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Complex Molecular Orbitals Method in the Non-Orthogonal Basis Set

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In order to avoid one transformation of integrals in the actual computation, the closed-shell Complex Molecular Orbitals (CMO) method is reformulated in the non-orthogonal basis set. The overlap matrix appears in a non-trivial way in the CMO secular equation. Some computational aspects are also briefly discussed.

INTRODUCTION

The Complex Molecular Orbitals (CMO) method has been recently developed[1-3] as a very convenient representation for the description of electronic correlations in molecules. This method belongs to the class of projected Hartree-Fock schemes of Löwdin[4]. It is based essentially on the *real part* of a single Slater determinant built out of complex orbitals, which is a trial function in the variational procedure. The operator (Re) of taking the real part plays the role of projector in this case. A comprehensive list of earlier papers dealing with complex orbitals is given in ref 3.

The most valuable feature of the CMO method is its ability to describe dominant electron correlations in a simple manner, which departs little from the SCF LCAO-MO method. Thus, the CMO method provides a scheme for the description of electron correlations in large molecules (and polymers[5]) which cannot be reliably treated by the currently popular method of configuration interaction (CI).

Numerical calculations with the closed-shell CMO method, performed so far, indicate that this method reproduces about two thirds of the correlation energy of an extended CI calculation[6]. Even if one wishes to perform the CI calculation for a certain molecule, the CMO calculation provides a better starting approximation than the LCAO-MO calculation, since it leads to a set of natural orbitals in which the convergence of the CI method is improved.

So far the CMO method has been formulated assuming an orthonormal set of basis functions. When larger molecules are described, the transformation of integrals into the orthogonalized basis consumes a large fraction of total computing time. Thus, it is often more efficient, although less elegant, to perform the computation in the non-orthogonal basis set. In fact, it is commonly done so in the usual LCAO-MO calculations.

Since the changes in the CMO secular equation caused by the non-orthogonality of the basis set are non-trivial, we shall carefully reformulate the closed-shell CMO formalism in the present paper. The algorithm for the numerical solution of the resulting equations will be also briefly discussed.

CMO ENERGY FORMULA IN THE NON-ORTHOGONAL BASIS SET

The wave function $|\Psi>$ of the CMO method is essentially a real part of the complex Slater determinant $|F>$

$$|\Psi> = \mathrm{Re}\,[e^{i\omega}\,|F>] \tag{1}$$

where ω is a conventional common phase angle and $|F>$ is given by an antisymmetrized product of complex spin-orbitals

$$|F> = A\,[\varphi_1\,\alpha\,\varphi_1\,\beta\,\varphi_2\,\alpha\,\varphi_2\,\beta \ldots \varphi_n\,\alpha\,\varphi_n\,\beta] \tag{2}$$

Here α and β are spin functions and φ_k are complex orbitals forming an orthonormal set. They are determined self consistently by minimizing the energy

$$E = [h_0 + \mathrm{Re}\,(e^{2i\omega}\,Dh_1)]\,/\,[1 + \mathrm{Re}\,(e^{2i\omega}\,D)] \tag{3}$$

with

$$h_0 \equiv <F\,|\,\hat{H}\,|\,F> \qquad D \equiv <F^*\,|\,F> \qquad h_1 \equiv <F^*\,|\,\hat{H}\,|\,F>/D \tag{4}$$

H is the electronic Hamiltonian and $|F^*>$ is the complex conjugate of $|F>$.

Assuming that the real basis set $\{\psi_\mu\}$, $\mu = 1, 2, \ldots m$ is orthonormal, the complex orbitals φ_k are defined by a unitary (complex) transformation

$$\varphi_k = \sum_{\mu=1}^{m} u_{\mu k}\psi_\mu \qquad \sum_{\mu=1}^{m} u^*_{\mu k}\,u_{\mu l} = \delta_{kl} \tag{5}$$

In that case, explicit expressions for D, h_o and h_1 are derived in ref. 1:

$$D = [\det_n|\sigma_{kl}|]^2 \qquad \sigma_{kl} = \sum_{\mu=1}^{m} u_{\mu k}u_{\mu l} \qquad k,\ l \leq n \tag{6}$$

$$h_0 = 2\sum_{\mu\nu} T_{\mu\nu}\varrho_{\mu\nu} + \sum_{\mu\nu\rho\sigma} [\mu\nu\,|\,\varrho\sigma]\,\varrho_{\mu\nu}\varrho_{\rho\sigma} \tag{7}$$

$$h_1 = 2\sum_{\mu\nu} T_{\mu\nu}\Omega_{\mu\nu} + \sum_{\mu\nu\rho\sigma} [\mu\nu\,|\,\varrho\sigma]\,\Omega_{\mu\nu}\,\Omega_{\rho\sigma} \tag{8}$$

The matrices ϱ and Ω are given by

$$\varrho_{\mu\nu} = \sum_{k=1}^{n} u^*_{\mu k}\,u_{\nu k} \qquad \Omega_{\mu\nu} = \sum_{kl=1}^{n} u_{\mu k}u_{\nu l}\omega_{lk} \qquad \omega = \sigma^{-1} \tag{9}$$

Other symbols denote one-electron and two-electron integrals familiar from the LCAO-MO theory, defined in the orthogonal basis set $\{\psi_\mu\}$.

Suppose that a set $\{\chi_\rho\}$ of real non-orthogonal normalized functions is given and that $\{\psi_\mu\}$ is the orthonormal set obtained from $\{\chi_\rho\}$ by Löwdin's orthogonalization[7]:

$$\int \chi_\rho\chi_\sigma\,d\tau = S_{\rho\sigma} \qquad \psi_\mu = \sum_{\rho=1}^{m} \mathbf{S}^{-1/2}_{\rho\mu}\,\chi_\rho \tag{10}$$

In this non-orthogonal basis set, complex MO's are defined by

$$\varphi_k = \sum_{\rho=1}^{m} v_{\rho k} \chi_\rho \qquad v_{\rho k} = \sum_{\mu=1}^{m} \mathbf{S}_{\rho\mu}^{-1/2} u_{\mu k} \tag{11}$$

where the matrix **v** is complex, but it is not unitary.

In order to keep the formalism as simple as possible, it is desirable that the expressions for h_0 and h_1 have the same structure in the non-orthogonal basis set as that in eqs (7) and (8). This is accomplished by defining the matrices $\tilde{\varrho}$ and $\tilde{\Omega}$ by

$$\tilde{\varrho}_{\mu'\nu'} \equiv \sum_{\mu\nu} \mathbf{S}_{\mu'\mu}^{-1/2} \mathbf{S}_{\nu'\nu}^{-1/2} \varrho_{\mu\nu} = \sum_{k=1}^{n} v_{\mu'k}^{*} v_{\nu'k} \tag{12}$$

$$\tilde{\Omega}_{\mu'\nu'} \equiv \sum_{\mu\nu} \mathbf{S}_{\mu'\mu}^{-1/2} \mathbf{S}_{\nu'\nu}^{-1/2} \Omega_{\mu\nu} = \sum_{kl=1}^{n} v_{\mu'k} v_{\nu'l} \omega_{lk} \tag{13}$$

As before, ω is the inverse of σ, which may be expressed in terms of the new transformation matrix **v** by

$$\sigma_{kl} = \sum_{\sigma\rho} v_{\sigma k} v_{\rho l} \mathbf{S}_{\sigma\rho} \tag{14}$$

In terms of these matrices, h_0 is given by

$$h_0 = 2 \sum_{\mu\nu} \tilde{T}_{\mu\nu} \tilde{\varrho}_{\mu\nu} + \sum_{\mu\nu\rho\sigma} \{\mu\nu \mid \varrho\sigma\} \tilde{\varrho}_{\mu\nu} \tilde{\varrho}_{\rho\sigma} \tag{15}$$

where $\tilde{T}_{\mu\nu}$ and $\{\mu\nu \mid \varrho\sigma\}$ are one-electron and two-electron integrals in *the non-orthogonal basis set* $\{\chi_\mu\}$. h_1 is given by an analogous expression containing Ω instead of ϱ matrices. This completes the energy formula in the non-orthogonal basis set. Note that every trace of Löwdin's orthogonalization is lost in the final expressions, so that the formulae are completely general.

SECULAR EQUATION

The secular equation of the closed-shell CMO method, eq (49) of ref 1, could also be transformed into the non-orthogonal basis set. The SCF matrix **G** in this equation is complex and non-hermitian. Since it is computationally more advantageous to work with hermitian matrices, this secular equation has been recently transformed into a pseudo-eigenvalue problem of a hermitian matrix by adding certain terms to **G**, ref 8. Thus, the CMO secular equation in the orthogonal basis set has the form

$$\sum_{\nu=1}^{m} \overline{G}_{\mu\nu} u_{\nu\gamma}^{*} = \varepsilon_\gamma u_{\mu\gamma}^{*} \qquad \mu = 1, 2 \ldots m \qquad \gamma = 1, 2 \ldots n \tag{16}$$

The SCF matrix $\overline{\mathbf{G}}$ is given by

$$\overline{G}_{\mu\nu} = h_{\mu\nu} + 2\,\mathrm{Re}\,\{e^{2i\omega} D\,[(h_1 - E)\,\Omega_{\mu\nu} - \sum_{\sigma\rho} \Omega_{\mu\sigma} k_{\sigma\rho} \Omega_{\rho\nu}]\}$$
$$+ e^{2i\omega} D \sum_{\sigma} k_{\mu\sigma} \Omega_{\sigma\nu} + e^{-2i\omega} D^{*} \sum_{\sigma} \Omega_{\mu\sigma}^{*} k_{\sigma\nu}^{*} - (E - h_o)\,\delta_{\mu\nu} \tag{17}$$

where matrices **h** and **k** are given by

$$h_{\mu\nu} = T_{\mu\nu} + \sum_{\mu'\nu'} [\mu\nu \mid \mu'\nu'] \varrho_{\nu'\mu'} \tag{18}$$

$$k_{\mu\nu} = T_{\mu\nu} + \sum_{\mu'\nu'} [\mu\nu \mid \mu'\nu'] \Omega_{\nu'\mu'} \tag{19}$$

The other symbols have already been defined in the text.

In order to transform the secular equation (16) into the non-orthogonal basis set $\{\chi_\mu\}$, we use the following relations

$$\begin{aligned} \varrho_{\mu\nu} &= \sum_{\rho\sigma} \mathbf{S}^{1/2}_{\mu\sigma} \tilde{\varrho}_{\sigma\rho} \mathbf{S}^{1/2}_{\rho\nu}, \qquad & \Omega_{\mu\nu} &= \sum_{\sigma\rho} \mathbf{S}^{1/2}_{\mu\sigma} \tilde{\Omega}_{\sigma\rho} \mathbf{S}^{1/2}_{\rho\nu}, \\ h_{\mu\nu} &= \sum_{\sigma\rho} \mathbf{S}^{-1/2}_{\mu\sigma} \tilde{h}_{\sigma\rho} \mathbf{S}^{-1/2}_{\rho\nu}, \qquad & k_{\mu\nu} &= \sum_{\sigma\rho} \mathbf{S}^{-1/2}_{\mu\sigma} \tilde{k}_{\sigma\rho} \mathbf{S}^{-1/2}_{\rho\nu} \end{aligned} \tag{20}$$

where

$$\begin{aligned} \tilde{h}_{\mu\nu} &= \tilde{T}_{\mu\nu} + \sum_{\mu'\nu'} \{\mu\nu \mid \mu'\nu'\} \tilde{\varrho}_{\nu'\mu'} \\ \tilde{k}_{\mu\nu} &= \tilde{T}_{\mu\nu} + \sum_{\mu'\nu'} \{\mu\nu \mid \mu'\nu'\} \tilde{\Omega}_{\nu'\mu'} \end{aligned} \tag{21}$$

Here the integrals are calculated in the basis $\{\chi_\mu\}$. If we also define $\tilde{\mathbf{G}}$ by

$$\overline{\mathbf{G}} \equiv \mathbf{S}^{-1/2} \tilde{\mathbf{G}} \mathbf{S}^{-1/2} \tag{22}$$

the secular equation (16) is transformed into

$$\sum_{\nu} \tilde{G}_{\mu\nu} v^{*}_{\nu\gamma} = \varepsilon_\gamma \sum_{\nu} S_{\mu\nu} v^{*}_{\nu\gamma} \qquad \mu = 1, 2 \ldots m \qquad \gamma = 1, 2 \ldots n \tag{23}$$

with

$$\begin{aligned} \tilde{G}_{\mu\nu} = \tilde{h}_{\mu\nu} &+ 2\,\mathrm{Re}\,\{e^{2i\omega} D\, [(h_1 - E) \sum_{\alpha\beta} S_{\mu\alpha} \tilde{\Omega}_{\alpha\beta} S_{\beta\nu} - \sum_{\alpha\beta\gamma\delta} S_{\mu\alpha} \tilde{\Omega}_{\alpha\beta} \tilde{k}_{\beta\gamma} \tilde{\Omega}_{\gamma\delta} S_{\delta\nu}]\} + \\ &+ e^{2i\omega} D \sum_{\alpha\beta} \tilde{k}_{\mu\alpha} \tilde{\Omega}_{\alpha\beta} S_{\beta\nu} + e^{-2i\omega} D^{*} \sum_{\alpha\beta} S_{\mu\alpha} \tilde{\Omega}^{*}_{\alpha\beta} \tilde{k}^{*}_{\beta\nu} - (E - h_0) S_{\mu\nu} \end{aligned} \tag{24}$$

With this, the reformulation of the closed-shell CMO method in the non-orthogonal basis set is completed. The single-determinant open-shell CMO formalism[3] may be transformed into the non-orthogonal basis essentially in the same way.

FINAL REMARKS

In the preceding sections, the CMO formalism was transformed into a non-orthogonal basis set in order to gain computational efficiency avoiding the transformation of integrals. The overlap matrix **S** of the functions in the basis set enters the SCF matrix **G** in a non-trivial way. It should also be noted that the transformation matrix $v_{\nu\gamma}$ is not unitary. Since it is computationally more convenient to solve a matrix eigenvalue problem which leads to a set of orthogonal vectors, Löwdin's orthogonalization *Ansatz* may be used once more to transform eq (23) into

$$\sum_{\nu=1}^{m} (\mathbf{S}^{-1/2} \tilde{\mathbf{G}} \mathbf{S}^{-1/2})_{\mu\nu} u^{*}_{\nu\gamma} = \varepsilon_{\gamma} u^{*}_{\mu\gamma} \qquad \begin{array}{l} \mu = 1, 2, \ldots m \\ \gamma = 1, 2, \ldots n \end{array} \qquad (25)$$

which may be solved iteratively by successive diagonalization of complex hermitian matrices. This equation is the only place where Löwdin's orthogonalization is applied effectively.

REFERENCES

1. J. Hendeković, *Intern. J. Quantum Chem.* **8** (1974) 799.
2. J. Hendeković, *Chem. Phys. Letters* **32** (1975) 597.
3. J. Hendeković, *Intern. J. Quantum Chem.* **10** (1976) 1025.
4. P.-O. Löwdin, *The Projected Hartree-Fock Method,* in P.-O. Löwdin (Ed.), *Quantum Theory of Atoms, Molecules and Solid State,* Academic Press, New York 1966, pp. 601—623.
5. J. Hendeković, *Chem. Phys.* **9** (1975) 105.
6. J. Hendeković and K. Vasudevan, *Theoret. Chim. Acta (Berlin)* **39** (1975) 119.
7. P.-O. Löwdin, *J. Chem. Phys.* **18** (1950) 365.
8. J. Hendeković, *Intern. J. Quantum Chem.,* to be published.

SAŽETAK

Metoda kompleksnih molekularnih orbitala u neortogonalnoj bazi

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Da bi se u stvarnom računu izbjegla jedna transformacija integrala, metoda kompleksnih molekularnih orbitala (CMO) za zatvorene ljuske reformulirana je u neortogonalnoj bazi. Matrica prekrivanja pojavljuje se na netrivijalan način u CMO sekularnoj jednadžbi. Neki aspekti numeričkog računanja također su ukratko razmatrani.

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