The Coupled-Cluster Method with a Multiconfiguration Reference State

AJIT BANERJEE AND JACK SIMONS*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Abstracts

The coupled-cluster approach to obtaining the bond-state wave functions of many-electron systems is extended, with a set of physically reasonable approximations, to admit a multiconfiguration reference state. This extension permits electronic structure calculations to be performed on correlated closed- or open-shell systems with potentially uniform precision for all molecular geometries. Explicit coupled cluster working equations are derived using a multiconfiguration reference state for the case in which the so-called cluster operator is approximated by its one- and two-particle components. The evaluation of the requisite matrix elements is facilitated by use of the unitary group generators which have recently received wide attention and use in the quantum chemistry community.

Le procédé des amas couplés pour obtenir des fonctions d'onde pour les états liés d'un système à N électrons a été généralisé dans le cadre d'un nombre d'approximations raisonnables du point de vue physique, pour utiliser un état de référence multiconfigurationnel. Cette extension permet des calculs de la structure électronique pour des systèmes à couches fermées ou ouvertes correlées avec une précision qui est uniforme pour toutes les géométries moléculaires. Des équations explicites sont obtenues avec un état de référence multiconfigurationnel dans le cas où le soi-disant opérateur d'amas est remplacé par ses composantes à une et deux particules. Le calcul des éléments matriciels nécessaires est facilité par l'utilisation des générateurs du groupe unitaire.

Das Verfahren mit gekoppelten "Clusters" für die Berechnung von Wellenfunktionen für gebundene Zustände eines Vielelektronensystems ist im Rahmen gewisser physikalisch angemessenen Näherungen erweitert worden, um einen multikonfigurationellen Referenzzustand zu erlauben. Mit dieser Erweiterung können Berechnungen der Elektronenstruktur von Systemen mit korrelierten abgeschlossenen oder offenen Schalen und mit einer potentiell einheitlichen Genauigkeit für alle Molekülgeometrien ausgeführt werden. Explizite Gleichungen werden mit einem multikonfigurationellen Referenzzustand für den Fall abgeleitet, wo der sogenannte Clusteroperator von seinem Ein- und Zweiteilchenkomponenten angenähert wird. Die Auswertung der erforderlichen Matrixelemente wird durch die Anwendung der Generatoren der unitären Gruppe erleichtert.

1. Introduction

A cluster expansion formalism was developed by Coester [1] for treating N-fermion nuclear systems. Cizek [2] and others [3] expressed this formalism such that it was more suitable for electronic structure calculations on closed-shell systems and actually applied the resulting equations in an *ab initio* framework to the ground states of a few closed-shell molecules [4]. More recently, attempts have been made to extend the formalism to open-shell systems [5, 6] and Freeman et al. [7] have applied the method to the uniform electron gas.

---

* Camille and Henry Dreyfus Teacher-Scholar, John Simon Guggenheim Fellow.

The basic idea of the coupled cluster (CC) method for closed-shell systems is to express the exact wave function ψ as a cluster expansion in the neighborhood of an independent-particle wave function (a single Slater determinant) Φ containing N electrons:

$$\psi = e^T \Phi = \exp\left(\sum_s T_s\right)(N!)^{-1/2} \det|\phi_\alpha, \phi_\beta, \ldots|, \tag{1}$$

where, for example, a second-order cluster operator $T_2 = \sum_{rs\alpha\beta} t_{\alpha\beta}^{rs} a_r^\dagger a_s^\dagger a_\beta a_\alpha$ produces $(T_2\Phi)$ two-particle "excited" configurations when operating on Φ. The Schrödinger equation

$$(H-E)\psi = (H-E)\,e^T\Phi = 0 \tag{2}$$

is then projected against sufficient set of excited functions $|\Phi_{\alpha\beta}^{rs\cdots}\rangle$ to generate a series of equations for determining the cluster amplitudes $t_{\alpha\beta}^{rs\cdots}$,

$$\langle \Phi_{\alpha\beta}^{rs\cdots}|e^{-T}H e^T|\Phi\rangle = 0 \tag{3a}$$

and the electronic energy

$$\langle \Phi|e^{-T}H e^T|\Phi\rangle = E. \tag{3b}$$

The fact that the excited functions $\Phi_{\alpha\beta}^{rs\cdots} = a_r^\dagger a_s^\dagger \cdots a_\beta a_\alpha|\Phi\rangle$ contain the same set of indices as in the corresponding T operators gives a unique set of equations for the amplitudes $t_{\alpha\beta}^{rs\cdots}$. Among the attractive features of this description are (i) that it determines the optimum cluster functions in a fully coupled manner, and (ii) that the method provides a mechanism for obtaining only the linked-cluster (i.e., operators T_s cannot be written as a product of other lower order T_i's) contributions to all physical properties. This latter fact then leads to so-called size-consistent or size-extensive results [unlike results of limited configuration interaction (CI) calculations].

In actual calculations, truncation of the cluster operator manifold (usually up to T_2) has, thus far, been an inevitable practical necessity. Treatment of the most general set of CC equations requires solutions of coupled fourth degree equations. For the T_2 truncated operator manifold, calculations performed at different bond lengths or angles will be of similar precision only if the reference state is of similar precision at these geometries. In general, a Hartree–Fock (HF) reference function would certainly not be expected to give a balanced description at both the equilibrium and distorted geometries of a molecule. In order to extend the CC method such that it is equally applicable to a much more general class of systems (closed- and open-shell molecules near and far from equilibrium geometries), we propose to employ the multiconfiguration reference state coupled cluster method (CCMC) described in detail below.

2. Formal Development

A. Notation

For reasons which are related to the computational efficiency of the resultant expressions as explained in more detail below, we develop the CC equations in

terms of the so called generators [7–10] of the unitary group $\{e_{ij}\}$. The initial applications of such unitary group methods [10, 11] to molecular systems have shown that this approach provides a systematic and very efficient procedure for organizing the density matrix element evaluations which arise in most quantum chemical problems and eliminating redundancies through introducing a "global" organization of the electronic configurations employed in the calculation. The generators of the unitary group can be defined in second quantized form as

$$e_{ij} = \sum_{\sigma} a^{\dagger}_{i\sigma} a_{j\sigma}, \tag{4}$$

where $a^{\dagger}_{i\sigma}$ and $a_{i\sigma}$, respectively, are creation and annihilation operators for an electron in spatial orbital ϕ_i and spin state σ (α or β). These generators satisfy the commutation relations

$$[e_{ij}, e_{kl}]_- = \delta_{jk}e_{il} - \delta_{li}e_{kj}. \tag{5}$$

In terms of these generators the nonrelativistic electronic Hamiltonian has the form

$$H = \sum_{ij} \langle i|h|j\rangle e_{ij} + \frac{1}{2} \sum_{ijkl} \langle ij|v|kl\rangle (e_{ik}e_{jl} - \delta_{jk}e_{il}) \equiv h + v, \tag{6}$$

where h and v are the one- and two-electron parts of the Hamiltonian, respectively, and the elements $\langle i|h|j\rangle \equiv h_{ij}$ and $\langle ij|V|kl\rangle \equiv V_{ijkl}$ refer to the one- and two-electron integrals over the spatial orbital basis $\{\phi_i\}$.

B. Choice of Reference State and Cluster Operators

The multiconfigurational (MC) reference state and the cluster operators T_s which we discuss below have been chosen to preserve some of the essential properties of the HF reference state. The MC reference state has the form

$$\Phi(\mathbf{C}, \boldsymbol{\phi}) = \sum_{k} \chi_K(\boldsymbol{\phi}) C_K, \tag{7}$$

where the $\chi_K(\boldsymbol{\phi})$ are configurations constructed from the set of orbitals $\{\phi_\alpha\}$, $\alpha = 1, \ldots, m$, with $m < \omega$, ω being the total number of basis orbitals. The reference function Φ is now assumed to be a full–CI wave function within the restricted space $\{m\}$. That is, the set χ_K contains all N-electron configurations which can be constructed from the orbital set $\{\phi_\alpha\}$. For calculation of properties in which core–electron correlation effects are of no importance, a well established *approximation* is to "freeze" the set of core orbitals in the description of the wave function. The occupancy of the core orbitals does not vary then among the set $\{\chi_K\}$. For such calculations Φ is taken to be a full-valence CI wave function within the restricted (valence) space $\{m\}$ and the core orbitals remain frozen throughout the calculation (in Φ as well as in the subsequent CC calculation). However, it should be pointed out that the development that follows is independent of whether or not this frozen-core approximation is made. The m orbitals over which Φ is defined are to be chosen as the minimum number of orbitals needed to give the qualitatively essential description of the potential surface. For example, for

the $H_2(^1\Sigma_g^+)$ molecule, $m = 2$, $\{m\} = \{\sigma_g, \sigma_u\}$ and the full-CI reference state is $\Phi = C_1\sigma_g^2 + C_2\sigma_u^2$. For a description of $NH(b^1\Sigma^+)$ in which $1\sigma^2 2\sigma^2$ is defined as the core, the essential configurations at R_e and R_∞ are $3\sigma^2 1\pi^2$ and $3\sigma 4\sigma 1\pi^2$. Thus, $\{m\} = \{3\sigma, 4\sigma\}$, and the full-valence CI reference function Φ contains the $\{3\sigma^2, 3\sigma 4\sigma, 4\sigma^2\}$ configurations. From these examples it is clear that, with a proper and judicious choice of the restricted orbital space $\{m\}$, Φ will contain only a few configurations and is therefore easily calculated. It is important to stress that our intention is to include in Φ only the qualitatively essential configurations needed to describe the state of the molecule at all geometries of interest. We are not, however, attempting to permit Φ itself to include high order electron correlation effects; the CC operator e^T is designed to take care of the latter effects. Particular choices of the orbitals appearing in the configurations of Φ (i.e., specific linear combinations $\phi_i = \sum_j^\omega a_{ij}\xi_j$ of the basis orbitals ξ_j), such as MCSCF or natural orbitals, which might be especially useful in solving the resulting CC equations will be discussed in Section 3.

The cluster operators defined with respect to the above MC reference state Φ are as follows:

$$T = \sum_{s=1}^N T_s,$$

with

$$T_1 = \sum_{r\alpha} t_\alpha^r e_{r\alpha}, \qquad T_2 = \sum_{(rs),\alpha,\beta} t_{\alpha\beta}^{rs} e_{r\alpha} e_{2\beta}, \dots \tag{8}$$

Here the Greek subscripts $\alpha, \beta, \dots$ refer to the "occupied" orbitals of Φ (within a "frozen core" approximation, α does not include the core orbitals) and Roman subscripts $r, s, \dots$ refer to the orbitals not occupied in any configurations of Φ. The notation (rs) implies the restrictions $r \leq s$. Subscripts i, j, k, and l are used later to denote unrestricted summation indices. Following a development very analogous to that arising in the case when Φ is the HF single configuration function, the above choices of MC reference state [Eq. (6)] and cluster operators [Eq. (8)] lead to the following results:

(i) Intermediate normalization of ψ is achieved

$$\langle\Phi|e^T\Phi\rangle = \langle\Phi|\Phi\rangle + \sum_{(rs)\alpha\beta} t_{\alpha\beta}^{rs}\langle\Phi|e_{r\alpha}e_{s\beta}|\Phi\rangle + \cdots = 1, \tag{9}$$

which occurs because $a_r|\Phi\rangle = 0$.

(ii) The Baker–Campbell–Housdorff expansion gives a *finite* commutator series having only five terms

$$e^{-T}He^T = H + [H, T] + \frac{1}{2!}[[H, T], T] + \frac{1}{3!}[[[H, T], T], T]$$

$$+ \frac{1}{4!}[[[[H, T], T], T], T], \tag{10}$$

since H contains at most two-particle operators. Terms of higher order in T in the above series involve commutators of the type $[e_{r\alpha}, e_{s\beta}]$ which are identically zero. This finite exact expansion holds whether or not T is truncated to some order T_s, $S \leq N$.

C. Working Equations

The coupled-cluster wave function has the form

$$\psi = e^T \Phi, \tag{11}$$

where Φ and T are given by Eqs. (7) and (8), respectively. The total energy cluster amplitudes $t_{\alpha\beta}^{rs}$ are determined by projecting the Schrödinger equation (2) against a sufficient set of "excited" functions $\{e_{r\alpha}e_{s\beta} \cdots |\Phi\rangle\}$,

$$\langle\Phi|e^{-T}H e^{-T}|\Phi\rangle = E \tag{12}$$

and

$$\langle\Phi_{\alpha\beta\cdots}^{rs\cdots}|e^{-T}H e^{T}|\Phi\rangle = 0, \tag{13}$$

where

$$e_{r\alpha}e_{s\beta} \cdots |\Phi\rangle \equiv |\Phi_{\alpha\beta\cdots}^{rs\cdots}\rangle. \tag{14}$$

Equation (13) reduces exactly to closed form nonlinear algebraic equations which can be solved for the cluster amplitudes $t_{\alpha\beta\cdots}^{rs\cdots}$. The nonlinearity of the equations is due to intercluster coupling; for example, the coupling between one- and two-particle clusters has the amplitude $t_\alpha^r t_{\lambda\sigma}^{pq}$. Since the qualitatively essential configurations are already contained in the MC reference state Φ, we expect the magnitudes of these amplitudes to be small. Thus it is likely that the difficulties involved in solving, by linearization or iteration methods, the resulting CC equations will be less severe than if Φ were taken to be a single configuration wave function. It is our intention to develop the CCMC equations within the approximation of $T \cong T_1 + T_2$ and retaining up to double commutators in the expansion of Eq. (10). This approximation, i.e., including up to two-particle clusters and their interactions, has been generally accepted to account for most of the electron correlation effects in atoms and molecules.

At this point a few observations regarding the general set of Eqs. (13) should be made. If $\{m\}$ is chosen so that Φ is a single configuration ($=\Phi_{HF}$ for closed shell systems), the above equations reduce exactly to the conventional CC equations with the Φ_{HF} reference state. The equations [Eqs. (13)] advocated here are *not*, in principle, *exact* (except when Φ is a single configuration). This is because the operator manifold T of Eq. (8) is not complete unless it also includes the terms $\sum_{\alpha\mu} t_\mu^\alpha e_{\alpha\mu}, \sum_{\alpha\beta\mu\nu} t_{\mu\nu}^{\alpha\beta} e_{\alpha\mu}e_{\beta\nu}$, etc., which have the effect of generating relaxed amplitudes $t_{\mu\nu\cdots}^{\alpha\beta\cdots}$, or relaxed mixing coefficients C_K for the configurations χ_K in Φ. Our stipulation that Φ be a full (valence) CI wave function within the restricted space $\{m\}$ was introduced to guarantee that these valence orbitals need not be further optimized to any major extent. That is, although the configurations Φ *span*

the configuration space defined over the orbital set $\{m\}$, the mixing coefficients C_K, having been calculated in the absence of configurations involving the remaining orbitals $\{\omega - m\}$, are not completely optimal.

The explicit expressions arising in Eqs. (13) with $T \simeq T_1 + T_2$ are as follows:

(i) The total energy is given by

$$E = \langle H \rangle + \langle [H, T_1] \rangle + \langle [H, T_2] \rangle + \tfrac{1}{2} \langle [[H, T_1], T_1] \rangle, \tag{15a}$$

with

$$\langle H \rangle = \sum_{ij} h_{ij} \langle e_{ij} \rangle + \frac{1}{2} \sum_{ijkl} V_{ijkl} \langle e_{ik,jl} \rangle, \tag{15b}$$

$$\langle [H, T_1] \rangle = \sum_{r\alpha} t_\alpha^r \left(\sum_i h_{ir} \langle e_{i\alpha} \rangle + \sum_{ijk} V_{ijkr} \langle e_{j\alpha,ik} \rangle \right), \tag{15c}$$

$$\langle [H, T_2] \rangle = \sum_{(rs),\alpha,\beta} t_{\alpha\beta}^{rs} \sum_{ij} V_{ijrs} \langle e_{i\alpha,j\beta} \rangle, \tag{15d}$$

$$\langle [[H, T_1], T_1] \rangle = \sum_{r\alpha} t_\alpha^r \sum_{p\lambda} t_\lambda^p \sum_{ij} V_{ijpr} \langle e_{j\alpha,i\lambda} \rangle, \tag{15e}$$

(ii) The cluster coefficients t_α^r and $t_{\alpha\beta}^{rs}$ result from solvings Eqs. (16) and (17):

$$\langle \Phi_\mu^m | e^{-T} H e^T | \Phi \rangle = 0, \tag{16a}$$

which leads to

$$\langle \Phi_\mu^m | H | \Phi \rangle = \sum_i h_{mi} \langle e_{\mu i} \rangle + \sum_{ijk} V_{imkj} \langle e_{ik,\mu j} \rangle, \tag{16b}$$

$$\langle \Phi_\mu^m | [H, T_1] | \Phi \rangle = \sum_{r\alpha} t_\alpha^r \left(h_{mr} \langle e_{\mu\alpha} \rangle - \delta_{mr} \sum_i h_{\alpha i} \langle e_{\mu i} \rangle \right.$$

$$+ \sum_{ij} \left(V_{imjr} \langle e_{\mu\alpha,ij} \rangle + V_{mijr} \langle e_{i\alpha,\mu j} \rangle \right)$$

$$\left. + \delta_{mr} \sum_{ijk} V_{i\alpha jk} \langle e_{\mu k,ij} \rangle \right), \tag{16c}$$

$$\langle \Phi_\mu^m | [H, T_2] | \Phi \rangle = \sum_{(rs)\alpha,\beta} t_{\alpha\beta}^{rs} \left[\delta_{ms} V_{\alpha\beta ir} \langle e_{\mu i} \rangle + (1 + P_{\alpha\beta}^{rs}) \right.$$

$$\left. \times \left(\delta_{ms} \sum_i h_{ir} \langle e_{\mu\beta,i\alpha} \rangle + \sum_i V_{mirs} \langle e_{\mu\alpha,i\beta} \rangle + \sum_{ijk} V_{ijkr} \langle e_{\mu\beta,j\alpha,ik} \rangle \right) \right], \tag{16d}$$

$$\langle\Phi_\mu^m|[[H, T_1], T_1]|\Phi\rangle = \sum_{r\alpha} t_\alpha^r \sum_{p\lambda} t_\lambda^p (1+P_{\alpha\lambda}^{rp})\Big(-\delta_{mp} h_{\lambda r}\langle e_{\mu\alpha}\rangle + \sum_i V_{impr}\langle e_{\mu\alpha,i\lambda}\rangle$$

$$+ \delta_{mp} \sum_{ij} (-V_{\lambda ijr}\langle e_{i\alpha,\mu j}\rangle - V_{i\lambda jr}\langle e_{\mu\alpha,ij}\rangle)\Big), \tag{16e}$$

$$\langle\Phi_\mu^m|[[H, T_2], T_1]|\Phi\rangle = \sum_{(rs),\alpha\beta} t_{\alpha\beta}^{rs} \sum_{p\lambda} t_\lambda^p (1+P_{\alpha\beta}^{rs})\Big(-V_{\beta\alpha rp}\langle e_{\mu\lambda}\rangle + \delta_{\beta r} \sum_i V_{\alpha iip}\langle e_{\mu\lambda}\rangle$$

$$+ \delta_{ms} \sum_i (-V_{i\beta pr}\langle e_{\mu\alpha,i\lambda}\rangle - V_{i\beta rp}\langle e_{\mu\lambda,i\alpha}\rangle - V_{i\alpha rp}\langle e_{\mu\beta,i\lambda}\rangle$$

$$+ V_{\alpha iip}\langle e_{\mu\beta,r\lambda}\rangle)\Big), \tag{16f}$$

$$\langle\Phi_\mu^m|[H, T_2], T_2]|\Phi\rangle = 0; \tag{16g}$$

finally,

$$\langle\Phi_{\mu\nu}^{mn}|e^{-T} H e^T|\Phi\rangle = 0, \qquad m \le n \tag{17a}$$

gives

$$\langle\Phi_{\mu\nu}^{mn}|H|\Phi\rangle = \tfrac{1}{2}(1+P_{\mu\nu}^{mn}) \sum_{ij} V_{mnij}\langle e_{\mu i,\nu j}\rangle, \tag{17b}$$

$$\langle\Phi_{\mu\nu}^{mn}|[H, T_1]|\Phi\rangle = \sum_{r\alpha} t_\alpha^r (1+P_{\mu\nu}^{mn})\Big(\sum_i V_{mnir}\langle e_{\nu\alpha,\mu i}\rangle + \delta_{mr} \sum_{ij} V_{n\alpha ji}\langle e_{\mu i,\nu j}\rangle\Big), \tag{17c}$$

$$\langle\Phi_{\mu\nu}^{mn}|[[H, T_1], T_1]|\Phi\rangle = \sum_{r\alpha} t_\alpha^r \sum_{p\lambda} t_\lambda^p \Big[\delta_{mr}\delta_{np} \sum_{ij} V_{\lambda\alpha ij}\langle e_{\nu i,\mu j}\rangle$$

$$+ (1+P_{\mu\nu}^{mn})(1+P_{\lambda\alpha}^{pr})\Big(\tfrac{1}{2} V_{nmpr}\langle e_{\mu\alpha,\nu\lambda}\rangle$$

$$+ \delta_{mp} \sum_i (V_{\lambda nir}\langle e_{\nu\alpha,\mu i}\rangle - V_{\lambda nir}\langle e_{\mu\alpha,\nu i}\rangle)\Big)\Big], \tag{17d}$$

$$\langle\Phi_{\mu\nu}^{mn}|[H, T_2]|\Phi\rangle = \sum_{(rs)\alpha\beta} t_{\alpha\beta}^{rs}\Big\{(1+P_{\alpha\beta}^{rs})(1+P_{\mu\nu}^{mn})$$

$$\times\Big[\tfrac{1}{2}V_{mnrs}\langle e_{\mu\alpha,\nu\beta}\rangle - \tfrac{1}{2}\delta_{mr}\delta_{ns} \sum_{ij} V_{\alpha\beta ij}\langle e_{\mu i,\nu j}\rangle + \delta_{mr}\delta_{ns}$$

$$\times\Big(-\sum_i h_{\alpha i}\langle e_{\nu\beta,\mu i}\rangle - \sum_{ijk} V_{i\alpha jk}\langle e_{\nu\beta,\mu k,ij}\rangle\Big) + \delta_{ms}$$

$$\times\Big(h_{nr}\langle e_{\mu\beta,\nu\alpha}\rangle + \sum_{ij} V_{injr}\langle e_{\mu\beta,\nu\alpha,ij}\rangle + \sum_{ij} V_{njir}\langle e_{\mu\beta,j\alpha,\nu i}\rangle\Big)\Big]\Big\}, \tag{17e}$$

$$\langle \Phi_{\mu\nu}^{mn} | [[H, T_2], T_1] | \Phi \rangle = \sum_{(rs)\alpha,\beta} t_{\alpha\beta}^{rs} \sum_{p\lambda} t_\lambda^p (1 + P_{\alpha\beta}^{rs})(1 + P_{\mu\nu}^{mn})$$

$$+ \left\{ \delta_{mp}\delta_{nr} \sum_i V_{\lambda\alpha si}\langle e_{\mu\beta,\nu i}\rangle + \delta_{ms}(\delta_{\beta\nu}V_{\alpha npr}\langle e_{\mu\lambda}\rangle \right.$$

$$+ \delta_{\alpha\nu}V_{n\beta pr}\langle e_{\mu\lambda}\rangle) - \delta_{mp}V_{n\lambda rs}\langle e_{\mu\beta,\nu\alpha}\rangle + (1 + P_{\alpha\lambda}^{rp})\left[\delta_{ms}\delta_{nr} \right.$$

$$\times \left(h_{\alpha p}\langle e_{\mu\beta,\nu\lambda}\rangle - \sum_i V_{\beta\alpha ip}\langle e_{\mu i,\nu\lambda}\rangle - \sum_{ij} V_{i\alpha jp}\langle e_{\mu\beta,\nu\lambda,ij}\rangle \right.$$

$$\left. \left. \left. - \sum_{ij} V_{i\alpha pj}\langle e_{\mu\beta,\nu j,i\lambda}\rangle \right) - \delta_{ms} \sum_i V_{inpr}\langle e_{\mu\beta,\nu\alpha,i\lambda}\rangle \right] \right\}, \qquad (17f)$$

$$\langle \Phi_{\mu\nu}^{mn} | [[H, T_2], T_2] | \Phi \rangle = \sum_{(rs)\alpha,\beta} t_{\alpha\beta}^{rs} \sum_{(pq)\lambda,\sigma} t_{\lambda\sigma}^{pq} (1 + P_{\alpha\beta}^{rs})(1 + P_{\lambda\sigma}^{pq})(1 + P_{\mu\nu}^{mn})$$

$$\times \left\{ \sum_{ij} V_{\bar{y}pr}\langle e_{\mu\beta,\nu\sigma}e_{j\alpha}e_{i\lambda}\rangle + (1 + P_{\alpha\lambda}^{rp}P_{\beta\sigma}^{sq}) \right.$$

$$\times \left[\delta_{mp}\delta_{nq}\left(-\tfrac{1}{2}V_{\sigma\lambda rs}\langle e_{\mu\beta,\nu\alpha}\rangle + \sum_i V_{i\lambda rs}\langle e_{\mu\beta,\nu\sigma,i\alpha}\rangle \right) + \delta_{ms}\delta_{nq} \right.$$

$$\times \left(\sum_i V_{i\beta pr}\langle e_{\mu\alpha,\nu\sigma,i\lambda}\rangle + \sum_i V_{i\beta rp}\langle e_{\mu\lambda,\nu\sigma,i\alpha}\rangle \right.$$

$$\left. \left. \left. + \tfrac{1}{2}\sum_i V_{i\alpha rp}\langle e_{\mu\beta,\nu\sigma,i\lambda}\rangle \right) \right] \right\}. \qquad (17g)$$

Here $\langle e_{\alpha\beta}\rangle$, $\langle e_{\alpha\beta,\mu\nu}\rangle$, $\langle e_{\alpha\beta,\mu\nu,\lambda r}\rangle$ are elements of the density matrices defined over the occupied orbitals of the reference state Φ:

$$e_{\alpha\beta,\mu\nu} = e_{\alpha\beta}e_{\mu\nu} - \delta_{\beta\mu}e_{\alpha\nu} \equiv \sum_{\sigma\sigma'} a_{\alpha\sigma}^+ a_{\mu\sigma'}^+ a_{\nu\sigma'}a_{\beta\sigma} \qquad (18)$$

and

$$e_{\alpha\beta,\mu\nu,\lambda\eta} = -e_{\alpha\beta}e_{\mu\nu}e_{\lambda\eta} + \delta_{\beta\mu}\delta_{\nu\lambda}e_{\alpha\eta} + \delta_{\beta\mu}e_{\alpha\nu,\lambda\eta} + \delta_{\nu\lambda}e_{\alpha\beta,\mu\eta} + \delta_{\beta\lambda}e_{\alpha\eta,\mu\nu}$$

$$\equiv \sum_{\sigma\sigma'\sigma''} a_{\alpha\sigma}^+ a_{\mu\sigma'}^+ a_{\lambda\sigma''}^+ a_{\beta\sigma}a_{\nu\sigma'}a_{\eta\sigma''}.$$

The expressions have been arranged in a form such that the summation indices including $i, j, k,$ and l sum over the occupied orbitals of Φ. In writing Eqs. (15)–(17) we have employed an exchange symmetry operator $P_{\alpha\beta}^{rs}$, which operating on a term to the right, interchange the indices (r, α) to (s, β).

3. Operational Considerations

As shown in Eqs. (15)–(18) the multiconfigurational coupled cluster (CCMC) equations reduce to a set of nonlinear algebraic equations which can be solved for the cluster amplitudes t_α^r and $t_{\mu\nu}^{pq}$. In the working CCMC equations, the factors which multiply such amplitudes are sums of products of one- and two-electron integrals and elements of reduced density matrices which must be efficiently evaluated and processed. We now turn our attention to these more practical considerations.

One advantage of employing the unitary group generators for expressing H, T_k and the requisite density matrix elements is that the cluster operators of Eq. (8) are automatically singlet coupled. i.e., they preserve the spin symmetry of the reference wave function. For example, an element of the T_2 operator written in terms of the one-particle creation and annihilation operators has the form $e_{r\mu}e_{s\nu} = \sum_{\sigma\sigma'} a_{r\sigma}^\dagger a_{\mu\sigma} a_{s\sigma'}^\dagger a_{\nu\sigma'}$, which is indeed singlet coupled. Therefore, the calculations of the density matrix elements $\langle e_{\alpha\beta} \rangle$, $\langle e_{\alpha\beta,\mu\nu} \rangle$, $\langle e_{\mu\beta,\mu\nu,\lambda\sigma} \rangle$ involve only nonredundant spin components. Shavitt [10] has developed very efficient algorithms for the calculations of such density matrix elements. We further stress that only the orbitals which are occupied in Φ appear in the needed density matrix elements since $a_r|\Phi\rangle \equiv \langle\Phi|a_r^\dagger \equiv 0$. Thus, the number of such density matrix elements is limited by the choice of the "occupied" orbital space. The symmetry properties of products of generators ($e_{\alpha\beta,\mu\nu} = e_{\mu\nu,\alpha\beta}$ and $e_{\alpha\beta,\mu\nu,\lambda\sigma} = e_{\alpha\beta,\lambda\sigma,\mu\nu} = e_{\mu\nu,\alpha\beta,\lambda\sigma} = e_{\mu\nu,\lambda\sigma,\alpha\beta} = e_{\lambda\sigma,\mu\nu,\alpha\beta} = e_{\lambda\sigma,\alpha\beta,\mu\nu}$) allow us to calculate the density matrices in a lower "triangular" array. Furthermore, only the nonzero matrix elements or those larger than a prescribed tolerance need be stored. In the above working equations we have chosen to arrange terms such that the unitary generators occur in the form $e_{ij,kl}$. This choice is motivated by the fact that Shavitt has shown that the evaluation of MC density matrix elements in terms of $e_{ij,kl}$ via unitary group methods gives rise to a very useful factorization of the contributions to the desired density matrices which would not occur if one were to evaluate $\langle e_{ij}e_{kl} \rangle$. Clearly, we wish to achieve this added efficiency in our computer programs.

In the above derivation, the partition of the Hamiltonian ($H = h + V$) was made in terms of one- and two-particle operators but the exact nature of the orbital basis was not specified, although we did indicate why MCSCF orbitals would probably be quite desirable (because then $T_1 \approx 0$). The fact that Φ is a full-valence CI wave function (and, is thus invariant with respect to a unitary transformation among the valence orbitals) gives a certain degree of freedom in the choice of orbital basis. Because the MCSCF optimization of the valence orbitals of Φ would be expected to lead to negligible one-particle cluster amplitudes $T_1 \approx 0$, and to thereby reduce the complexity of the MCCC equations, we favor the use of the MCSCF basis for actual calculations. Alternatively, one could choose the orbital basis such that either the one-particle density matrix or the "generalized Fock operator" $F_{ij} = \langle i|u|j \rangle + \sum_{\alpha\beta} \langle e_{\alpha\beta} \rangle V_{i\alpha j\beta}$ is diagonal, where u contains the kinetic energy and the electron nuclear attraction energy terms. There is no one choice

which is obviously "correct"; more experience in actually applying the CCMC method to atomic and molecular problems is needed.

4. Concluding Remarks

We have obtained explicit equations for the exponential one- and two-electron cluster operators which act on a reference state of MC form to yield an approximation to the true Schrödinger eigenfunction. The resulting equations have been cast in a computationally tractable form through the use of the generators of the unitary group in a way which makes them applicable to closed- or open-shell systems. By stipulating that Φ be a full (valence) CI reference function, we were able to obtain CCMC equations which are no more complicated in form than those arising in HF–reference function CC approaches. As pointed out clearly in our development, the resulting equations are not exact since we do not properly treat the readjustment of the "occupied" orbitals $\{\phi_\alpha\}$ which takes place due to the interaction (through e^T) with new configurations which involve the orbitals $\{\phi_p\}$. Nevertheless, we feel that this extension of the CC framework to permit a very important new family of reference functions represents a significant step forward in this area.

Bibliography

[1] F. Coester, Nucl. Phys. **7**, 421 (1958).
[2] J. Cízek, J. Chem. Phys. **45**, 4256 (1966); Adv. Chem. Phys. **24**, 35 (1969).
[3] O. Sinanoglu, J. Chem. Phys. **36**, 706, 3198 (1962); R. K. Nesbet, Adv. Chem. Phys. **9**, 521 (1965); H. Kümmel, *Lectures on Many-Body Problem*, E. R. Caianiello, Ed. (Academic, New York, 1962); F. E. Harris, Int. J. Quantum Chem. Symp. **11**, 403 (1977).
[4] J. Paldus, J. Cízek, and I. Shavitt, Phys. Rev. A **5**, 50 (1972).
[5] I. Lindgren, Int. J. Quantum Chem. Symp. **12**, 33 (1978).
[6] B. Jeziorski and H. J. Monkhorst (unpublished).
[7] D. L. Freeman, Phys. Rev. B (to be published); M. Moshinsky, *Group Theory and the Many-Body Problem* (Gordon and Breach, New York, 1968).
[8] J. Paldus, J. Chem. Phys. **61**, 5321 (1974); Int. J. Quantum Chem. **10**, 525 (1976); *Group Theoretical Methods in Physics*, W. Beiglboeck, A. Bohm, and E. Takasugi, Eds. (Springer, Heidelberg, 1979).
[9] G. W. F. Drake and M. Schlesinger, Phys. Rev. A **15**, 1990 (1977).
[10] I. Shavitt, Int. J. Quantum Chem. Symp. **11**, 131 (1977); **12**, 5 (1978); Annual Report on "New Methods in Computational Quantum Chemistry and their Application on Modern Super-Computers," Battelle Colombus Laboratories (1979).
[11] B. R. Brooks and H. F. Schaefer III, J. Chem. Phys. **70**, 5092 (1979); R. Shepard and J. Simons (unpublished).