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Application of the AMO Method to the Naphthalene Molecule

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The alternant molecular orbital (AMO) method was applied to the ground state of naphthalene. Both the single and the many-parameter variants lead to substantial improvement in the energy. Comparison with a limited configurational interaction treatment shows that the AMO method is better in the many-parameter variant.

Die Methode der alternierenden MO (AMO) wurde auf den Grundzustand des Naphthalins angewandt. Beide Varianten der Methode, mit einem sowie mit mehreren Parametern, bringen wesentliche Verbesserung in der Energie. Vergleich mit einer beschränkten Konfigurations-Wechselwirkungs-Methode zeigt, daß die AMO-Methode besser ist, wenn mehrere Parameter angewandt werden.

La méthode des orbitales moléculaires alternantes (AMO) est appliquée a l'état-fondamental du naphthalène. Les variantes a un ou plusieurs parametres de cette methode produisent des améliorations substantielles pour l'énergie. La comparison avec une application de la méthode d'interaction de configurations limitée montre que la méthode AMO est plus efficace dans la variante avec plusieurs parametres.

1. Introduction

The alternant molecular orbital method (AMO) proposed by Löwdin [1] is an extension of the independent-particle model. It is intended for an improved description of the electronic correlation especially between electrons having antiparallel spins. The α and β spin functions are allotted to two different sets of spatial orbitals which have maxima in different regions in the molecule. The general theory of the method and the relevant energy expressions have been treated in a series of papers [2] and recently summarized in a monograph [3]. The method has been successfully applied to benzene [4], other cyclic systems [5] and some small conjugated molecules [6]. These systems are somewhat special: the cyclic systems have molecular orbitals completely determined by symmetry and in the case of small systems even the full configuration interaction treatment involves only a small number of configurations[1]. The aim of the present paper is to apply the method to a system which is free of the limitations mentioned above. The naphthalene molecule has been chosen as a convenient test case. Our purpose is twofold: we want to test the applicability of the AMO method to a medium size aromatic system and to investigate different ground state properties of the molecule as obtained from a wave function which gives a better representation of the π-electronic correlation.

The electronic structure of naphthalene has been the subject of numerous investigations. Among the recent publications we refer to the paper of Gonzalez et al. [8] and to the bibliography contained in it. The only common feature of these studies is the assumption about the σ-π separability but from this point

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[1] For a distinction between the full and complete configuration interaction treatment see [7].

on the methods and treatments diverge considerably. In our work the emphasis will be on testing the AMO method so that we shall try to keep the simplifications and approximations to a minimum. The method of computation will be presented in Section 2. Results of the AMO calculations for the energy are given in Section 3 while the charge and bond order matrix is analysed in Section 4. A brief conclusion is given in Section 5.

2. Determination of the Molecular Orbitals

The alternant molecular orbitals are linear combinations of the bonding and antibonding molecular orbitals. They are given in the following form

$$\begin{aligned} a_{\mathrm{I}} &= \cos\vartheta_i\,\psi_i + \sin\vartheta_i\,\psi_{\bar{i}}\,, \\ \bar{a}_{\mathrm{I}} &= \cos\vartheta_i\,\psi_i - \sin\vartheta_i\,\psi_{\bar{i}}\,. \end{aligned} \tag{1}$$

For the molecular orbitals we have chosen two sets a) self-consistent field (Roothaan) orbitals, b) eigenvectors of the overlap matrix. The first set is characterized by the fact that in the single-determinantal wave function it yields the lowest energy. The second set has interesting properties [9] and it makes the calculation of the matrix elements much easier.

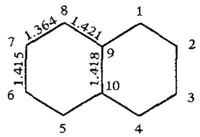

Fig. 1. The geometry of naphthalene

The geometrical data of the molecule were taken from Cruickshank and Sparks [10] and they are given in Fig. 1. The molecular orbitals are given in the form

$$\psi_i = \sum_{\mu} \chi_\mu c_{\mu i}\,, \tag{2}$$

where χ_μ is an atomic $2p_z$ orbital centered on atom μ. The matrix elements of the Hamiltonian over the basic atomic orbitals are determined using Ruedenberg's analysis [11]. It is essential the distinction between short range and long range parts in the Hamiltonian; neutral atom potential and kinetic energy belong to the first kind while electron interaction to the second kind. Electron interaction integrals were evaluated by a consistent use of the Mulliken approximation [12]. Overlap integrals were retained in the calculations. Table 1 contains the integrals between the atomic orbitals; overlap integrals, Coulomb integrals and the matrix elements of the one-electron Hamiltonian are given[2].

Self-consistent orbitals have been determined previously by Moser [13], Kolboe and Pullman [14] and Gladney [15]. The approximations used in the present paper differ from the ones used in the previous investigations.

Table 2 contains the molecular orbitals as determined from the Roothaan procedure and by the diagonalization of the overlap matrix.

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[2] Some preliminary results are reported in [3]. The calculations given here are more complete than those given in [3] as all the elements of the overlap matrix are retained.

Table 1. *Overlap integrals, Coulomb integrals and matrix elements of the one-electron Hamiltonian between atomic orbitals for naphthalene*

μ	ν	$S_{\mu\nu}$	$\gamma_{\mu\nu}$(eV)	$h_{\mu\nu}$(eV)
1	1	1.	17.228953	−74.348748
2	1	0.261999	9.210997	−21.386803
2	2	1.	17.228953	−70.978411
3	1	0.035500	5.674943	− 2.354295
3	2	0.240674	8.955520	−19.150509
4	1	0.015313	4.943846	− 1.041624
5	1	0.001765	3.762717	− 0.120031
5	2	0.000560	3.354074	− 0.037138
5	3	0.001873	3.786945	− 0.124200
5	4	0.030685	5.530827	− 2.087293
6	1	0.000560	3.354074	− 0.037138
6	2	0.000074	2.827982	− 0.004805
6	3	0.000124	2.944496	− 0.008041
6	4	0.001873	3.786945	− 0.124200
9	1	0.238258	8.926210	−20.769529
9	2	0.035500	5.674943	− 2.504516
9	3	0.015517	4.953707	− 1.094701
9	4	0.033046	5.603038	− 2.387688
9	9	1.	17.228953	−84.130520
10	9	0.239464	8.940845	−21.892623

Table 2. *Molecular orbitals for naphthalene*

Sym.	MO	Roothaan scheme			Eigenvectors of the overlap matrix		
	AO:	1	2	9	1	2	9
b_{3u}	1	0.21715	0.18410	0.36904	0.23401	0.19645	0.33265
b_{2g}	2	0.23200	0.34670	0	0.22939	0.34844	0
b_{1g}	3	0.33580	0.19985	0.29140	0.35475	0.16327	0.28903
b_{3u}	4	0.06695	0.33860	−0.44166	−0.01643	0.36264	−0.40462
a_{1u}	5	0.39170	0.27065	0	0.39754	0.26187	0
b_{2g}	6	0.46895	−0.31150	0	0.47023	−0.30956	0
b_{1g}	7	−0.02770	−0.41085	0.58980	0.01168	−0.46756	0.49508
b_{3u}	8	0.48690	−0.26055	−0.35263	0.48337	−0.21568	−0.42534
a_{1u}	9	0.35865	−0.53020	0	0.53213	−0.53456	0
b_{1g}	10	0.42770	−0.38070	−0.55437	0.41292	−0.33188	−0.63860

Symmetry Considerations

The molecule belongs to the D_{2h} symmetry and each of the molecular orbitals belongs to a certain irreducible representation of the symmetry group. The alternant molecular orbitals themselves do not belong to a given irreducible representation as they are combinations of molecular orbitals belonging to different symmetries. Table 3 shows the behaviour of the alternant molecular orbitals under the symmetry operations of the group. Considering the total wave function

$$\Psi = \mathscr{A} a_{\mathrm{I}}(1) \dots a_{\mathrm{V}}(5)\, \bar{a}_{\mathrm{I}}(6) \dots \bar{a}_{\mathrm{V}}(10)\, \mathcal{O}_{00}\, \alpha(1) \dots \alpha(5)\, \beta(6) \dots \beta(10) \tag{3}$$

we see that there are two possibilities. The wavefunction either remains invariant or it goes over to the following function

$$\Psi' = \mathscr{A} \bar{a}_{\mathrm{I}}(1) \dots \bar{a}_{\mathrm{V}}(5)\, a_{\mathrm{I}}(6) \dots a_{\mathrm{V}}(10)\, \mathcal{O}_{00}\, \alpha(1) \dots \alpha(5)\, \beta(6) \dots \beta(10)\,. \tag{4}$$

Let us apply the permutation (1, 6) ... (5, 10) to this function.

$$(1,6)\ldots(5,10)\,\Psi' = -\Psi' = \mathscr{A}\, a_{\mathrm{I}}(1)\ldots\bar{a}_{\mathrm{V}}(10)\,\mathcal{O}_{00}\,\beta(1)\ldots\alpha(10)\,. \tag{5}$$

From the symmetry properties of the projected spin function follows the identity [16]

$$\mathcal{O}_{00}\beta(1)\ldots\beta(5)\alpha(6)\ldots\alpha(10) = -\mathcal{O}_{00}\alpha(1)\ldots\alpha(5)\beta(6)\ldots\beta(10)\,, \tag{6}$$

so that the wavefunction remains invariant under all symmetry operations and it belongs to the representation ${}^1A_{1g}$.

Table 3. *Transformation of AMO orbitals under operations of the elements of the symmetry group*

E	C_2^x	C_2^y	C_2^z	I	IC_2^x	IC_2^y	IC_2^z
a_{I}	$-\bar{a}_{\mathrm{I}}$	$-a_{\mathrm{I}}$	$\bar{a}_{\mathrm{I}}$	$-\bar{a}_{\mathrm{I}}$	a_{I}	$\bar{a}_{\mathrm{I}}$	$-a_{\mathrm{I}}$
$\bar{a}_{\mathrm{I}}$	$-a_{\mathrm{I}}$	$-\bar{a}_{\mathrm{I}}$	a_{I}	$-a_{\mathrm{I}}$	$\bar{a}_{\mathrm{I}}$	a_{I}	$-\bar{a}_{\mathrm{I}}$
a_{II}	$-\bar{a}_{\mathrm{II}}$	a_{II}	$-\bar{a}_{\mathrm{II}}$	$\bar{a}_{\mathrm{II}}$	$-a_{\mathrm{II}}$	$\bar{a}_{\mathrm{II}}$	$-a_{\mathrm{II}}$
$\bar{a}_{\mathrm{II}}$	$-a_{\mathrm{II}}$	$\bar{a}_{\mathrm{II}}$	$-a_{\mathrm{II}}$	a_{II}	$-\bar{a}_{\mathrm{II}}$	a_{II}	$-\bar{a}_{\mathrm{II}}$
a_{III}	$\bar{a}_{\mathrm{III}}$	$-a_{\mathrm{III}}$	$-\bar{a}_{\mathrm{III}}$	$\bar{a}_{\mathrm{III}}$	a_{III}	$-\bar{a}_{\mathrm{III}}$	$-a_{\mathrm{III}}$
$\bar{a}_{\mathrm{III}}$	a_{III}	$-\bar{a}_{\mathrm{III}}$	$-a_{\mathrm{III}}$	a_{III}	$\bar{a}_{\mathrm{III}}$	$-a_{\mathrm{III}}$	$-\bar{a}_{\mathrm{III}}$
a_{IV}	$-\bar{a}_{\mathrm{IV}}$	$-a_{\mathrm{IV}}$	$\bar{a}_{\mathrm{IV}}$	$-\bar{a}_{\mathrm{IV}}$	a_{IV}	$\bar{a}_{\mathrm{IV}}$	$-a_{\mathrm{IV}}$
$\bar{a}_{\mathrm{IV}}$	$-a_{\mathrm{IV}}$	$-\bar{a}_{\mathrm{IV}}$	a_{IV}	$-a_{\mathrm{IV}}$	$\bar{a}_{\mathrm{IV}}$	a_{IV}	$-\bar{a}_{\mathrm{IV}}$
a_{V}	$\bar{a}_{\mathrm{V}}$	a_{V}	$\bar{a}_{\mathrm{V}}$	$-\bar{a}_{\mathrm{V}}$	$-a_{\mathrm{V}}$	$-\bar{a}_{\mathrm{V}}$	$-a_{\mathrm{V}}$
$\bar{a}_{\mathrm{V}}$	a_{V}	$\bar{a}_{\mathrm{V}}$	a_{V}	$-a_{\mathrm{V}}$	$-\bar{a}_{\mathrm{V}}$	$-a_{\mathrm{V}}$	$-\bar{a}_{\mathrm{V}}$

3. AMO Calculations

Two kind of AMO calculations were performed. In the simpler one a common mixing parameter $\lambda = \cos 2\vartheta$ is used for all the orbital pairs. In the refined treatment different mixing parameters were obtained for the pairs. There are many physical reasons why the second treatment should yield a more correct description of the ground state of the molecule (de Heer [17]).

The energy expressions for the single-parameter and the many-parameter wavefunctions are given in [3]. For the many-parameter case the minimization was carried out using a program written by Gershgoren [18]. Table 4 contains the results of the single-parameter calculation while the many-parameter results are displayed in Table 5. Both calculations are performed using the two different sets for the molecular orbitals. The zero point of the energy was chosen as the energy corresponding to the single determinant using SCF orbitals (−494.4805 eV). Comparing the tables we see that the energy improvements are greater in the case of the molecular orbitals which are eigenvectors of the overlap matrix than

Table 4. *One-parameter AMO calculation for naphthalene*

MO	$E(\lambda = 1)$[a]	$\lambda_{\min}$	$E(\lambda_{\min})$[a]	ΔE[b]
SCF	−494.4805	0.689	−498.5394	−4.0589
Top.	−494.0243	0.675	−498.3510	−3.8705

[a] Energy in electron volt.

[b] Zeropoint of the energy = E (SCF, $\lambda = 1$).

for the SCF orbitals but the final energy values are lower in the latter case because the corresponding starting point (the energy of a single determinant) is better by 0.4562 eV.

The energy improvements obtained are quite considerable. We see that in the one-determinantal wavefunction going over from the Δ orbitals to the SCF ones means an improvement of only 0.4562 eV while the subsequent application of the AMO method leads to an improvement of 4.0589 eV in the single-parameter approach and to an additional improvement of about 1 eV in the many-parameter scheme. The energy improvements obtained are of the same order of magnitude as those achieved in the case of cyclic systems with the same number of atoms.

Table 5. *Many-parameter AMO calculation for naphthalene*

MO	λ_1	λ_2	λ_3	λ_4	λ_5	ΔE[a]
SCF	0.8236	0.7286	0.6431	0.5249	0.4648	−5.0454
Top.	0.8159	0.7210	0.6366	0.5196	0.4365	−4.9276

[a] Energy in electron volt. Zero-point of the energy: −494.4805.

Comparison with CI *Treatment*

The full configuration interaction treatment for the ground state of naphthalene involves 4936 configurations of the type ${}^1A_{1g}$. Evidently this number is too high for performing a full configuration interaction treatment. The AMO wavefunction actually corresponds to a limited and constrained configuration interaction in which only certain selected configurations appear (those in which a given orbital is replaced by its antibonding partner) and the coefficients of the configurations are determined by the values of the non-linear mixing parameters λ_k.

Let us determine the number of configurations appearing in the AMO wavefunction. For the sake of simplicity we shall choose the single-parameter wavefunction. The AMO function can be expanded in the following form

$$\Psi = \sum_{i=0} a^{10-i} b^i \Psi_i , \tag{7}$$

where $a = \cos\vartheta$ and $b = \sin\vartheta$.

$$\Psi_i = \mathscr{A} \Phi_i \Theta_{00} \vartheta_1 \tag{8}$$

with
$$\vartheta_1 = \alpha(1) \ldots \alpha(5) \beta(6) \ldots \beta(10) . \tag{9}$$

Ψ_0 corresponds to the single determinant with doubly occupied orbitals.

$$\Phi_0 = \psi_1(1) \ldots \psi_5(5) \psi_1(6) \ldots \psi_5(10) . \tag{10}$$

Φ_i can be obtained in the form

$$\Phi_i = \sum_{\kappa=\mu}^{\nu} (-1)^{-\kappa} \{\kappa | i - \kappa\} , \tag{11}$$

where
$$\mu = \max(0, i-5) \tag{12}$$
$$\nu = \min(i, 5) ,$$

and $\{\kappa|\lambda\}$ is defined as the sum of all functions which are obtained from Φ_0 as κ of the first 5 functions and λ of the last 5 functions are replaced by their antibonding partners. For example:

$$\Phi_6 = -\{1|5\} + \{2|4\} - \{3|3\} + \{4|2\} - \{5|1\}\,. \tag{13}$$

To any function in $\{\kappa|\lambda\}$ corresponds a function in $\{\lambda|\kappa\}$ which can be obtained from the former by applying the permutation $\tau = (1,6)\ (2,7)\ \ldots\ (5,10)$. Using Eq. (6) one can easily see that the projections of these two functions yield the same configurations. We have to apply special considerations to the case when $\kappa = \lambda$. We have to consider two possibilities: a) the functions replaced in the first part are identical to those replaced in the second part. In this case the application of the permutation τ does not produce any new function. b) if the set of functions selected in the first part is different from the one replaced in the second part, then similar considerations apply as for the case $\kappa \neq \lambda$. The number of terms in $\{\kappa|\lambda\}$ is equal to $\binom{5}{\kappa}\binom{5}{\lambda}$, so that the number of total configurations obtained from Φ_i is given as

$$N_i = \frac{1}{2}\sum_{\kappa=\mu}^{\nu}\binom{5}{\kappa}\binom{5}{i-\kappa} + \frac{1}{2}\binom{5}{i/2}. \tag{14}$$

It has been shown by one of us (R. P.) [16] that for the ground singlet state only those configurations contribute which correspond to an even number of excitations ($i = 2j$).

Table 6 contains the number of configurations corresponding to different i's. The total number is 272.

Table 6. *Number of configurations in the AMO function*

i	N_i
0	1
2	25
4	110
6	110
8	25
10	1

In order to test the effectiveness of the AMO method a limited configuration interaction treatment was performed. The starting molecular orbitals were the eigenvectors of the overlap matrix and we selected 50 configurations from those appearing in the AMO method. Table 7 contains the configurations and their coefficients determined from the secular equations. Table 8 compares the energy improvements obtained by this limited configuration interaction treatment with the single-parameter and many-parameter AMO method. The latter procedure with a single variable parameter comes very close to the result obtained by the CI treatment using 49 (linear) parameters while the many-parameter AMO method with 5 non-linear parameters surpasses the limited CI treatment. The reason for this result lies in the fact that the AMO method introduces a larger number (272) of configurations even that their coefficients are not determined by a free variation. As judged from previous experience and also from the present case, the coefficients obtained via the non-linear parameters are not far from the ones obtained from

Table 7. *Configuration interaction treatment for naphthalene*

Configuration			Coefficient	Configuration				Coefficient
Basic conf.			1.	2→9	3→8		a	0.12088
$5 \rightrightarrows 6$			−0.31126				b	0.06580
$4 \rightrightarrows 7$			−0.23321	1→10	3→8		a	0.11048
$3 \rightrightarrows 8$			−0.14539				b	0.04376
$2 \rightrightarrows 9$			−0.10805					
$1 \rightrightarrows 10$			−0.05525	1→10	2→9		a	0.08159
$4 \rightrightarrows 7$	$5 \rightrightarrows 6$		0.08858				b	0.03770
$3 \rightrightarrows 8$	$5 \rightrightarrows 6$		0.05418	3→8	4→7	$5 \rightrightarrows 6$	a	−0.05324
$2 \rightrightarrows 9$	$5 \rightrightarrows 6$		0.03842				b	−0.04784
$1 \rightrightarrows 10$	$5 \rightrightarrows 6$		0.01907					
$3 \rightrightarrows 8$	$4 \rightrightarrows 7$		0.03411	2→9	4→7	$5 \rightrightarrows 6$	a	−0.05578
$2 \rightrightarrows 9$	$4 \rightrightarrows 7$		0.02697				b	−0.02855
4→7	5→6	a	0.22655	1→10	4→7	$5 \rightrightarrows 6$	a	−0.04340
		b	0.19723				b	−0.02120
3→8	5→6	a	0.23725	2→9	3→8	$5 \rightrightarrows 6$	a	−0.04399
		b	0.09092				b	−0.02406
2→9	5→6	a	0.18474	1→10	3→8	$5 \rightrightarrows 6$	a	−0.03809
		b	0.10414				b	−0.01795
1→10	5→6	a	0.13945	1→10	2→9	$5 \rightrightarrows 6$	a	−0.02865
		b	0.07591				b	−0.01390
3→8	4→7	a	0.15943	3→8	5→6	$4 \rightrightarrows 7$	a	−0.05729
		b	0.13987				b	−0.01959
2→9	4→7	a	0.15908	2→9	5→6	$4 \rightrightarrows 7$	a	−0.04680
		b	0.08043				b	−0.02686
1→10	4→7	a	0.13506	1→10	5→6	$4 \rightrightarrows 7$	a	−0.03446
		b	0.06058				b	−0.01988

a and b denote the two different spin coupled configurations for the case of four unpaired electrons.

Table 8. *Comparison of the energy improvements in different methods*[a]

Method	CI	One-parameter AMO	Many-parameter AMO
Energy improvement[b]	4.3825	4.3267	5.3838

[a] MO's: eigenvectors of the overlap matrix.

[b] Zero-point of the energy: −494.0243. Energies given in eV.

the free variation. The AMO method therefore compares quite favorably with a large, limited configuration interaction treatment.

4. Charge Densities and Bond Orders

Based on the energetic results we are justified to assume that the AMO wavefunction represents an improved description of the electronic correlation in the ground state. It is interesting therefore to see the values of the charge and bond order matrix. Chirgwin and Coulson formulae [19] were used for the calculation of the charge densities and bond orders. We note that the molecular orbitals diagonalize the first-order spinless density matrix. The occupation numbers n_i are given in [16].

$$q_\mu = \sum_\lambda \sum_i n_i c_{\lambda i} S_{\lambda\mu} c_{\mu i}, \tag{15}$$

$$p_{\mu\nu} = \frac{1}{2} \sum_\lambda \sum_i n_i (c_{\lambda i} S_{\lambda\nu} c_{\mu i} + c_{\lambda i} S_{\lambda\mu} c_{\nu i}). \tag{16}$$

Table 9 gives the occupation numbers of the molecular orbitals and Table 10 contains the charges and bond orders. For the occupation numbers one can observe the following points. The sum of the occupation numbers for the paired orbitals is equal to 2 as the electrons transferred from a given orbitals are placed in their corresponding paired orbitals. We see also a gradual decrease in the occupation numbers as the energy of the orbital increases. The first one is the closest to 2, which simply shows that it is energetically unfavorable to transfer electron from the lowest occupied into the highest unoccupied orbitals.

Table 9. *Occupation numbers of the molecular orbitals in the AMO wavefunction*[a]

i	n_i	$n_{\bar{i}}$
1	1.8961	0.1039
2	1.8301	0.1699
3	1.7638	0.2362
4	1.6604	0.3396
5	1.6021	0.3979

[a] SCF molecular orbitals.

Table 10. *Charge and bond orders for naphthalene*

Method		SCF orbitals	SCF+AMO
Charge	1	0.967	0.972
	2	0.996	0.993
	9	1.074	1.070
Bond orders	1—2	0.8146	0.6189
	2—3	0.4910	0.4133
	1—9	0.4689	0.3940
	9—10	0.6453	0.4935

For the charges and bond orders one can compare the results of the SCF calculation with that of the AMO method. There is comparatively small change in the value of the charges and all of them are close to unity. The largest net positive charge is on atom 1. When one neglects overlap then the charge distribution is completely uniform. In Kolboe and Pullman's calculation the charges are more close to unity than in ours.

It is interesting to follow the changes in the bond orders as one goes over from the SCF function to the AMO wavefunction. Here one sees a quite substantial decrease in the bond orders. It is well known that if one includes higher orbitals with a larger number of nodes than the bond orders should come out smaller. If one compares the bond orders with the distances used in the calculations then the shortest and longest bonds correspond to the highest and smallest bond orders. The bond orders of the bond 2–3 and 1–9 do not conform to the geometrical distances, the central bond 9–10 has the higher bond order but its bond length is somewhat longer than that of the bond 2–3. These conclusions are similar for the SCF and for the AMO wavefunction so it has nothing to do with an improved description of the electronic correlation.

5. Conclusions

The results of the calculations show that it is feasible to apply the AMO method to a system of the size of naphthalene and it leads to considerable improvement in the total energy of the π-electrons and accordingly to an improved description of the ground state of the system. The many-parameter approach gives a better result than a configuration interaction treatment with 50 configurations and the reason is that in the AMO method we include automatically a large number (272) of configurations. The charge densities show small variations from the ones obtained by the SCF method while there is a considerable decrease in the values of the bond orders.

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