L \tilde{\epsilon}'[\hat{f}^K \times \hat{f}^L] \right\} = 0, \quad (47)$$

(sym. rel. set)

$$\delta_{\text{sym}} \left\{ \sum_K \sum_{k < l} \sum_m |C_K|^2 \tilde{\epsilon}_{kl;m}^{K} (1 + \rho_{kl;m} \langle \hat{f}_{kl;m}^K, \hat{f}_{kl;m}^K \rangle)^{-1} + \sum_{K < L} C_K C_L \tilde{\epsilon}'[\hat{f}^K \times \hat{f}^L] \right\} = 0, \quad (48)$$

(sym. rel. set)

$$\delta_{\text{sym}} \left\{ \sum_K \sum_{k < l} |C_K|^2 \tilde{\epsilon}_{kl}^{K} (1 + \rho_{kl} \langle \hat{u}_{kl}^K, \hat{u}_{kl}^K \rangle)^{-1} + \sum_{K < L} C_K C_L \tilde{\epsilon}'(ij; kl) \right\} = 0. \quad (49)$$

(sym. rel. set)

The summations in each case run over a set of correlation functions interrelated by symmetry (symmetry-related set). The δ_{sym} indicates that symmetry relations must hold during the variation. Note that some $\hat{f}_{kl;m}$ are related to \hat{f}_i [Eq. (47)] while others are not [Eq. (48)]. The $\tilde{\epsilon}'[\hat{f}^K \times \hat{f}^L]$ and $\tilde{\epsilon}'(ij; kl)$ stand for significant cross-correlation terms. "Diagonal" two-determinant terms are meant to be included implicitly in the diagonal or cross-correlation terms. (For the relation of variational equations to the corresponding differential equations, and for a discussion of other possible choices of the portion of E to be minimized in the closed-shell case, see Refs. 4 and 5.)

Anonymous Parentage

In the χ'_s case [Eq. (9)] we can easily find equations similar to Eqs. (47)–(49). First define the average correlation energies [c.f. Eqs. (33)–(35)] without unlinked cluster effects. For instance,

$$[\tilde{\epsilon}_k^{(P)}]_{\text{Av}} = \rho_k^{-1} \sum_K |C_K|^2 \tilde{\epsilon}_k^{(P)K} \quad (k \text{ in } K) \quad (50)$$

and similarly for $[\tilde{\epsilon}_{kl;m}]_{\text{Av}}$ and $[\tilde{\epsilon}_{kl}]_{\text{Av}}$. Then the corresponding variational equations appropriate for χ'_s are, e.g.,

$$\delta_{\text{sym}} \left\{ \sum_k \rho_k [\tilde{\epsilon}_k^{(P)}]_{\text{Av}} (1 + \rho_k \langle \hat{f}_k^{(P)}, \hat{f}_k^{(P)} \rangle)^{-1} + \sum_{k < l} \sum_m \rho_{kl;m} [\tilde{\epsilon}_{kl;m}]_{\text{Av}} (1 + \rho_{kl;m} \langle \hat{f}_{kl;m}, \hat{f}_{kl;m} \rangle)^{-1} + \sum_{K < L} C_K C_L \tilde{\epsilon}'[\hat{f} \times \hat{f}] \right\} = 0 \quad (51)$$

(sym. rel. set)

and similarly for $[\tilde{\epsilon}_{kl}]_{\text{Av}}$, etc. Note that cross-correlation terms in Eq. (51) are more inclusive than those in Eq. (47), because correlation functions from separate configurations may now be related by symmetry.

It is interesting to note that the $[\tilde{\epsilon}]_{\text{Av}}$ represent energies for the correlation processes occurring in average Coulomb and exchange fields. For instance, let

$$V_k = \rho_k^{-1} \sum_K |C_K|^2 \sum_{a=1}^N \tilde{S}_{ka} \quad (k \text{ in } K) \quad (k_a \neq k) \quad (52)$$

and

$$\eta_k = \rho_k^{-1} \sum_K |C_K|^2 \eta_k^K \quad (k \text{ in } K) \quad (53)$$

Then,

$$[\tilde{\epsilon}_k^{(P)}]_{\text{Av}} = 2 \langle k, (h^0 + V_k) \hat{f}_k^{(P)} \rangle + \langle \hat{f}_k^{(P)}, (h^0 + V_k - \eta_k) \hat{f}_k^{(P)} \rangle. \quad (54)$$

Again analogous equations hold for the other $[\tilde{\epsilon}]_{\text{Av}}$.

Comments on Nonempirical Calculations

The basic variation-perturbation equations for calculating χ'_a are Eqs. (47)–(49), and for χ'_s are Eq. (51) and its equivalent. A \hat{u}_{ij} (or \hat{f}) is obtained independently of other \hat{u} 's (or \hat{f} 's) to which the \hat{u}_{ij} (or \hat{f}) is not related by symmetry. To keep the correct symmetry relations in a nonempirical calculation, express the related correlation functions in terms of "irreducible" correlation functions,^{4,10} and then vary the individual irreducible components. To varying approximations, other types of pairs may be varied too (for closed-shell case see Ref. 4).

Use of Eqs. (47)–(49) or (51), etc., *without any cross terms* may be sometimes justifiable numerically as mentioned above. In perturbation theory [I, Eqs. (52)–(58)] neglect or retention of cross terms leads to identical results.

The $\hat{f} \times \hat{u}$ and other cross-correlation terms coupling symmetry-unrelated functions were neglected to obtain decoupled equations. If in a specific problem some of these terms are large, one may have to solve coupled equations for the symmetry-unrelated functions.

We also made the unlinked cluster cancellation approximations [Eqs. (41)–(46)] to decouple the correlation functions. When the correlation functions have been calculated, one can make better estimates of the A 's and B 's. These more accurate values are probably more important in calculating E'_a than in calculating the correlation functions themselves.

When calculating E'_a , *all* significant cross-correlation terms should be included, even though some were not included in the part of E'_a minimized. To obtain an upper bound to the exact E , the remainder terms [R'/D' , Eq. (36)] must also be estimated.

VI. SEMIEMPIRICAL CORRELATION THEORY

Equation (36) forms a theoretical basis for a semiempirical correlation theory. The average pair correlation energies $[\bar{\epsilon}_{kl}]'$ are of the dynamical type,^{11,12} vary slowly as the system changes, and may be evaluated empirically. The significant $\bar{\epsilon}'(ij; kl)$ "cross correlations" can be found empirically using symmetry. We expect the $[\bar{\epsilon}_k^{(P)}]'$, $[\bar{\epsilon}_{kl;m}]'$, and $\bar{\epsilon}[\hat{f} \times \hat{f}]$ cross-correlation terms to be quite sensitive to symmetry and exclusion effects and not available for empirical evaluation. The ϕ_{GRHF} , E_{GRHF} , ρ_k , $\rho_{kl;m}$, ρ_{kl} , the polarization and semi-internal correlation energies, and the $\bar{\epsilon}[\hat{f} \times \hat{f}]$ cross-correlation terms must be obtained nonempirically. If the theory is to be based on a Roothaan-type RHF, the $E_{\text{int}}^{\text{RHF}} \approx E_{\text{GRHF}} - E_{\text{RHF}}$ (which is essentially the near-degeneracy-type nondynamical correlation energy) is extremely sensitive to exclusion effects^{2b,12} and must be obtained nonempirically.

¹¹ D. F. Tuan and O. Sinanoğlu, *J. Chem. Phys.* **41**, 2677 (1964).

¹² V. McKoy and O. Sinanoğlu, in *Modern Quantum Chemistry—Istanbul Lectures*, O. Sinanoğlu, Ed. (Academic Press Inc., New York, 1965), Pt. II.

A workable semiempirical correlation energy procedure would be:

- (1) Calculate ϕ_{RHF} by Roothaan's procedure. (See I, Refs. [13] and [14].)
- (2) Estimate ϕ_{GRHF} and $E_{\text{int}}^{\text{RHF}}$ by near-degeneracy-type CI [Eq. (17) of I].
- (3) Calculate $[\bar{\epsilon}_k^{(P)}]'$, $[\bar{\epsilon}_{kl;m}]'$, and $\bar{\epsilon}'[\hat{f} \times \hat{f}]$ terms nonempirically [Eqs. (54), (48), (47), (34), and (33)].
- (4) Evaluate empirically the remaining pair terms according to the formula

$$\sum_{k < l} \rho_{kl} [\bar{\epsilon}_{kl}]' + \{\text{significant cross-correlation terms}\}.$$

VII. EXAMPLES

The following examples illustrate some aspects of the nonclosed-shell many-electron theory. This theory has also been applied to atomic valence state energy calculations on C, N, and O for use in the π -electron treatment of molecules such as pyridine, furane, etc.¹³ (See also the appendix of that paper,¹³ for general Hartree-Fock and correlation theory of valence states).

Lithium

Orbital Wavefunction

$$\phi_{\text{GRHF}}(^2S\text{-Li}) = \phi_{\text{RHF}} = \alpha \{ (1s\alpha)(1s\beta)(2s\alpha) \}. \quad (55)$$

The spin orbitals are eigenfunctions of a one-electron Hamiltonian with the Roothaan SCF potential V_R given by

$$\begin{aligned} V_R(\text{Li}) = & 2J_{1s} - K_{1s} - \frac{1}{2}(2J_{2s} - K_{2s}) \\ & + (|1s\rangle\langle 1s| + \frac{1}{2}|2s\rangle\langle 2s|)(2J_{2s} - K_{2s}) \\ & + (2J_{2s} - K_{2s})(|1s\rangle\langle 1s| + \frac{1}{2}|2s\rangle\langle 2s|), \quad (56) \end{aligned}$$

where the J_i and K_i are (spinless) Coulomb and exchange operators.

Correlation Wavefunction

Since ϕ_{GRHF} is a single determinant, $\chi'_a = \chi'_s$. Explicitly, χ'_a is

$$\begin{aligned} \chi'_a = & \alpha \{ (\hat{f}_{1s\alpha}^{(P)})(1s\beta)(2s\alpha) + 2^{-\frac{1}{2}} \hat{f}_{1s\alpha}^{(P)} \hat{u}_{1s\beta, 2s\alpha} \\ & + (1s\alpha)(\hat{f}_{1s\beta}^{(P)})(2s\alpha) + 2^{-\frac{1}{2}} \hat{f}_{1s\beta}^{(P)}(\mathbf{X}_2) \hat{u}_{1s\alpha, 2s\alpha}(\mathbf{X}_1, \mathbf{X}_3) \\ & + (1s\alpha)(2s\beta)(\hat{f}_{1s\beta, 2s\alpha; 2s\beta}) + 2^{-\frac{1}{2}} \hat{u}_{1s\alpha, 2s\beta} \hat{f}_{1s\beta, 2s\alpha; 2s\beta} \\ & + 2^{-\frac{1}{2}} \hat{u}_{(1s)^2}(2s\alpha) + 2^{-\frac{1}{2}}(1s\alpha) \hat{u}_{1s\beta, 2s\alpha} \\ & + 2^{-\frac{1}{2}}[1s\beta(\mathbf{X}_2)] \hat{u}_{1s\alpha, 2s\alpha}(\mathbf{X}_1, \mathbf{X}_3) \}. \quad (57) \end{aligned}$$

Symmetry Relationships

Equations (58) and (59) express the spin-polarizing nature of the $\hat{f}_{1s}^{(P)}$. Equation (60) is a consequence of

¹³ M. K. Orloff and O. Sinanoğlu, *J. Chem. Phys.* **43**, 49 (1965).

symmetry and Eqs. (58) and (59). Write

$$\hat{f}_{1s\alpha}^{(P)} = \hat{f}\alpha. \quad (58)$$

Then

$$\hat{f}_{1s\beta}^{(P)} = -\hat{f}\beta, \quad (59)$$

$$\hat{f}_{1s\beta, 2s\alpha; 2s\beta} = -2\hat{f}\alpha. \quad (60)$$

For the pair functions, it is easy to show from Eqs. (39) and (40), or from more direct considerations,^{4,5,8,9} that \hat{u}_{1s^2} is a 1S function, $\hat{u}_{1s\alpha, 2s\alpha}$ and $\hat{u}_{1s\beta, 2s\beta}$ are two components of a 3S , the third component contributing equally to $\hat{u}_{1s\alpha, 2s\beta}$ and $\hat{u}_{1s\beta, 2s\alpha}$, and that the remaining 1S parts of $\hat{u}_{1s\alpha, 2s\beta}$ and $\hat{u}_{1s\beta, 2s\alpha}$ differ only in sign.

Variational Equation for \hat{f}

With Eqs. (58)–(60), Eq. (47) becomes an equation for \hat{f} . We write this equation explicitly. Define

$$\eta = \langle (1s), h^0(1s) \rangle + J_{1s, 1s} + J_{1s, 2s} - \frac{3}{2}K_{1s, 2s} \quad (61)$$

and

$$\Delta V \equiv J_{1s} - K_{1s} + J_{2s} + \frac{1}{2}K_{2s} - V_R. \quad (62)$$

Then, using Eqs. (58)–(60) to make a better unlinked

cluster cancellation approximation than Eqs. (44) and (45),

$$D_{1s\alpha}/D' \approx D_{1s\beta}/D' \approx D_{1s\beta, 2s\alpha; 2s\beta}/D' \approx [1 + 6\langle \hat{f}, \hat{f} \rangle]^{-1}. \quad (63)$$

We obtain after some manipulation the variational equation for \hat{f} :

$$\begin{aligned} \delta_{\text{sym}} \{ & (\bar{\epsilon}_{1s\alpha}^{(P)} + \bar{\epsilon}_{1s\beta}^{(P)} + \bar{\epsilon}_{1s\beta, 2s\alpha; 2s\beta} \\ & + \bar{\epsilon}[f_{1s\alpha}^{(P)} \times f_{1s\beta}^{(P)}] + \bar{\epsilon}[f_{1s\alpha}^{(P)} \times \hat{f}_{1s\beta, 2s\alpha; 2s\beta}] \\ & + \bar{\epsilon}[f_{1s\beta}^{(P)} \times f_{1s\beta, 2s\alpha; 2s\beta}]) / (1 + 6\langle \hat{f}, \hat{f} \rangle) \} \\ = & 6\delta_{\text{sym}} \{ [2\langle \hat{f}, (-\frac{1}{2}K_{2s})(1s) \rangle \\ & + \langle \hat{f}, (h^0 + V_R + \Delta V - \eta)\hat{f} \rangle] \\ & \times (1 + 6\langle \hat{f}, \hat{f} \rangle)^{-1} \} = 0. \end{aligned} \quad (64)$$

Carbon

The 1S -state of the $(1s)^2(2s)^2(2p)^2$ configuration of carbon has symmetry orbital average polarizations and is also a case where the anonymous parentage approximation cannot be used. The ϕ_{GRHF} has the form

$$\begin{aligned} \phi_{\text{GRHF}} = & \mathcal{G} \left\{ C_1(1s\alpha)(1s\beta)(2s\alpha)(2s\beta) \frac{(2p_x\alpha)(2p_x\beta) + (2p_y\alpha)(2p_y\beta) + (2p_z\alpha)(2p_z\beta)}{\sqrt{3}} \right. \\ & + \left[C_2(1s\alpha)(1s\beta) + C_3(2s\alpha)(2s\beta) + C_4 \frac{(1s\alpha)(2s\beta) + (2s\alpha)(1s\beta)}{\sqrt{2}} \right] \\ & \times \left[\frac{(2p_x\alpha)(2p_x\beta)(2p_y\alpha)(2p_y\beta) + (2p_x\alpha)(2p_x\beta)(2p_z\alpha)(2p_z\beta) + (2p_y\alpha)(2p_y\beta)(2p_z\alpha)(2p_z\beta)}{\sqrt{3}} \right. \\ & \left. \left. + C_5(2p_x\alpha)(2p_x\beta)(2p_y\alpha)(2p_y\beta)(2p_z\alpha)(2p_z\beta) \right\}. \end{aligned} \quad (65)$$

Let d_m , ($m=2, 1, 0, -1, -2$), denote five one-electron functions corresponding to d symmetry ($l=2$). The function $\phi(d)$ mixes directly with ϕ_{GRHF} .

$$\begin{aligned} \phi(d) = & 5^{-1/2} \mathcal{G} \left\{ (1s\alpha)(1s\beta) \left[(2s)(d_{-2})(2p_+)(2p_+) - (2s)(d_{-1}) \frac{(2p_+)(2p_0) + (2p_0)(2p_+)}{\sqrt{2}} \right. \right. \\ & + (2s)(d_0) \frac{2(2p_x)(2p_x) - (2p_x)(2p_x) - (2p_y)(2p_y)}{(6)^{1/2}} \\ & \left. \left. - (2s)(d_1) \frac{(2p_-)(2p_0) + (2p_0)(2p_-)}{\sqrt{2}} + (2s)(d_2)(2p_-)(2p_-) \right] \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \alpha\beta \right\}. \end{aligned} \quad (66)$$

From $\phi(d)$ there are contributions to $f_{2s\beta}^{(P)}$ given (symbolically) by Eqs. (67)–(69). [X denotes $(1s)^2(2s)^2(2p_x)^2$, Y denotes $(1s)^2(2s)^2(2p_y)^2$, and Z denotes $(1s)^2(2s)^2(2p_z)^2$]

$$\hat{f}_{2s\beta}^{(P)X} = [-(1/20)^{1/2}d_0 + (3/40)^{1/2}(d_2 + d_{-2})]\beta, \quad (67)$$

$$\hat{f}_{2s\beta}^{(P)Y} = [-(1/20)^{1/2}d_0 - (3/40)^{1/2}(d_2 + d_{-2})]\beta, \quad (68)$$

$$\hat{f}_{2s\beta}^{(P)Z} = (1/5)^{1/2}d_0\beta. \quad (69)$$

Note first that these symmetry polarizations “add d character to the $(2s\beta)$ spin orbital”, and second

that the average $\hat{f}_{2s\beta}^{(P)}$ vanishes, making the anonymous parentage approximation inappropriate. Note also that Eqs. (67)–(69) may be used to simplify the energy expressions.

Ethylene Positive Ion

The HF ϕ_0 for the ground state of the ethylene positive ion (C_2H_4^+) can be written

$$\begin{aligned} \phi_{\text{GRHF}} = & \phi_{\text{RHF}} \\ = & \mathcal{G} \{ \sigma_1^2 \sigma_2^2 \sigma_3^2 \sigma_4^2 \sigma_5^2 \sigma_6^2 \sigma_7^2 \pi_1 \}. \end{aligned} \quad (70)$$

The σ_i , ($i=1, 2, \dots, 7$), are the seven HF σ orbitals, and π_1 is the HF orbital of the π electron. There is no significant (first-order) internal correlation. Spin polarizing $f_i^{(P)}$'s, and $f_{ij,k}$'s arise from excitations ($\sigma \rightarrow g$ where g is an arbitrary excited orbital) of the type

$$\sigma_i^2 \pi_1 \rightarrow g \sigma_i \pi_1 (\alpha\beta\alpha + \beta\alpha\alpha - 2\alpha\alpha\beta), \quad (71)$$

$$\hat{f}_{\sigma_i\alpha}^{(P)} = g\alpha, \quad (72)$$

$$\hat{f}_{\sigma_i\beta}^{(P)} = -g\beta, \quad (73)$$

$$\hat{f}_{\sigma_i\beta, \pi_1\alpha; \pi_1\beta} = -2g\beta, \quad (74)$$

$$\Delta V_{\sigma_i} = \sum_{j=1}^7 (\bar{S}_{\sigma_j\alpha} + \bar{S}_{\sigma_j\beta}) + \bar{S}_{\pi_1\alpha} - \bar{S}_{\sigma_i} - V_R. \quad (75)$$

These $\hat{f}_{\sigma_i}^{(P)}$ are very important in electron spin resonance, since they are responsible for the nonzero spin densities at the protons. The pair functions $\hat{u}_{\sigma_i\sigma_i}$, $\hat{u}_{\sigma_i\sigma_j}$ (for all spin combinations), and $\hat{u}_{\sigma_i\pi_1}$ (for all spin combinations), are one-electron orthogonal to $\sigma_i\alpha$, $\sigma_i\beta$, ($i=1, 2, \dots, 7$), and to $\pi_1\alpha$ and $\pi_1\beta$. Excitations of the type $\sigma_i^2 \pi_1 \rightarrow \sigma_i g \pi_1 (\alpha\beta\alpha - \beta\alpha\alpha)$ should not contribute

significantly to $f_{\sigma_i}^{(P)}$ because of the extremum property of ϕ_{GRHF} .

VIII. SUMMARY

We obtained a variational nonclosed-shell many-electron wavefunction by making the first-order correlation functions "exact to all orders" and by including unlinked clusters. The variational energy contains energies for each correlation process (orbital average polarizations, semi-internal correlations, and external pair correlations), weighted by the fractional occupancy of the spin orbitals, and significant cross-correlation energies not found in closed-shell states. By neglecting terms coupling correlation functions not related by symmetry, we obtain independent variational equations for sets of symmetry-related functions. The members of each set, however, are coupled to one another (at least by symmetry). The pair correlation energies and cross-correlation terms may be obtained semiempirically, but the other significant correlation terms are quite sensitive to symmetry and exclusion effects and must be calculated nonempirically.

Kinetic Isotope Effects in the Reaction between Atomic Chlorine and Molecular Hydrogen. Tunnel Coefficients of the Hydrogen Atom through an Asymmetric Potential Barrier

AVIGDOR PERSKY AND FRITZ S. KLEIN

Isotope Department, Weizmann Institute of Science, Rehovoth, Israel

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Kinetic isotope effects for the reactions between atomic chlorine and molecular hydrogen have been measured in the range of -30° to $+70^\circ\text{C}$. The following expressions were obtained:

$$R_{\text{H}_2/\text{HT}} = (1.27 \pm 0.03) \exp[(797 \pm 14)/RT],$$

$$R_{\text{H}_2/\text{D}_2} = (1.44 \pm 0.06) \exp[(1128 \pm 17)/RT],$$

$$R_{\text{H}_2/\text{DT}} = 1.53_4 \exp(1422/RT),$$

$$R_{\text{H}_2/\text{T}_2} = 1.54_5 \exp(1693/RT).$$

The isotope effect of HD,

$$R_{\text{H}_2/\text{HD}} = (1.24 \pm 0.03) \exp[(490 \pm 6)/RT],$$

has been redetermined and found to agree with previous measurements.

Theoretical calculations of these isotope effects, using (1) a Sato model, (2) a generalized Sato model, and (3) the Johnston-Parr method, were made to compare the calculated effects with experimental results.

Tunnel corrections were applied using (1) an asymmetric Eckart barrier, or (2) the Johnston-Rapp method with an asymmetric barrier. Best agreement (within 15%) of calculated values with experiment was obtained for a generalized Sato model including Johnston-Rapp tunnel corrections. Empirical sets of four force constants describing the transition state H-H-Cl are also given. These are used to calculate isotope effects which are in excellent agreement with experimental values.

ONE of the strongest experimental supports for the transition-state theory¹ has been coming forth in recent years from precision measurements of kinetic isotope effects² in elementary reactions,³⁻⁶ while the

most successful theoretical approach to reactions between atoms or radicals and simple molecules has been given by the quantum-chemical concept of the transition state.⁷⁻⁹

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