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Complete Multi-Configuration Self-Consistent Field Theory

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The two-configuration self-consistent field formalism previously presented in this Journal is extended and the CMC SCF LCAO MO (complete multi-configuration self-consistent field LCAO MO) technique is presented. The single Slater determinant for a $2n$ electron system is replaced by a combination of determinants built from two sets of MO's, one containing n orbitals; the second, $(\omega - n)$ orbitals. All the possible double excitations from the (n) set to the $(\omega - n)$ set are considered. The orbitals as well as the linear combination of determinants are simultaneously optimized making use of the self-consistent field technique.

On expose la méthode du champ self-consistant pour un ensemble complet de plusieurs configurations, dans l'approximation LCAO-MO (CMC SCF LCAO MO). Le déterminant de Slater pour un système de $2n$ électrons est remplacé par une combinaison de déterminants construits a partir de deux ensembles d'orbitales moléculaires, l'un contenant (n) orbitales et l'autre $(\omega - n)$ orbitales. On considère toutes les doubles excitations possibles, de l'ensemble (n) à l'ensemble $(\omega - n)$. La technique du champ self-consistant permet d'optimiser simultanément les orbitales ainsi que les coefficients dans la combinaison linéaire de determinants. La méthode CMC SCF tient plainement compte de la corrélation associée à chaque paire d'électrons et fait intervenir toutes les interactions paire-paire. L'optimisation simultanée des orbitales des deux ensembles (n) et $(\omega - n)$ garantit une convergence rapide.

Es wird die Methode des „self-consistent field" für eine Gesamtheit mehrerer Konfigurationen in der LCAO-Näherung entwickelt. Ein $2n$-Elektronensystem wird nicht mehr durch eine einzige Slaterdeterminante, sondern durch eine Kombination von Determinanten beschrieben, die aus zwei Sätzen von Molekülfunktionen mit n bzw. $(\omega - n)$ Orbitalen aufgebaut werden. Alle möglichen zweifachen Anregungen vom (n) zum $(\omega - n)$ Satz werden berücksichtigt. Mit Hilfe der SCF-Technik werden sowohl die Orbitale als auch die Kombination der Determinanten gleichzeitig optimiert.

Introduction

The Hartree-Fock approximation is often used as zero order approximation in a perturbation series. Alternatively one can use the configuration interaction technique, where the starting approximation to the total energy (the zero order energy) can be any one-electron function (generally inferior to the Hartree-Fock). In a previous work [*1*, *3*] a two-configuration SCF technique was developed and applied to the first row atoms. The inclusion of only one additional configuration decreased the correlation error for example in Be(^1S), B(^2P), C(^3P), N(^2P), O(^1S) from 0.0942 a.u., 0.1241 a.u., 0.1580 a.u., 0.232 a.u., 0.306 a.u. to 0.052 a.u., 0.094 a.u., 0.141 a.u., 0.198 a.u., 0.252 a.u. respectively. In this paper the number of configurations is no longer restricted to only two, but one can include as many configurations as needed to obtain an accurate wavefunction. As previously, the coefficients of the configuration mixing as well as the form for the orbitals are simultaneously optimized to ensure fast convergency in the series. For additional references to the multi-configuration SCF approach we refer to previous work [*1*], for references on the correlation energy problem we refer to Ref. [*2*].

I. CMC SCF MO Equations

We assume that the $2n$ electrons of a given closed shell system are distributed in n double occupied orbitals $\phi_1 \ldots \phi_n$ and we shall refer to this set as the "(n)" set. A second set of orbitals $\phi_{(n+1)} \ldots \phi_\omega$ is used and this will be referred to as the "$(\omega - n)$" set. We consider all the possible double excitations from the (n) to the $(\omega - n)$ set, i.e., we consider $n(\omega - n)$ configurations. A given excitation from the (n) set to the $(\omega - n)$ set will be indicated as $t \to u$ where t is a number from 1 to n and u is a number from $n + 1$ to ω.

We shall designate as complete multi-configuration self-consistent field (CMC SCF) technique the one where each orbital of the (n) set is excited to all orbitals of the $(\omega - n)$ set; if an orbital of the (n) set is excited to one or more, but not all orbitals of the $(\omega - n)$ set, then we shall describe the technique as incomplete MC SCF (IMC SCF).

The wavefunction of the system is

$$\Psi = a_{oo}\psi_{oo} + \sum_t \sum_u a_{tu}\psi_{tu} \,.$$

In the above summation and in the following of this paper the summation for the indices t or t' extends from 1 to n and the summation for the indices u or u' extends from 1 to $\omega - n$. If one wishes to exclude a number of occupied orbitals from the excitations, i.e., if a number of orbitals are left uncorrelated, then this requires simply starting the summation over the index t at some value of t larger than one (see Appendix). We shall use t or t' as indices for the (n) set and u or u' as indices for the $(\omega - n)$ set.

The energy corresponding to Ψ is

$$\begin{aligned} E = {} & a_{oo}^2 \langle\psi_{oo}^* \,|\, H \,|\, \psi_{oo}\rangle + \sum_t \sum_u a_{tu}^2 \langle\psi_{tu}^* \,|\, H \,|\, \psi_{tu}\rangle + \\ & + \sum_t \sum_u a_{tu} \sum_{t'} \sum_{u'} a_{t'u'} \langle\psi_{tu}^* \,|\, H \,|\, \psi_{t'u'}\rangle (1 - \delta_{tt'}\delta_{uu'}) + \\ & + 2a_{oo} \sum_t \sum_u a_{tu} \langle\psi_{oo}^* \,|\, H \,|\, \psi_{tu}\rangle \end{aligned} \tag{1}$$

$$\begin{aligned} E = {} & a_{oo}^2 E_{oo} + \sum_t \sum_u a_{tu}^2 E_{tu} + \sum_t \sum_u a_{tu} \sum_{t'} a_{t'u} I_{tt'} (1 - \delta_{tt'}) + \\ & + \sum_t \sum_u a_{tu} \sum_{u'} a_{tu'} I_{uu'} (1 - \delta_{uu'}) + 2a_{oo} \sum_t \sum_u a_{tu} I_{tu} \end{aligned} \tag{2}$$

where

$$E_{oo} = \sum_t 2h_t + 2\sum_t \sum_{t'} P_{tt'} \tag{3}$$

$$E_{tu} = E_{oo} - 2h_t + 2h_u - 4\sum_{t'} P_{tt'} + 4\sum_{t'} P_{t'u} - 4P_{tu} + 2P_{uu} + 2P_{tt} \tag{4}$$

$$I_{ij} = K_{ij} \tag{5}$$

$$P_{ij} = J_{ij} - \tfrac{1}{2}K_{ij} \,. \tag{6}$$

By simple algebraic manipulations the energy expression can be rewritten as

$$\begin{aligned} E = {} & 2\sum_t [h_t + \sum_{t'} P_{tt'} - A_t (h_t + 2\sum_{t'} P_{tt'} - P_{tt})] + \\ & + 2\sum_u B_u(h_u + P_{uu} + 2\sum_t P_{tu}) + \\ & + 2\sum_t \sum_u a_{tu}(a_{oo}K_{tu} - 2a_{tu}P_{tu}) + \\ & + \sum_t \sum_{t'} A_{tt'}K_{tt'}(1 - \delta_{tt'}) + \sum_u \sum_{u'} B_{uu'}K_{uu'}(1 - \delta_{uu'}) \end{aligned} \tag{7}$$

where

$$1 = a_{oo}^2 + \sum_t \sum_u a_{tu}^2 \tag{8}$$

$$A_{tt'} = \sum_u a_{tu}a_{t'u} \tag{9a}$$

$$A_t \equiv A_{tt} = \sum_u a_{tu}^2 \tag{9b}$$

$$B_{uu'} = \sum_t a_{tu}a_{tu'} \tag{10a}$$

$$B_u \equiv B_{uu} = \sum_t a_{tu}^2 \,. \tag{10b}$$

The coefficients A_t and B_u are related by the following equations:

$$1 = a_{oo}^2 + \sum_t A_t = a_{oo}^2 + \sum_u B_u \tag{11}$$

or

$$\sum_t A_t = \sum_u B_u \,. \tag{12}$$

The coefficient A_t represents the "fraction of an electron" which is excited from the ϕ_t orbital of the (n) set to the ϕ_u orbitals of the entire $(\omega - n)$ set. The coefficient B_u represents the "fraction of an electron" in the ϕ_u orbital of the $(\omega - n)$ set as a result of excitation from the entire (n) set. It is therefore tempting to reexamine the configuration structure of a $2n$ electron system. The standard electronic configuration for the $2n$ electrons is a set of n orbitals. For example ψ_{oo} has configuration

$$\phi_1^2\,\phi_2^2 \ldots \phi_n^2 \,.$$

Let us call such a configuration a "zero-order electronic configuration". The MC SCF LCAO MO function will be a sum of $(\omega n - n^2)$ zero-order configurations with appropriate coefficients, a_{tu}. It is rather difficult to visualize in a simple way the effect of such a rather long expansion. However, we can make use of the A_t and B_u coefficients and write the following configuration:

$$\underset{(n)\ \text{set}}{\phi_1^{2(1-A_1)} \cdots \phi_n^{2(1-A_n)}} \qquad\qquad \underset{(\omega - n)\ \text{set}}{\phi_{n+1}^{2B_1} \cdots \phi_\omega^{2B_{\omega-n}}}$$

which we shall refer to as the "complete electronic configuration". The set of (n) orbitals has a fractional occupation equal to $(1 - A_t)$ for the orbital ϕ_t, whereas the remaining orbitals [the ϕ_u's of the $(\omega - n)$ set] will have in general relatively small fractional occupation values B_u. Clearly the sum of the fractions of electrons annihilated from the (n) set is equal to the sum of the fractions created in the $(\omega - n)$ set, since $\sum_t A_t = \sum_u B_u$ [Eq. (12)].

The energy E_{oo} defined in Eq. (3) is formally the SCF MO closed shell energy expansion; however the ϕ_t in the CMC SCF formalism are not equal to the ϕ_t of the usual Hartree-Fock formalism. If we indicate with E_{HF} the Hartree-Fock energy, we can state that E_{HF} is somewhat lower than E_{oo}, by an amount which is almost proportional to the correlation error of E_{HF} as can be seen by analysis of CLEMENTI and VEILLARD's ICM results for first row atoms. We now define a quantity $E_c = E - E_{oo}$ which is larger than the correlation energy by the amount that E_{oo} is larger than E_{HF}. It is noted that the correlation energy is commonly defined as $E - E_{HF}$. Therefore the CMC SCF formalism differs from most many-body techniques presented to date insofar as we do not take the Hartree-Fock energy as the zero-order energy.

We shall briefly analyze the energy expression 7 in terms of E, E_c and E_{oo}. For this purpose we introduce the following definitions:

$$E_c(t) = -2h_t - 2\sum_{t'} 2P_{tt'} + 2P_{tt} \tag{13}$$

$$E_c(u) = 2h_u + 2P_{uu} + 2\sum_{t} 2P_{tu} \tag{14}$$

$$E_c(tu) = 2a_{oo}K_{tu} - 4a_{tu}P_{tu} \tag{15}$$

$$E_c(tt') = K_{tt'}(1 - \delta_{tt'}) \tag{16}$$

$$E_c(uu') = K_{uu'}(1 - \delta_{uu'})\,. \tag{17}$$

We can now write

$$E = E_{oo} + \sum_{t} A_t E_c(t) + \sum_{u} B_u E_c(u) + \sum_{tu} a_{tu} E_c(tu) + \\ + \sum_{tt'} A_{tt'} E_c(tt') + \sum_{uu'} B_{uu'} E_c(uu')\,. \tag{18}$$

The first term is the contribution to E given by the one-electron model. The second term is a correction to E_{oo} obtained by annihilation of electrons in the (n) set. The third term is the energy of the electrons created in the $(\omega - n)$ set. The fourth term is interaction of created and annihilated electrons. The fifth term is the interaction energy resulting from any pair of electrons in a ϕ_t orbital interacting with any pair of electrons in a $\phi_{t'}$ orbital. Therefore it is the pair-pair interaction in the (n) set. The last term is the pair-pair interaction in the $(\omega - n)$ set.

Let us now continue with the development of the CMC SCF LCAO MO theory. We wish to obtain the best ϕ_t's and ϕ_u's, making use of the variational principle, i.e., by requiring that $(\partial E/\partial\phi_t) = 0$ and $(\partial E/\partial\phi_u) = 0$. In addition we have to satisfy the equation $(\partial E/\partial a_{oo}) = 0$ and $(\partial E/\partial a_{tu}) = 0$ in order to obtain the best multiconfiguration expansion. We shall make use of the Lagrangian multiplier technique for determining ϕ_t and ϕ_u, and of the solution of the secular equation for determining the a_{tu} coefficients.

Let us define the following operators:

$$F_t = (1 - A_t)\,h_t + 2\sum_{t'} (1 - A_t - A_{t'})\,P_{t'} + 2A_tP_t + 2\sum_{u} B_uP_u + \\ + \sum_{u} (a_{oo}a_{tu}K_u - 2a_{tu}^2P_u) + \sum_{t'} A_{tt'}K_{t'}(1 - \delta_{tt'}) \tag{19a}$$

and

$$F_u = B_u(h_u + 2P_u + \sum_t 2P_t) + \sum_t (a_{tu}\, a_{oo} K_t - 2a_{tu}^2\, P_t) + \\ + \sum_{u'} B_{uu'}\, K_{u'}\, (1 - \delta_{uu'}) \tag{19b}$$

where $P_{ij} = \langle \phi_i^* \mid P_j \mid \phi_i \rangle$ and $K_{ij} = \langle \phi_i^* \mid K_j \mid \phi_j \rangle$. Differentiation of E with respect to the variational parameters ϕ_t, ϕ_u, a_{oo}, a_{tu}, brings about the following relation:

$$\begin{aligned}\delta E = {} & 2\sum_t \langle \delta\phi_t^* \mid F_t \mid \phi_t \rangle + 2\sum_t \langle \phi_t^* \mid F_t \mid \delta\phi_t \rangle + 2\sum_u \langle \delta\phi_u^* \mid F_u \mid \phi_u \rangle + \\ & + 2\sum_u \langle \phi_u^* \mid F_u \mid \delta\phi_u \rangle + 2\sum_t \delta A_t\, (-h_t - 2\sum_t P_{tt'} + P_{tt}) + \\ & + 2\sum_u \delta B_u\, (h_u + P_{uu} + 2\sum_t P_{tu}) + 2\delta a_{oo} \sum_t \sum_u a_{tu}\, K_{tu} + \\ & + 2\sum_t \sum_u \delta a_{tu}\, [a_{oo}\, K_{tu} - 4a_{tu}\, P_{tu} + \sum_{t'} a_{t'u}\, K_{tt'}(1 - \delta_{tt'}) + \\ & + \sum_{u'} a_{tu'} K_{uu'}(1 - \delta_{uu'})]\,.\end{aligned} \tag{20}$$

The variational principle is satisfied for ϕ_t and ϕ_u if $(\partial E/\partial\phi_t) = 0$ and $(\partial E/\partial\phi_u) = 0$. However the variation in the ϕ's is constrained by imposition of the orthogonality relations

$$\langle \phi_i \mid \phi_j \rangle = \delta_{ij} \tag{21}$$

where the indices i and j run over the full (n) and $(\omega - n)$ sets. By setting Eq. (20) to zero, then by differentiation of the above equation, and finally by joining the resulting equations, we obtain the relation which defines ϕ_t and ϕ_u:

$$F_t\, \phi_t - \sum_{t'}{}^{(t)}\, \phi_{t'}\, \vartheta_{tt'} - \sum_u \phi_u\, \vartheta_{ut} = \phi_t\, \vartheta_{tt} \tag{22a}$$

$$F_u\, \phi_u - \sum_{u'}{}^{(u)}\, \phi_{u'}\, \vartheta_{uu'} - \sum_t \phi_t\, \vartheta_{tu} = \phi_u\, \vartheta_{uu} \tag{22b}$$

where $\sum_{t'}{}^{(t)}$ and $\sum_{u'}{}^{(u)}$ exclude the terms with $t' = t$ and $u' = u$ from the summations and ϑ are proportional to the yet undetermined Lagrangian multipliers, $-\vartheta_{ij}/2$. The above equations can be written as

$$\mid F_t \mid \phi_t \rangle - \sum_{t'}{}^{(t)} \mid \phi_{t'} \rangle \langle \phi_{t'} \mid F_t \mid \phi_t \rangle - \sum_u \mid \phi_u \rangle \langle \phi_u \mid F_t \mid \phi_t \rangle = \mid \phi_t \rangle\, \vartheta_{tt} \tag{23a}$$

$$\mid F_u \mid \phi_u \rangle - \sum_{u'}{}^{(u)} \mid \phi_{u'} \rangle \langle \phi_{u'} \mid F_u \mid \phi_u \rangle - \sum_t \mid \phi_t \rangle \langle \phi_t \mid F_u \mid \phi_u \rangle = \mid \phi_u \rangle\, \vartheta_{uu} \tag{23b}$$

which can be rewritten as

$$\mid F_t - T_t - T_u \mid \phi_t \rangle = \mid \phi_t \rangle\, \vartheta_{tt} \tag{24a}$$

$$\mid F_u - U_u - U_t \mid \phi_u \rangle = \mid \phi_u \rangle\, \vartheta_{uu} \tag{24b}$$

where T_t and T_u are the hermitean operators corresponding to second and third operators in Eq. (23a) and U_u and U_t are the hermitean operators corresponding to second and third operators in Eq. (23b).

We now turn our attention to the variables a_{oo}, A_t, B_u and a_{tu}. These are not independent, because of Eqs. (11) and (12). Differentiation of Eqs. (8), (9b), and (10b) brings about the following relations:

$$0 = a_{oo}\delta a_{oo} + \sum_t \sum_u a_{tu}\delta a_{tu} \tag{25}$$

$$\delta A_t = 2\sum_u a_{tu}\delta a_{tu} \tag{26a}$$

$$\delta B_u = 2\sum_t a_{tu}\delta a_{tu}\,. \tag{26b}$$

Joining Eqs. (26a) and (26b) with Eq. (20) we obtain, taking into account the constraints of Eq. (25) by the Lagrangian multipliers $-\lambda/2$:

$$\sum_t \sum_u a_{tu}K_{tu} - \lambda a_{oo} = 0 \tag{27}$$

$$\begin{aligned} a_{tu}(-2h_t - 4\sum_{t'} P_{tt'} + 2P_{tt} + 2h_u + 2P_{uu} + 4\sum_{t'} P_{t'u} - 4P_{tu} - \lambda) + \\ + a_{oo}K_{tu} + \sum_{t'} a_{t'u}K_{tt'}(1 - \delta_{tt'}) + \sum_{u'} a_{tu}\, K_{uu'}(1 - \delta_{uu'}) = 0\,. \end{aligned} \tag{28}$$

It can be proved easily that $\lambda = E - E_{oo}$. We can now write

$$(E_{oo} - E)\, a_{oo} + \sum\sum a_{tu}K_{tu} = 0 \tag{29}$$

$$(E_{tu} - E)\, a_{tu} + a_{oo}K_{tu} + \sum\sum a_{t'u'}(K_{tt'}\delta_{uu'} + K_{uu'}\delta_{tt'})(1 - \delta_{uu'}\delta_{tt'}) = 0\,. \tag{30}$$

One will recognize in the above equations the standard secular equations for the configuration interaction (C.I.) treatment. Indeed, E_{oo} and E_{tu} are the diagonal elements, the second term in Eq. (29) represents the interaction energy between the zero-order configuration and the configurations arising from $t \rightarrow u$ excitations, and finally the third term of Eq. (30) represents the interaction energy between excited configurations.

In the past, use has been made of "virtual orbitals" in the configuration interaction technique. It is noted in this regard, that the ϕ_u of the $(\omega - n)$ set are quite different from the virtual orbitals of a standard SCF LCAO MO computation. The reason is that virtual orbitals have very little physical meaning: they are obtained from diagonalization of the Fock equation, are orthogonal to the occupied orbitals, but the variational principle can not act on them, since they do not contribute to the total energy. In general the virtual orbitals have very little overlap with the occupied orbitals and therefore are of little use in correlating the electrons of the occupied orbitals.

It is noted that a given ϕ_u will mainly be used to correlate one, or at most two or three ϕ_t and therefore the remaining $(n - 1)$ or $(n - 2)$ or $(n - 3)$ ϕ_t's which are promoted to that given ϕ_u will add little to the correlation correction. However, by including the $(n - 1)$ or $(n - 2)$ or $(n - 3)$ remaining orbitals of ϕ_t's we will include part of the pair-pair correction in the total energy at no extra cost. In addition the inclusion of the additional excitation allows us to make use of the equality $\sum B_u = \sum A_t$ with the simple physical meaning for each B_u and A_t as previously explained. Therefore, for a given A_t and a given B_u there are one or at most very few leading terms in the $\sum_u a_{tu}^2$ or in the $\sum_t a_{tu}^2$ summation, respectively. The IMC SCF treatments consider only the leading terms in A_t or B_u, and this requires more accurate optimization of the basis set for the ϕ_t and ϕ_u which is very time-consuming in the computation.

Inspection of the energy expression Eq. (18) reveals the reason for the often-found poor agreement between computed orbital energies ε_t (the eigenvalues of the Fock equations) and ionization potentials or excitation potentials in the standard SCF computations, where $E_{oo} = \sum_t (\varepsilon_t + h_t)$. As known, one reason is that the orbitals in the excited configuration or in the ionized molecule often differ sufficiently from the ground state orbitals even in the SCF LCAO MO approximation. The second reason is clearly obvious by inspection of Eq. (18), namely that the numerical values of the A_t and B_u coefficients will, in general, vary from the ground state to the excited states of a neutral molecule or from the ground state of the neutral molecule to the ground state of the ionized molecule.

It is tempting to consider the possibility of a semiempirical scheme whereby the correct ionization potential or the correct excitation energies are obtained by empirically determining the A_t and B_u fractional occupation values. It is noted that the justification of the use of empirical parameters in the Pariser-Parr technique lies in the fact that the one-electron approximation assumes $A_t = B_u = 0$, whereas in an exact theory A_t and B_u are different from zero.

II. The CMC SCF LCAO MO Equations

Let us continue with the CMC SCF LCAO MO analysis and let us consider the consequences of the LCAO approximation to a given MO, or the consequences of expanding an orbital in terms of a given basis set.

Since the orbitals $\phi_1 \ldots \phi_n \ldots \phi_\omega$ are expanded as linear combinations of a given basis set χ_l we can write

$$\phi_i = \sum_p c_{ip} \chi_p \tag{31}$$

and, noticing that a given orbital will transform as one of the irreducible representations λ (or μ) of the symmetry group appropriate to the $2n$ electron systems, we shall have

$$\phi_{\lambda\alpha i} = \sum_p c_{\lambda i p} \chi_{\lambda\alpha p} = \boldsymbol{c}_{\lambda i} \boldsymbol{\chi}_{\lambda\alpha} \tag{32}$$

where the index α (or β) specifies the degenerate component in the case λ is a degenerate representation and where $\boldsymbol{c}_{\lambda i}$ and $\boldsymbol{\chi}_{\lambda\alpha}$ express in vector notation the orbital $\phi_{\lambda\alpha i}$. By introducing the following notation

$$(d_\lambda) S_{\lambda pq} = \sum_\alpha \langle \chi_{\lambda p\alpha} \mid \chi_{\lambda q\alpha} \rangle \tag{33}$$

$$(d_\lambda) H_{\lambda pq} = \sum_\alpha \langle \chi_{\lambda p\alpha} \mid H \mid \chi_{\lambda q\alpha} \rangle \tag{34}$$

$$(d_\lambda d_\mu) K_{\lambda pq,\mu rs} = \sum_{\alpha\beta} \langle \chi^{(1)}_{\lambda\alpha p} \chi^{(2)}_{\mu\beta r} \mid r^{-1}_{12} \mid \chi^{(1)}_{\mu\beta s} \chi^{(2)}_{\lambda\alpha q} \rangle \tag{35}$$

$$(d_\lambda d_\mu) P_{\lambda pq,\mu rs} = \sum_{\alpha\beta} \langle \chi^{(1)}_{\lambda\alpha p} \chi^{(2)}_{\mu\beta r} \mid r^{-1}_{12} \mid \chi^{(1)}_{\lambda\alpha q} \chi^{(2)}_{\mu\beta s} \rangle - \tfrac{1}{2} K_{\lambda pq,\mu rs} \tag{36}$$

where d_λ and d_μ are the dimensions of the degeneracy in the λ and μ representations, we can define the matrices $\boldsymbol{H}_\lambda$, $\boldsymbol{S}_\lambda$, $\boldsymbol{P}_{\lambda\mu}$, $\boldsymbol{K}_{\lambda\mu}$ and the matrices $\mathscr{H} = \sum_\lambda \boldsymbol{H}_\lambda$, $\mathscr{S} = \sum_\lambda \boldsymbol{S}_\lambda$, $\mathscr{P} = \sum_\lambda \sum_\mu \boldsymbol{P}_{\lambda\mu}$, $\mathscr{K} = \sum_\lambda \sum_\mu \boldsymbol{K}_{\lambda\mu}$. The SCF technique in the matrix

Hartree-Fock formalism reduces to the problem of finding the best set of components $c_{\lambda i p}$ for any orbital $\phi_{\lambda i \alpha}$ described by a given basis set $\chi_{\lambda\alpha}$.

We shall drop in the following the subscript α since in our program the n degenerate vectors appear explicitly as n vectors. This does not require any additional computation time, since only one of the set is computed and the remaining $(n-1)$ vectors are put equal to the first.

Let us introduce the following density matrices:

$$D_{\lambda t, rs} = N_{\lambda t}\, c_{\lambda t r}\, c_{\lambda t s} \tag{37}$$

$$D_{\lambda t} = N_{\lambda t}\, \boldsymbol{c}^{\dagger}{}_{\lambda t}\, \boldsymbol{c}_{\lambda t} \tag{38}$$

$$D_{\lambda} = \sum_{t}^{(n)} D_{\lambda t} \tag{39}$$

$$D_{\lambda, \mu u} = \sum_{t}^{(n)} a_{\lambda t, \mu u}\, D_{\lambda t} \tag{40}$$

$$D^{*}_{\lambda, \mu u} = \sum_{t}^{(n)} a^{2}_{\lambda t, \mu u}\, D_{\lambda t} \tag{41}$$

$$D_{\lambda, A} = \sum_{t}^{(n)} A_{\lambda t}\, D_{\lambda t} \tag{42}$$

$$D_{\lambda u} = N_{\lambda u}\, \boldsymbol{c}^{\dagger}{}_{\lambda u}\, \boldsymbol{c}_{\lambda u} \tag{43}$$

$$D_{\lambda, \mu t} = \sum_{u}^{(\omega)} a_{\mu t, \lambda u}\, D_{\lambda u} \tag{44}$$

$$D^{*}_{\lambda, \mu t} = \sum_{u}^{(\omega)} a^{2}_{\mu t, \lambda u}\, D_{\lambda u} \tag{45}$$

$$D_{\lambda, B} = \sum_{u}^{(\omega)} B_{\lambda u}\, D_{\lambda u} \tag{46}$$

where the $a_{\lambda t, \mu u}$ is the mixing coefficient for the excitation $\lambda t \to \mu u$; $A_{\lambda t}$ and $B_{\mu u}$ are the A_t and B_u previously defined. The notation $\sum\limits_{b}^{(n)}$ stands for $\sum\limits_{b=1}^{n_a}$ and the notation $\sum\limits_{b}^{(\omega)}$ stands for $\sum\limits_{b=1}^{\omega_a - n_a}$.

The equations which define the ϕ_t and ϕ_u are now written in the form

$$F_{\lambda t}\, \boldsymbol{c}_{\lambda t} = (\boldsymbol{c}_{\lambda t}\, \boldsymbol{S}_{\lambda} \vartheta_{\lambda t t}/N_{\lambda t}) + \sum_{t'}{}^{(t)} (\boldsymbol{c}_{\lambda t'}\, \boldsymbol{S}_{\lambda} \vartheta_{\lambda t' t}/N_{\lambda t}) + \sum_{u} (\boldsymbol{c}_{\lambda u}\, \boldsymbol{S}_{\lambda} \vartheta_{\lambda u t}/N_{\lambda t}) \tag{47}$$

$$F_{\lambda u}\, \boldsymbol{c}_{\lambda u} = (\boldsymbol{c}_{\lambda u}\, \boldsymbol{S}_{\lambda} \vartheta_{\lambda u u}/N_{\lambda u}) + \sum_{u'}{}^{(u)} (\boldsymbol{c}_{\lambda u'}\, \boldsymbol{S}_{\lambda} \vartheta_{\lambda u' u}/N_{\lambda u}) + \sum_{t} (\boldsymbol{c}_{\lambda t}\, \boldsymbol{S}_{\lambda} \vartheta_{\lambda t u}/N_{\lambda u}) \tag{48}$$

where

$$\begin{aligned} F_{\lambda t} = {} & (1 - A_{\lambda t})\, H_{\lambda} + (1 - A_{\lambda t})\, P_{\lambda} - P^{A}_{\lambda} + A_{\lambda t}\, P^{t}_{\lambda} + P^{B}_{\lambda} + \tfrac{1}{2} a_{oo}\, K^{t}_{\lambda} - \\ & - \tfrac{1}{2} P^{\lambda t *}_{\lambda} + \tfrac{1}{2} \sum_{\mu} \sum_{u}^{(\omega)} \sum_{\lambda'} \sum_{t'}^{(n)} a_{\lambda t, \mu u}\, a_{\lambda' t', \mu u}\, (1 - \delta_{\lambda t, \lambda' t'})\, K^{\lambda' t'}_{\lambda} \end{aligned} \tag{49}$$

$$F_{\lambda u} = B_{\lambda u}(H_\lambda + P_\lambda^u + P_\lambda) + \tfrac{1}{2} a_{oo} K_\lambda^u - P_\lambda^{\lambda u *} + \\ + \tfrac{1}{2} \sum_\mu \sum_t^{(n)} \sum_{\lambda'} \sum_{u'}^{(\omega)} a_{\mu t,\lambda u}\, a_{\mu t,\lambda' u'} (1 - \delta_{\lambda u,\lambda' u'}) K_\lambda^{\lambda' u'} . \tag{50}$$

In the Eqs. (49) and (50) we have made use of the following definitions:

$$P_{\lambda pq} = \sum_\mu \sum_{rs} P_{\lambda pq,\mu rs} D_{\mu rs} \tag{51}$$

$$P_{\lambda pq}^A = \sum_\mu \sum_{rs} P_{\lambda pq,\mu rs} D_{\mu rs,A} \tag{52}$$

$$P_{\lambda pq}^i = \sum_{rs} P_{\lambda pq,\lambda rs} D_{\lambda i,rs} \tag{53}$$

$$K_{\lambda pq}^i = \sum_\mu \sum_{rs} K_{\lambda pq,\mu rs} D_{\mu,rs,\lambda i} \tag{54}$$

$$P_{\lambda pq}^B = \sum_\mu \sum_{rs} P_{\lambda pq,\mu rs} D_{\mu rs,B} \tag{55}$$

$$P_{\lambda pq}^{\lambda i *} = \sum_\mu \sum_{rs} P_{\lambda pq,\mu rs} D^*_{\mu rs,\lambda i} \tag{56}$$

$$K_{\lambda pq}^{\lambda' i} = \sum_{rs} K_{\lambda pq,\lambda' rs} D_{\lambda' i,rs} \tag{57}$$

where the index i stands for t or u in Eqs. (49) and (50). The off-diagonal Lagrangian multipliers $\vartheta_{\lambda ij}$ with $i \neq j$ can be eliminated by introducing the U and T operators as previously done Eq. (24). In the LCAO approximation we obtain

$$(F_{\lambda t} + T_{\lambda t} + T'_{\lambda t}) \boldsymbol{c}_{\lambda t} = \boldsymbol{c}_{\lambda t} \boldsymbol{S}_\lambda \vartheta_{\lambda tt} / N_{\lambda t} \tag{58}$$

and

$$(F_{\lambda u} + U_{\lambda u} + U'_{\lambda u}) \boldsymbol{c}_{\lambda u} = \boldsymbol{c}_{\lambda u} \boldsymbol{S}_\lambda \vartheta_{\lambda uu} / N_{\lambda u} \tag{59}$$

where

$$T_{\lambda t} = - \sum_{t'}^{(t)} (\boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda t'} F_{\lambda t} \boldsymbol{c}_{\lambda t} + F_{\lambda t} \boldsymbol{c}_{\lambda t'} \boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda t'}) \tag{60}$$

$$T'_{\lambda t} = - \sum_u (\boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda u} F_{\lambda t} \boldsymbol{c}_{\lambda u} + F_{\lambda t} \boldsymbol{c}_{\lambda u} \boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda u}) \tag{61}$$

$$U_{\lambda u} = - \sum_t (\boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda t} F_{\lambda u} \boldsymbol{c}_{\lambda t} + F_{\lambda u} \boldsymbol{c}_{\lambda t} \boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda t}) \tag{62}$$

$$U'_{\lambda u} = - \sum_{u'}^{(u)} (\boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda u'} F_{\lambda u} \boldsymbol{c}_{\lambda u} + F_{\lambda u} \boldsymbol{c}_{\lambda u'} \boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda u'}) . \tag{63}$$

Eqs. (58) and (59) are the CMC SCF LCAO MO equations, where the Lagrangian multipliers ϑ are to be identified with the orbital energies. The above formalism can be easily modified into the IMC SCF LCAO MO formalism.

In the appendix we report the necessary modifications of the above equations for the case where a number of orbitals of the (n) set are left uncorrelated (for example the core electrons). In the computer program we have written, this is an optional input specification.

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Appendix

The CMC SCF LCAO MO Equations with Core

Let us introduce now some "core" orbitals ϕ_k which are left uncorrelated: the corresponding electrons are never excited to orbitals of the second set. We use k and l as indices for this core set, running from 1 to n_c. The energy expression can be written exactly as in Eq. (7) with an additional term:
E = formula (7) +

$$2\sum_{k=1}^{n_c}\left[h_k+\sum_{l=1}^{n_c}P_{kl}+2\sum_{t=1}^{n}(1-A_t)\,P_{kt}+2\sum_{u=1}^{\omega-n}B_uP_{ku}\right]. \tag{64}$$

The variational principle is now applied for ϕ_k, ϕ_t and ϕ_u. We define the following operators on the LCAO approximation:

$$F_\lambda^{Core}=H_\lambda+P_\lambda^{Core}+P_\lambda-P_\lambda^A+P_\lambda^B \tag{65}$$

$$F_{\lambda t}=\text{Formula (49)}+(1-A_{\lambda t})\,P_\lambda^{Core} \tag{66}$$

$$F_{\lambda u}=\text{Formula (50)}+B_{\lambda u}\,P_\lambda^{Core}\,. \tag{67}$$

We made use of the following definitions:

$$D_\lambda^{Core}=\sum_{k=1}^{n_c}N_{\lambda k}\,\boldsymbol{c}^{\dagger}{}_\lambda\boldsymbol{c}_{\lambda k} \tag{68}$$

$$P_{\lambda pq}^{Core}=\sum_{\mu}P_{\lambda,\mu}D_\mu^{Core}. \tag{69}$$

It is found easily that the equations which define ϕ_k, ϕ_t and ϕ_u are now written in the form

$$\begin{aligned}F_\lambda^{Core}\boldsymbol{c}_{\lambda k}=&\sum_{l}(\boldsymbol{c}_{\lambda l}\,\boldsymbol{S}_\lambda\vartheta_{\lambda lk}/N_k)+\sum_{t}(\boldsymbol{c}_{\lambda t}\,\boldsymbol{S}_\lambda\vartheta_{\lambda tk}/N_{\lambda k})+\\&+\sum_{u}(\boldsymbol{c}_{\lambda u}\,\boldsymbol{S}_\lambda\vartheta_{\lambda uk}/N_{\lambda k})\end{aligned} \tag{70}$$

$$\begin{aligned}F_{\lambda t}\,\boldsymbol{c}_{\lambda t}=&(\boldsymbol{c}_{\lambda t}\,\boldsymbol{S}_\lambda\vartheta_{\lambda tt}/N_{\lambda t})+\sum_{t'}{}^{(t)}(\boldsymbol{c}_{\lambda t'}\,\boldsymbol{S}_\lambda\vartheta_{\lambda t't}/N_{\lambda t})+\\&+\sum_{u}(\boldsymbol{c}_{\lambda u}\,\boldsymbol{S}_\lambda\vartheta_{\lambda ut}/N_{\lambda t})+\sum_{k}(\boldsymbol{c}_{\lambda k}\,\boldsymbol{S}_\lambda\vartheta_{\lambda kt}/N_{\lambda t})\end{aligned} \tag{71}$$

$$\begin{aligned}F_{\lambda u}\,\boldsymbol{c}_{\lambda u}=&(\boldsymbol{c}_{\lambda u}\,\boldsymbol{S}_\lambda\vartheta_{\lambda uu}/N_{\lambda u})+\sum_{u'}{}^{(u)}(\boldsymbol{c}_{\lambda u'}\,\boldsymbol{S}_\lambda\vartheta_{\lambda u'u}/N_{\lambda u})+\\&+\sum_{t}(\boldsymbol{c}_{\lambda t}\,\boldsymbol{S}_\lambda\vartheta_{\lambda tu}/N_{\lambda u})+\sum_{k}(\boldsymbol{c}_{\lambda k}\,\boldsymbol{S}_\lambda\vartheta_{\lambda ku}/N_{\lambda u})\,.\end{aligned} \tag{72}$$

Eqs. (71) and (72) are the exact counterparts of Eqs. (47) and (48). By eliminating the off-diagonal Lagrangian when necessary we obtain the following equations:

$$(F_\lambda^{Core}+R_\lambda+R'_\lambda)\,\boldsymbol{c}_{\lambda k}=\sum_{l}(\boldsymbol{c}_{\lambda l}\,\boldsymbol{S}_\lambda\vartheta_{\lambda lk}/N_{\lambda k}) \tag{73}$$

$$(F_{\lambda t}+T_{\lambda t}+T'_{\lambda t}+T''_{\lambda t})\,\boldsymbol{c}_{\lambda t}=\boldsymbol{c}_{\lambda t}\,\boldsymbol{S}_\lambda\vartheta_{\lambda tt}/N_{\lambda t} \tag{74}$$

$$(F_{\lambda u}+U_{\lambda u}+U'_{\lambda u}+U''_{\lambda u})\,\boldsymbol{c}_{\lambda u}=\boldsymbol{c}_{\lambda u}\,\boldsymbol{S}_\lambda\vartheta_{\lambda uu}/N_{\lambda u}\,. \tag{75}$$

T, T', U, U' are the operators defined in Eqs. (60) to (63). R, R', T'' and U'' are new operators defined as:

$$R_\lambda = -\sum_t (\boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda t} F_\lambda^{Core} \boldsymbol{c}_{\lambda t} + F_\lambda^{Core} \boldsymbol{c}_{\lambda t} \boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda t}) \tag{76}$$

$$R'_\lambda = -\sum_u (\boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda u} F_\lambda^{Core} \boldsymbol{c}_{\lambda u} + F_\lambda^{Core} \boldsymbol{c}_{\lambda u} \boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda u}) \tag{77}$$

$$T''_\lambda = -\sum_k (\boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda k} F_{\lambda t} \boldsymbol{c}_{\lambda k} + F_{\lambda t} \boldsymbol{c}_{\lambda k} \boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda k}) \tag{78}$$

$$U''_\lambda = -\sum_k (\boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda k} F_{\lambda u} \boldsymbol{c}_{\lambda k} + F_{\lambda u} \boldsymbol{c}_{\lambda k} \boldsymbol{S}_\lambda \boldsymbol{c}_{\lambda k}) \,. \tag{79}$$

The secular Eqs. (29) and (30) are only changed through the expressions of E Eq. (64), E_{oo} and E_{tu}.

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