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An Analysis of the Complex Molecular Orbitals Method

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Numerical results for the ground state of the HN_2^+ and HCO^+ molecular ions at their near equilibrium geometry, obtained by the complex molecular orbitals (CMO) method in the extended basis set, are reported. The CMO wavefunction of the HN_2^+ ion is compared with the CI wavefunction obtained in the same basis set. This reveals the nature of approximations inherent in the CMO method. A peculiar feature of the occupation numbers of the CMO natural orbitals is also explained.

Key words: Complex molecular orbitals method – Closed shell complex MO formalism

1. Introduction

The complex molecular orbitals (CMO) method which was recently developed [1–3] incorporates dominant electron correlations into the zero-order molecular wavefunction. This is substantiated by the numerical results for the N_2 and CO molecules, obtained with a minimal basis set, which are close to those derived from limited configuration interaction (CI) calculations [2]. It was recently shown that the method could also be understood as a natural unification of the molecular orbital and valence bond theories of a chemical bond [4].

In the light of the usefulness of the method, it seems necessary to examine the scope and limitations of the CMO calculational scheme. To this end, a comparative study of the wavefunctions obtained using both the CMO and conventional CI methods is essential. In the present communication, such an analysis of the results on molecular ions, HN_2^+ and HCO^+, is carried out.

2. Survey of the Closed-Shell CMO Formalism

Since the theory of the complex molecular orbital method for a closed-shell system has been recently given in detail [2], only the essential features will be outlined. For a closed-shell system of $2n$ electrons, a set of m orthonormal orbitals ψ_j is assumed to be given. ψ_j's could be either LCAO-MO's or orthonormalized symmetry orbitals. A new equivalent set of "complex" orbitals χ_k is introduced by an appropriate unitary (complex) transformation

$$\chi_k = \sum_j U_{jk}\psi_j . \tag{1}$$

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A molecular ground state could be described by an unnormalized wavefunction $|\Psi\rangle$ [2],

$$|\Psi\rangle = \mathscr{R}e(e^{i\phi}|\Phi\rangle) \tag{2}$$

where $|\Phi\rangle$ is an antisymmetric normalized product (Slater determinant) formed from doubly occupied orbitals, χ_k,

$$|\Phi\rangle = A[\chi_1\alpha\chi_1\beta\chi_2\alpha\chi_2\beta\ldots\chi_n\alpha\chi_n\beta]\,. \tag{3}$$

The operation $\mathscr{R}e$ (taking the real part) acts only on the phase factor ϕ and on coefficients, U_{jk}. It does not affect the basis vectors ψ_j even if they happen to be complex functions. The common phase factor was explicitly introduced in (2) since absolute phases of complex orbitals χ_k cannot be determined from a secular equation of the pseudo-eigenvalue form. The phase factor allows for a convention that the diagonal elements of the unitary matrix U_{jj} are real and non-negative.

The wavefunction in Eq. (2) leads to the energy formula

$$E = [h_0 + \mathscr{R}e(e^{2i\phi}Dh_1)]/[1 + \mathscr{R}e(e^{2i\phi}D)] \tag{4}$$

where

$$h_0 = \langle\Phi|\hat{H}|\Phi\rangle\,,$$

$$D = \langle\Phi^*|\Phi\rangle\,, \quad \text{and}$$

$$h_1 = \langle\Phi^*|\hat{H}|\Phi\rangle/D\,. \tag{5}$$

Since $|\Phi^*\rangle$ and $|\Phi\rangle$ are two nonorthogonal Slater determinants, D and h_1 may be calculated by the method of Löwdin [5]. Using Löwdin's method, one obtains [2]:

$$D = (\det_n|\boldsymbol{\sigma}|)^2\,, \tag{6}$$

$$h_0 = 2\textstyle\sum_{ij} T_{ij}\varrho_{ij} + \sum_{iji'j'} [ij|i'j']\varrho_{ij}\varrho_{i'j'}\,, \tag{7}$$

and

$$h_1 = 2\textstyle\sum_{ij} T_{ij}\Omega_{ij} + \sum_{iji'j'} [ij|i'j']\Omega_{ij}\Omega_{i'j'}\,, \tag{8}$$

where $\boldsymbol{\sigma}$ is the overlap matrix given by

$$\sigma_{ij} \equiv \langle\chi_i^*|\chi_j\rangle \equiv \textstyle\int \chi_i\chi_j d\tau = \sum_{k=1}^{m} U_{ki}U_{kj} \tag{9}$$

and where matrices $\boldsymbol{\varrho}$ and $\boldsymbol{\Omega}$ have elements

$$\varrho_{ij} = \textstyle\sum_{k=1}^{n} U_{ik}^* U_{jk}\,; \qquad \Omega_{ij} = \sum_{kl=1}^{m} U_{ik}U_{jl}(\boldsymbol{\sigma}^{-1})_{lk} \tag{10}$$

T_{ij} and $[ij|i'j']$ in Eqs. (7) and (8) denote one- and two-electron integrals which are exactly the same as those that appear in the LCAO-MO method.

The optimal set of coefficients U_{jk} and the phase angle ϕ may be obtained directly by a numerical minimization of the energy given in Eq. (4). Alternatively, one could solve the corresponding secular equations. One of these secular equations follows from the energy variation with respect to ϕ [3].

$$\sin(2\phi + \omega) = R/S \tag{11}$$

where real numbers R, S and ω are determined from

$$R = |D|^2 \mathrm{Im}\,h_1\,; \qquad e^{i\omega}S = D(h_0 - h_1)\,. \tag{12}$$

For the other secular equation, the following pseudo-eigenvalue equation has been recently derived [2]:

$$\sum_{j=1}^{m} G_{ij} U_{jl}^{*} = \varepsilon_l U_{il}^{*} , \quad \substack{i=1,m \\ l=1,n} . \tag{13}$$

The complex non-hermitian matrix $\boldsymbol{G}$ is given by

$$\boldsymbol{G} = \boldsymbol{h} + e^{2i\phi} D[(h_1 - E)\boldsymbol{\Omega} + (\boldsymbol{I} - \boldsymbol{\Omega})\boldsymbol{k}\boldsymbol{\Omega}] . \tag{14}$$

Matrices $\boldsymbol{h}$ and $\boldsymbol{k}$ are defined by

$$h_{ij} = T_{ij} + \sum_{i'j'} [ij|i'j'] \varrho_{j'i'} ; \qquad k_{ij} = T_{ij} + \sum_{i'j'} [ij|i'j'] \Omega_{j'i'} \tag{15}$$

and $\boldsymbol{I}$ is the identity matrix δ_{ij}.

The secular Eq. (13) is solved by successive matrix triangularization accompanied by solving the Eq. (11) in each iterational step. The matrix triangularization may be conveniently performed by a set of elementary unitary transformations with nontrivial (2 × 2) part of the form

$$U = \begin{pmatrix} c & s \\ -s^{*} & c \end{pmatrix} ; \qquad \begin{aligned} c &= \cos\theta \\ s &= \sin\theta \cdot e^{i\beta} . \end{aligned} \tag{16}$$

Since resulting orbital energies should be monotonically increasing so that complex orbitals of lowest energies are occupied when the self-consistency is reached, the appropriate ordering should be built into the triangularization algorithm.

3. CMO Numerical Results in the Extended Basis Set

The CMO secular Eqs. (11) and (13) were solved for the linear HN_2^+ molecule ion in the ground state at its near equilibrium geometry ($R_{NN} = 2.0674$ bohr; $R_{NH} = 2.0$ bohr). As the initial basis set of orbitals the LCAO-MO-SCF solutions of Ref. [6] were utilized. In order to compare our results with the CI results (the details of the CI calculation whose results are here used are given in Ref. [6]), the three lowest σ-orbitals ($1\sigma 2\sigma 3\sigma$) in the above set were left in "core" (as in Ref. [6]). The "core" orbitals are not subjected to a complex unitary transformation. The remaining orbitals in the set contain ten σ and four π orbitals of which 4σ, 5σ, and 1π are occupied in the ground state configuration, $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4$.

The solution of the CMO secular equation yields an electronic energy $E_{CMO} = -109.1876$ hartree which is 0.1138 hartree below the LCAO-MO energy. This makes 66.9% of the CI energy lowering, 0.1700 hartree [6]. The following values of h_0, h_1, D and ϕ correspond to the CMO solution: $h_0 = -22.0227$ hartree, $h_1 = (-22.96500 - 0.1597i)$ hartree, $D = (0.4860 - 0.0261i)$, $\phi = -0.0978$ radian, while the energy contribution of the core electrons and of nuclear repulsion is $E_0 = -86.1652$ hartree. Coefficients U_{ki} (σ) for the occupied complex σ-orbitals ($i = 4, 5$) are given in Table 1. The coefficients of the occupied π-orbital are as follows: $U_{11}(\pi) = 0.9616$; $U_{21}(\pi) = (0.0143 - 0.2626i)$; $U_{31}(\pi) = (-0.0150 + 0.0298i)$; $U_{41}(\pi) = (0.0055 - 0.0709i)$.

Table 1. Coefficients $U_{ki}(\sigma)$ of the occupied HN_2^+ σ-orbitals, $i=4, 5$

k	$U_{k4}(\sigma)$	$U_{k5}(\sigma)$
4	0.9958	-0.0398 + 0.0220 i
5	0.0418 + 0.0215 i	0.9930
6	-0.0023 + 0.0354 i	-0.0091 + 0.0165 i
7	-0.0010 + 0.0071 i	-0.0028 + 0.0089 i
8	0.0014 + 0.0038 i	0.0028 - 0.0085 i
9	-0.0029 + 0.0189 i	-0.0076 + 0.0307 i
10	-0.0009 + 0.0630 i	0.0058 - 0.0470 i
11	0.0057 - 0.0041 i	0.0157 - 0.0841 i
12	0.0002 + 0.0202 i	0.0034 - 0.0288 i
13	0.0003 + 0.0112 i	0.0015 - 0.0058 i

The one-electron reduced density matrix $\varrho^{(1)}$

$$\varrho^{(1)} = \mathscr{Re}(\varrho + e^{2i\phi} D\Omega)/\mathscr{Re}(1 + e^{2i\phi} D)$$

was diagonalized and the corresponding CMO natural orbitals and their occupation probabilities γ_k were obtained. In the σ-space only four natural orbitals have non zero occupation probabilities, which are in the decreasing order 0.9981, 0.9958, 0.0042, and 0.0019. Also, out of four π natural orbitals, only two have non-zero occupation; i.e. $\gamma_1(\pi)=0.9780$ and $\gamma_2(\pi)=0.0220$. A similar feature of the CMO results was also noticed in the minimal basis set CMO calculations [2]. These results indicate that the CMO wavefunction (2) may be generally transformed into a form in which the number of occupied complex orbitals equals the number of empty complex orbitals, while all other orbitals are real. Although we do not have a formal proof of this equivalence, we shall show that the number of independent variational parameters is the same in these two cases.

Suppose that in the CMO wavefunction, as in Eq. (2), the number of occupied σ-orbitals is μ, and the number of empty σ-orbitals is v, with $v>\mu$. According to Ref. [3] the corresponding transformation unitary matrix $U_{jk}(\sigma)$ is given essentially by $2\mu v$ generalized Euler angles $\theta_k^{(l)}$ and $\phi_k^{(l)}$ which may be considered as independent variational parameters. It is indicated above that the same result could be obtained if 2μ orbitals are allowed to be complex and remaining $(v-\mu)$ orbitals are real. In order to determine these real orbitals in the minimization procedure according to [3] we need $(v-\mu)\times 2\mu$ Euler angles, since the corresponding orthogonal transformation matrix may be assumed in parts triangular. Indeed, an arbitrary orthogonal transformation of these $(v-\mu)$ real orbitals between themselves does not change the wavefunction, while the remaining 2μ real orbitals form a basis for the subsequent CMO treatment, thus permitting also an arbitrary orthogonal transformation between themselves. To determine μ occupied complex orbitals in the space of 2μ basis orbitals, additional $2\mu^2$ generalized Euler angles are needed. Thus, total number of variational parameters would be $2\mu(v-\mu)+2\mu^2=2\mu v$, which is the same as in the complete CMO treatment.

This seems to explain the peculiar results for the occupation probabilities of the CMO natural orbitals.

The CMO calculation was also performed for the near equilibrium geometry of the linear HCO^+ ion in the ground state, using the LCAO-MO-SCF vectors [7] which contain 13σ- and 5π-orbitals of which two lowest σ orbitals were left in "core". An energy decrease 0.1487 hartree with respect to the LCAO-MO energy was obtained. This amounts to 69.7% of the energy lowering obtained in the CI calculation [7].

In the case of HCO^+ molecule ion, 25 seconds of the CPU time of the IBM/370 were needed for 16 iterations on the solution of the CMO secular equations, when the integrals were prepared in advance. Initial vectors were constructed by a small CMO treatment of two π-orbitals.

4. Comparison of the CMO and CI Wavefunctions

In order to gain an insight into the nature of approximations inherent in the CMO "ansatz", we compare in Table 2 a few largest components $\chi_k(\mathrm{CI})$ of the CI ground state wavefunction of HN_2^+ [6] with the corresponding components contained in the CMO result, $\chi_k(\mathrm{CMO})$. Since the CI and CMO calculations were performed using the same basis set, components $\chi_k(\mathrm{CMO})$ are obtained as the overlap of the (normalized) CMO wavefunction $|\Psi\rangle$ and the Slater determinant $|\Psi_k\rangle$ of an appropriate configuration.

$$\begin{aligned}\chi_k(\mathrm{CMO}) &= (\langle\Psi_k|\Psi\rangle/\langle\Psi|\Psi\rangle^{1/2}) \\ &= \mathcal{R}e(e^{i\phi}\langle\Psi_k|\Phi\rangle)/(0.5(1+\mathcal{R}e\,e^{2i\phi}D))^{1/2} \end{aligned} \tag{18}$$

Table 2. Dominant components of the CI wavefunction [6] of the HN_2^+ molecule ion compared with corresponding components extracted from the CMO wavefunction

c	k	Slater Determinant $\|\Psi_k\rangle$	N	χ_k(CI)	χ_k(CMO)
1	1	$4\sigma^2\ 5\sigma^2\ 1\pi^4$	1	0.957	0.974
2	2	$4\sigma^2\ 5\sigma^2\ 1\pi_x^2\ 2\pi_y^2$	2	-0.113	-0.073
	3	$4\sigma^2\ 5\sigma^2\ 1\pi_x\alpha\ 1\pi_y\beta\ 2\pi_x\beta\ 2\pi_y\alpha$	2	-0.074	-0.073
	4	$4\sigma^2\ 5\sigma^2\ 1\pi_x\alpha\ 2\pi_y\beta\ 2\pi_x\beta\ 1\pi_y\alpha$	2	-0.047	-0.073
	5	$4\sigma^2\ 5\sigma^2\ 1\pi_x\alpha\ 1\pi_y\beta\ 2\pi_y\beta\ 2\pi_x\alpha$	2	-0.026	$\pi_x\alpha\pi_y\beta \leftrightarrow \pi_x\beta\pi_y\alpha$
	6	$4\sigma^2\ 5\sigma^2\ 1\pi_x^2\ 2\pi_x^2$	2	-0.013	$\pi_x^2 \leftrightarrow \pi_y^2$
3	7	$4\sigma^2\ 1\pi^4\ 2\pi_x^2$	2	-0.042	$\sigma^2 \leftrightarrow \pi^2$
4	8	$5\sigma^2\ 1\pi^4\ 2\pi_x^2$	2	-0.022	$\sigma^2 \leftrightarrow \pi^2$
5	9	$4\sigma^2\ 5\sigma^2\ 1\pi_x^2\ 2\pi_y\alpha\ 4\pi_y\beta$	4	-0.038	-0.020
	10	$4\sigma^2\ 5\sigma^2\ 1\pi_x\alpha\ 1\pi_y\beta\ 2\pi_x\beta\ 4\pi_y\alpha$	4	-0.025	-0.020
	11	$4\sigma^2\ 5\sigma^2\ 1\pi_x\alpha\ 1\pi_y\alpha\ 2\pi_y\beta\ 4\pi_x\beta$	4	-0.016	-0.020
	12	$4\sigma^2\ 5\sigma^2\ 1\pi_x\alpha\ 1\pi_y\beta\ 2\pi_y\beta\ 4\pi_x\alpha$	4	-0.008	$\pi_x\alpha\pi_y\beta \leftrightarrow \pi_x\beta\pi_y\alpha$
	13	$4\sigma^2\ 5\sigma^2\ 1\pi_x^2\ 2\pi_x\alpha\ 4\pi_x\beta$	4	-0.004	$\pi_x^2 \leftrightarrow \pi_y^2$
6	14	$4\sigma^2\ 5\sigma\alpha\ 11\sigma\beta\ 1\pi_x^2\ 2\pi_y\alpha\ 1\pi_y\beta$	4	-0.020	-0.023
	15	$4\sigma^2\ 5\sigma\alpha\ 11\sigma\beta\ 1\pi_x^2\ 1\pi_y\alpha\ 2\pi_y\beta$	4	-0.017	-0.023
	16	$4\sigma^2\ 5\sigma\alpha\ 11\sigma\alpha\ 1\pi_x^2\ 1\pi_y\beta\ 2\pi_y\beta$	4	-0.003	$\sigma\alpha\pi\beta \leftrightarrow \sigma\beta\pi\alpha$
7	17	$4\sigma_\alpha\ 5\sigma_\beta\ 1\pi^4\ 2\pi_x^2$	4	0.016	$\sigma^2 \leftrightarrow \pi^2$

$\langle \Psi_k | \Phi \rangle$ is the overlap of two nonorthogonal Slater determinants, and it is equal to the determinant of the overlap matrix of basis orbitals in $|\Psi_k\rangle$ and occupied complex orbitals in $|\Phi\rangle$. Thus, this is certain submatrix of the transformation matrix U in (1).

It is seen from Table 2 that certain configurations are not present at all in the CMO wavefunction, although they contribute to the CI wavefunction ($c = 3$, for example). In the present CMO "ansatz" they are not allowed by symmetry since the transformation (1) is performed separately for σ and π orbitals (like in the restricted HF). As indicated in the entry χ_k(CMO) of Table 2 the $c = 3$ configuration is characterized by the promotion of an electron pair from the σ-space into the π-space, which cannot be expressed by the "restricted" CMO wavefunction.

Only representative Slater determinants are explicitly given in Table 2. The number N suggests how many equivalent Slater determinants may be obtained by substituting α for β or π_x for π_y and *vice versa*. Each interacting configuration c contains a symmetrized set of determinants [8]; i.e. spin and space adapted.

In the present analysis of the CI ground state wavefunction of the HN_2^+ ion, all configurations with CI expansion coefficients larger than 0.01 (427 Slater determinants in 51 configurations) were considered. The Slater determinants thus taken into consideration were distributed into five classes. In Table 3, the sum of squares of the CI coefficients for the given classes of Slater determinants are presented. Class 1 contains all Slater determinants which may be obtained from the main ground state configuration by redistributing electrons inside of each symmetry subspace of orbitals. All such Slater determinants could be generated (accounted for), in principle, by the "restricted" CMO transformation (1). Class 2 corresponds to Slater determinants in which two electrons were exchanged between σ- and π-spaces. It is clear that the CMO wavefunction is an approximation to that part of the CI wavefunction which contains the main ground state configuration and Slater determinants of class 1. According to Table 3 about 88% of a departure of the CI wavefunction from the main ground state configuration belongs to class 1, and remaining 12% to all other classes. Assuming that the perturbation in the energy is proportional to a square of the perturbation in the wavefunction (as the perturbation theory suggests), it is clear that about 10% of the correlation energy is out of reach of the CMO "ansatz" for the symmetry reason alone. A refinement of the CMO method which would cover also this part of electron correlations would require few additional configurations to be considered explicitly.

Table 3. Relative weights of different types of the CI components

Class	1	2 $\sigma^2 \leftrightarrow \pi^2$	3 $\pi_x\alpha\pi_y\beta \leftrightarrow \pi_y\alpha\pi_x\beta$	4 $\sigma\alpha\pi\beta \leftrightarrow \pi\alpha\sigma\beta$	5 $\pi^2_x \leftrightarrow \pi^2_y$
$\sum_j \chi_j^2$(CI)	0.0694	0.0064	0.0016	0.0009	0.0004

From Table 2 it is also seen that coefficients of Slater determinants which appear in the CMO wavefunction for a particular configuration are given by a single value. This value is an approximation to the average of the corresponding CI coefficients. In a few dominant configurations (like $c = 2$ in Table 2) this averaging may represent quite a drastic approximation. Thus, in a more ambitious calculational scheme based on complex MO's few dominant configurations should be treated explicitly like in the multiconfigurational Hartree-Fock method. The role of complex orbitals would be to collect large number of small CI components around the multiconfigurational skeleton. However, due to nonorthogonalities the simplicity of the CMO method will be lost in such a scheme.

5. Conclusion

Numerical results for the HN_2^+ and HCO^+ ions obtained by the CMO method in the extended basis set demonstrate that about 2/3 of the electron correlations described by present CI calculations [6, 7] may be reproduced. The significance of this result lies in the simplicity of the secular equation which is comparable to that of the LCAO-MO method. From the detailed analysis of the HN_2^+ ground state CI wavefunction certain limitations of the CMO "ansatz" were recognized. It seems clear that a significant improvement over the CMO "ansatz" would require a multiconfigurational treatment, in which, however, the simplicity of the CMO method would be considerably reduced.

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