

## Regular article

# An orthogonal approach to determine extremely localised molecular orbitals

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**Abstract.** The introduction of extremely localised molecular orbitals, a current issue in modern physical chemistry, justifies chemical intuition and provides a useful tool towards the description of large molecules. In this paper, a possible strategy to determine these orbitals is proposed. The algorithm implemented has been tested by effecting computations on water, ammonia, benzene and naphthalene by employing different intramolecular partitionings. Ethane and biphenyl have been considered for application of the algorithm to the study of rotational barriers. Our scheme also includes the possibility to compute derivatives with respect to nuclear coordinates.

**Key words:** Localised molecular orbitals – Nonorthogonal orbitals

## 1 Introduction

The description of the electronic structure of large molecules remains one of the most appealing targets of computational chemistry. The theory of molecular orbitals (MOs) contributed significantly to the achievement of this aim, but introduced the idea of delocalised orbitals, which does not support the intuitive concepts of chemistry.

MO theory can be considered the natural evolution of the electronic structure of polyelectronic atoms. The electronic structure of a molecule is obtained by filling, according to the aufbau principle, the various MOs pertinent to the nuclei which compose the system. This delocalised-orbital-based construction is in contrast with the more chemically intuitive idea of a molecule as a collection of functional groups, upon which the concepts of chemical reactivity, molecular conformation analysis and functional group interaction are based.

The introduction of local concepts allows other extremely interesting applications. For example, the study of the receptor site of a protein naturally requires the treatment of a restricted molecular portion as part of a more extended region whose detailed knowledge, though not negligible, is not essential.

Moreover, local concepts call for the possibility to transfer the information obtained for small fragments to larger molecules, and may therefore be the ideal starting point for fundamental computational developments in applied quantum chemistry.

These factors account for the great number of publications regarding the extension of local concepts to MO theory, for example, the various well-known localisation schemes for MOs and the diverse approaches to the determination of the wavefunction of a restricted molecular region [1, 2].

Recently Rubio et al. [3] have demonstrated that it is possible to apply an iterative scheme based directly on localised MOs, instead of localising orbitals previously determined on the whole structure. This approach was proposed as a method to determine self-consistent-field (SCF) wavefunctions of large molecules by employing MOs built on smaller fragments, and it constitutes a valid alternative for the investigation of periodical systems. Related work on this approach is also due to Sano and Matsuoka [4].

It is to be noted, however, that the use of orbitals obtained by a localisation procedure is always accompanied by the presence of tails on the regions surrounding the localisation area; these tails are essential to guarantee the orthogonality of MOs. A complete localisation is therefore associated with nonorthogonality [5–7]. It should be underlined that the presence of tails prevents the transferability of the relative orbitals.

Combined quantum mechanics/molecular mechanics (QM/MM) methods [8, 9], which are becoming very popular for the modelling of large molecular systems, can take advantage of extremely localised MO techniques. In fact, QM/MM approaches, in which a subsystem is treated quantum mechanically while its surroundings are described by classical molecular mechanics, can easily deal with solvent-effect investigations [10, 11] because of

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the natural discontinuity between the solute and the solvent molecules. Nevertheless, when the quantum description is limited to a small fragment of a larger molecule, an artificial discontinuity is introduced between the quantum and the classical part of the system. In these cases, localised MOs can play the role of a buffer between the two parts. Furthermore, it is to be noted that such orbitals strictly depend on all atomic orbitals of the system, since there are no special reasons, excluding computational or chemical motives, to limit this zone to a bond. Therefore, as pointed by Assfeld and Rivail [12], a sufficiently realistic expression should be adopted, even if the simple exclusion of the other basis functions centred on external atoms has also been employed.

In this paper we describe a possible approach to the determination of MOs strictly localised in defined molecular regions. The total system containing  $N_f$  arbitrary molecular fragments can be described by a wavefunction of the form

$$\Psi = \left| \prod_{k=1}^{N_f} \prod_{j=1}^{N_k} \varphi_j^{(k)} \overline{\varphi_j^{(k)}} \right|,$$

where each fragment consists of  $N_k$  appropriate doubly occupied MOs expanded in a subset of the total atomic functions (the subset which determines the molecular fragment). These orbitals, therefore, are nonorthogonal and are extremely localised.

This type of localisation was originally proposed by Stoll et al. [5] and more recently by Couty et al. [6], who determined the orbitals appearing in Eq. (1) maintaining their non-orthogonality and hence employing Lowdin's formulae for the computation of the matrix elements. The proposed formulation adopts a second-order approach by determining approximate diagonal blocks of the inverse Hessian matrix, while the other blocks are calculated through Davidon–Fletcher–Powell or Broyden–Fletcher–Goldfarb–Shanno methods [13].

In this work we propose a different approach, which, though maintaining the rigorous extremely localised nature of the MOs, does not require the use of the Lowdin's formulae. This approach is developed in the framework of the SCF theory, thus allowing the calculation of wavefunction energy derivatives with respect to nuclear coordinates by standard algorithms [14].

It is well known that double occupation allows a considerable freedom in the choice of the orbitals: the SCF wavefunction is invariant upon linear transformation of the constituent MOs. This freedom can be used to transform a group of nonorthogonal MOs  $|\varphi^{(k)}\rangle$ , whose expectation value of the energy can be determined by Lowdin formulae, into a set of orthogonal orbitals with the same energy value, obtained through application of Slater's rules.

This problem is solved through a direct extension of the SCF-MI (SCF for Molecular Interactions) wavefunction [15], recently introduced for the calculation of intermolecular forces in the absence of basis set superposition error (BSSE). In the SCF-MI wavefunction, the MOs of each interacting molecule are expanded employing only their own atomic functions, thus realising a BSSE-free wavefunction. While fragments approach, the

MOs tend to superimpose on each other, losing their orthonormality. Gianinetti and coworkers [15] and Famulari [16] have demonstrated that the determination of MOs in this case is reducible to the solution of an eigenvalue–eigenvector problem for each molecular fragment.

This paper demonstrates that the equations proposed can easily be generalised to include the case of overlapping molecular fragments. It is therefore possible, for example, to describe a chain of atoms 1-2,...- $N$  by defining a first fragment containing the first and second atom, a second fragment constituted by the atomic functions of the second and third atoms and so on, so that all fragments share part of the basis functions (contrary to the SCF-MI formulation). The algorithm presented in this paper has been inserted into GAMESS-US [17] together with the calculation of analytical derivatives with respect to the nuclear coordinates, and, therefore, allows the determination of the molecular geometry through a localised wavefunction. Moreover, the numerical determination of the second derivatives and of vibrational frequencies is possible.

This strategy has been applied to water and ammonia molecules, including full geometry optimisation. Preliminary calculations have been accomplished on benzene and naphthalene by employing diverse localisation schemes, and MOs localised over two or more centres to describe C–C and C–H bonds and over one centre to describe carbon atom cores. Ethane and biphenyl molecular systems have also been treated with the aim to analyse delocalisation contributions to rotational barriers. The results are interesting, and we believe that the algorithm can be employed in future to treat systems of larger dimensions.

## 2 Theory

Consider a system of  $N_f$  molecular fragments. The  $k$ th fragment is defined by  $M_k$  atomic functions  $\{\chi_i^{(k)}\}_{i=1}^{M_k} = |\chi^{(k)}\rangle$  and  $N_k$  doubly occupied MOs,  $\{\varphi_i^{(k)}\}_{i=1}^{M_k} = |\varphi^{(k)}\rangle$ . By employing the orbitals  $|\varphi^{(k)}\rangle$  the following Slater determinant can be defined:

$$\Psi = \left| \prod_{k=1}^{N_f} \prod_{j=1}^{N_k} \varphi_j^{(k)} \overline{\varphi_j^{(k)}} \right|. \quad (1)$$

The orbitals  $|\varphi^{(k)}\rangle$  can be obtained through a generalisation of the recent equations proposed by Gianinetti and coworkers [15] and Famulari [16] developed in the framework of the SCF-MI wavefunction, devised to exclude BSSE in the study of molecular interactions.

A brief review of the SCF-MI equations is reported here, in order to understand the present generalisation. The SCF-MI wavefunction has the same structure as Eq. (1), where the orbitals of the  $k$ th fragment are described by a linear combination of atomic functions centred only on the atoms of the fragment itself:

$$\varphi_i^{(k)} = \sum_j^{M_k} [\mathbf{T}_k]_{ji} \chi_j^{(k)}.$$

The different monomers do not share any atomic function, thus avoiding the BSSE.

In order to determine the coefficient matrices  $\mathbf{T}_k$ , the following  $N_f$  eigenvalue–eigenvector equations must be solved iteratively:

$$\mathbf{F}'_k \mathbf{T}_k = \mathbf{S}'_k \mathbf{T}_k \mathbf{E}_k \quad (2)$$

The matrices  $\mathbf{F}'_k$  and  $\mathbf{S}'_k$ , each of dimension  $M_k \times M_k$  are defined by the following equations:

$$\begin{aligned} \mathbf{F}'_k &= \left[ (\mathbf{I}^M - (\tilde{\mathbf{T}}\tilde{\mathbf{V}}\tilde{\mathbf{T}}^\dagger)\mathbf{S} + \tilde{\mathbf{Q}})^\dagger \mathbf{F} (\mathbf{I}^M - (\tilde{\mathbf{T}}\tilde{\mathbf{V}}\tilde{\mathbf{T}}^\dagger)\mathbf{S} + \tilde{\mathbf{Q}}) \right]_{kk} \\ \mathbf{S}'_k &= [\mathbf{S} - \tilde{\mathbf{S}}\tilde{\mathbf{T}}\tilde{\mathbf{V}}\tilde{\mathbf{T}}^\dagger\mathbf{S} + \mathbf{S}\tilde{\mathbf{Q}}]_{kk} \end{aligned} \quad (3)$$

where  $\mathbf{F}$  and  $\mathbf{S}$  are the Fock matrix and the overlap matrix between atomic functions, respectively, both of dimension  $M \times M$ , where  $M$  is the total number of basis functions (which is equal to  $\sum_k^{N_f} M_k$  in the present discussion).

The  $M \times N$  matrix  $\tilde{\mathbf{T}}$  (where  $N = \sum_k^{N_f} N_k$ ) can be considered as a block diagonal supermatrix, defined as

$$[\tilde{\mathbf{T}}]_{hk} = \delta_{hk} \mathbf{T}_k \quad h, k = 1, K, N_f,$$

where the  $(h, k)$  block is of dimension  $M_h \times N_k$ . The other matrices in Eq. (3) have a similar block diagonal structure:

$$\tilde{\mathbf{V}}_{hk} = [(\tilde{\mathbf{T}}^\dagger \mathbf{S} \tilde{\mathbf{T}})^{-1}]_{hk} \quad \text{of dimension } N_h \times N_k$$

$$\tilde{\mathbf{Q}}_{hk} = [\tilde{\mathbf{T}}\tilde{\mathbf{V}}]_{hk} [\tilde{\mathbf{V}}\tilde{\mathbf{T}}^\dagger \mathbf{S}]_{kk} \quad \text{of dimension } M_h \times M_k.$$

In the present work we are interested in fragments which can share one or more atoms, i.e. the same atomic function can belong to more than one group  $\chi^{(k)}$ . If we denote by  $M_t$  the total number of atomic functions employed,  $M_t = \sum_k^{N_f} M_k$ , then in general  $M_t \geq M$  (where  $M$  is the number of the unique atomic functions). Equality will be obtained when a basis function belongs to just one fragment, as seen before for the SCF-MI wavefunction. Consequently the supermatrix  $\tilde{\mathbf{T}}$  loses its block diagonal structure. Anyway, it can be shown that it is still possible to use Eq. (2) or Eq. (3), by substituting the  $\mathbf{S}$  and  $\mathbf{F}$  matrices with two supermatrices, of dimension  $M_t \times M_t$  defined as:

$$[\tilde{\mathbf{S}}_{xy}] = \langle \chi^{(x)} | \chi^{(y)} \rangle \quad \text{or} \quad [\tilde{\mathbf{S}}_{xy}]_{ij} = \langle \chi_i^{(x)} | \chi_j^{(y)} \rangle \quad (4)$$

$$[\tilde{\mathbf{F}}_{xy}]_{ij} = \langle \chi_i^{(x)} | \tilde{\mathbf{F}} | \chi_j^{(y)} \rangle.$$

By employing the above definitions, the  $\mathbf{F}'_k$  and  $\mathbf{S}'_k$  matrices can be expressed as follows:

$$\mathbf{F}'_k = \sum_{xy} \tilde{\mathbf{P}}_{kx}^\dagger \tilde{\mathbf{F}}_{xy} \tilde{\mathbf{P}}_{yk} \quad (5)$$

where

$$\tilde{\mathbf{P}}_{xy} = \mathbf{1}_{xx} \delta_{xy} - \mathbf{T}_x [\tilde{\mathbf{W}}_{xy} - \tilde{\mathbf{V}}_{xy} \tilde{\mathbf{W}}_{yy}]$$

$$\mathbf{S}'_k = \tilde{\mathbf{S}}_{kk} + \tilde{\mathbf{W}}_{kk}^\dagger \tilde{\mathbf{W}}_{kk} - \sum_x \tilde{\mathbf{S}}_{kx} \mathbf{T}_x \tilde{\mathbf{W}}_{xk},$$

where

$$\tilde{\mathbf{W}}_{xy} = \sum_z \tilde{\mathbf{V}}_{xz} \mathbf{T}_z^\dagger \tilde{\mathbf{S}}_{zy} \quad \text{and } \mathbf{1}_{xx} \text{ is the identity matrix of}$$

dimension  $M_x \times M_x$ .

It should be noted that the determination of the supermatrices  $\tilde{\mathbf{S}}$  and  $\tilde{\mathbf{F}}$  does not require any additional calculation, since they contain the same elements of the  $\mathbf{S}$  and  $\mathbf{F}$  matrices. Actually, these supermatrices have been introduced only in the formal treatment, since the algorithm to calculate Eq. (5) makes use of the  $\mathbf{S}$  and  $\mathbf{F}$  matrices. It should be noted, in effect, that the introduction of a great number of fragments with diverse common functions will result in  $M_t \gg M$ .

Due to the presence of the same atomic function in different fragments, the supermatrix  $\mathbf{S}$  now becomes singular. This singularity is also induced in the  $\mathbf{S}'$  matrix, which appears in the eigenvalue–eigenvector equations (Eq. 2). Anyway, it is possible to overcome this problem and to solve Eq. (2) by means of the canonical orthogonalization method [18].

The convergence properties of the algorithm are still under study. Convergence is not very fast with a great number of fragments which strongly interact, as in the examples reported later. It should be observed that the dependence of the  $\mathbf{F}'$  matrix upon the coefficients  $\mathbf{T}$  is complicated by the transformation (Eq. 5), indicating that an estimation of the second derivatives could be useful to realise a robust algorithm, and this will be the subject of future work.

Anyway, the algorithm implemented so far was able to converge even when considering an “extreme” localisation scheme as in the naphthalene and biphenyl examples Sect. 3.

The theory reported is compatible with the usual formulation of the analytic derivatives of the SCF energy. This allowed the implementation of gradient optimisation algorithms and force constant matrix computations in both the direct and conventional SCF approaches. The present algorithm has been inserted into the GAMESS-US package.

### 3 Computational examples

In this section, some results showing the accuracy and the potential applications of the method are presented. The systems considered as examples for gradient optimisation applications under localisation constraints are water and ammonia, while benzene and naphthalene have been investigated with different localisation patterns. Preliminary studies have also been performed for ethane and biphenyl molecules including rotational barrier analysis using extremely localised molecular orbital calculations.

A triple- $\zeta$  + polarisation basis set [19] was employed for water, ammonia, ethane and benzene a 6-31G\*\* basis set [20] for naphthalene and a 6-31G basis set [20] for biphenyl.

The results for water and ammonia are reported in Table 1. The calculation for the water molecule was carried out by considering the electrons to be partitioned in three fragments. The first two are identified by the oxygen atom and each of the two hydrogen atoms; they contain two electrons and describe the two O–H bonds. The third fragment is identified only by the oxygen atom and it contains six electrons; it describes the core electrons of the oxygen atom and the two lone pairs.

Similarly, the ammonia molecule was described by four fragments: three of them describe the N—H bonds and are identified by the nitrogen atom and one of the three hydrogen atoms. The fourth fragment, identified only by the nitrogen atom contains four electrons and describes the core electrons of the nitrogen and the lone pair.

The calculation was first carried out at the SCF optimised geometry, then the geometry was optimised by maintaining the localised nature of the MOs. As is evident from Table 1, the optimised geometry in the framework of the localised MOs does not differ substantially from the SCF optimised geometry. These results indicate that a wavefunction built up using extremely localised MOs is also a good candidate to describe geometric properties.

The calculations on the benzene and naphthalene molecules were carried out to investigate different localisation schemes for the  $\pi$  system so as to test our program thoroughly. The geometry optimised at the SCF level was used.

The  $\sigma$  systems were described with a set of fragments, each constituted by pairs of bonded atoms. A strongly overlapping pattern of fragments results: with the exception of the carbon atoms involved in the fusion of the two rings, each carbon atom belongs to three fragments (two  $\sigma$  C—C bonds and one C—H bond). The same partitioning of the  $\sigma$  system was used with different descriptions of the  $\pi$  system.

The  $\pi$  electrons of the benzene molecule were described using four different localisation schemes (Fig. 1) consisting, respectively, of three fragments, each containing a couple of adjacent carbon atoms (1) (a Kekulé partition), three fragments containing three adjacent carbon atoms each (2), three fragments constituted by four adjacent carbon atoms (3) and a fragment containing all the carbon atoms (4) (full  $\pi$ -delocalisation model).

The  $\pi$  electrons of the naphthalene molecule were described using five fragments constituted by the func-

tions of two adjacent carbon atoms (1) (this set contains the resonance structure which maintains a double bond at the fusion of the two rings) and a fragment containing all the carbon atoms (2) (full  $\pi$ -delocalisation model).

The results are reported in Table 2, together with the value of the norm of the energy gradient with respect to the variational coefficients at the end of the calculation.

The rationalisation of steric effects represents a very challenging field for ab initio calculation methods. The simplest aliphatic chain involving a rotational barrier is represented by the ethane molecule. Always keeping in mind the possibility to transfer extremely localised MOs, we performed preliminary calculations on ethane: the results are reported in Table 3. Eclipsed and staggered SCF optimised geometry conformations have been considered by using a triple- $\zeta$ +polarisation basis set. Our extremely localised MO calculations were performed with a full localisation scheme by employing seven two-atom bonds (one C—C bond and six C—H bonds) and two carbon core fragments. A lowering of the C—C torsional barrier is observed with respect to the fully delocalised standard SCF value. Our result (2.87 kcal/mol), smaller by 22.6%, is in good accordance with the experimental (2.93 kcal/mol [21]) and theoretical (see, e.g. Ref. [5]) data. It is to be noted that this outcome could be fortuitous [5].

The biphenyl molecule represents the prototype for the study of delocalisation contributions to rotational barriers in biaryl systems. Great interest has been devoted to the conformational problems regarding biphenyl and its derivatives. Experimental studies [22] reveal a nonplanar equilibrium conformation with a torsional angle ( $\theta$ ) of 44.4° for the biphenyl molecule in the gaseous state. Two barriers ( $\theta = 0^\circ$  and  $\theta = 90^\circ$ ) characterise the potential function of the C—C rotation. The planar and orthogonal SCF optimised geometry conformations have been considered by using the 6-31G basis set [20]. As in the case of benzene and naphthalene,

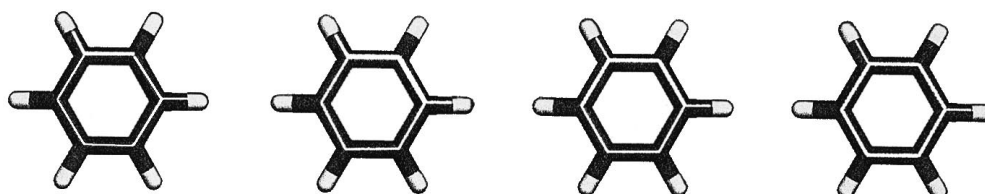
**Table 1.** Results for water and ammonia molecules for self-consistent-field (SCF) and (ELMO) optimised geometries

Water	Ammonia
SCF optimised geometry: O—H = 0.9407 a.u. HOH angle = 106.98° $E(\text{SCF}) = -76.056014$ a.u. $E(\text{ELMO}) = -76.045428$ a.u.	SCF optimised geometry: N—H = 0.9982 a.u. HOH angle = 108.90° $E(\text{SCF}) = -56.216625$ a.u. $E(\text{ELMO}) = -56.208131$ a.u.
ELMO optimised geometry: O—H = 0.9448 a.u. HOH = 108.33° $E(\text{ELMO}) = -76.045527$ a.u.	ELMO optimised geometry: N—H = 0.9998 a.u. HOH = 109.49° $E(\text{ELMO}) = -56.208167$ a.u.

**Table 2.** Results for benzene and naphthalene molecules

Localisation pattern (see text)	Energy value (a.u.)	Norm of the gradient
(1) – Benzene	-230.579446	1.48D-05
(2) – Benzene	-230.685634	1.31D-04
(3) – Benzene	-230.717852	2.25D-10
(4) – Benzene	-230.725393	2.15D-11
SCF – Benzene	-230.771570	
(1) – Naphthalene	-383.074923	2.20D-08
(2) – Naphthalene	-383.287746	2.78D-05
SCF – Naphthalene	-383.369365	

**Fig. 1.** Different localisation schemes for  $\pi$  electrons of benzene (see text)



at the Extremely Localized Molecular Orbitals (ELMO) level, the  $\sigma$  system was described with a set of fragments constituted by pairs of bonded atoms representing C—C and C—H bonds and by 12 carbon core fragments. The  $\pi$  electrons were described using two fragments constituted by the six carbon atoms of each ring (full internal ring  $\pi$ -delocalisation model). The results of our calculations are presented in Table 4 and Fig. 2. The qualitative accordance of ELMO and SCF rotational barriers is satisfactory when considering that the absolute energies of the two approaches differ by more than 50 kcal/mol.

In order to appreciate the extremely localised nature of the MOs we report in Fig. 2 the superimposed contour plots of the orbitals corresponding to the  $\sigma$  C—C bond and the C—H bonds for the biphenyl system.

In the case of the planar conformation of biphenyl, the energy of the MOs obtained by Pipeck and Mezey [23] with localisation and removal of the tails is 129 kcal/mol higher than ELMO result. It is to be noted that tail

deletion from localised SCF orbitals has a strong effect on the system energy, and so it becomes of crucial importance to dispose of realistic MOs in order to transfer local concepts.

It should be pointed out that, as underlined by Couty et al. [6], delocalisation effects can be, in principle, partially included by a Jacobi correction scheme. This supplementary procedure permits a better reproduction of Hartree–Fock energies while still maintaining accuracy and low computational cost.

#### 4 Conclusions

The use of extremely localised MOs provides a useful tool to describe large molecules using building blocks determined on smaller fragments. It must be pointed out

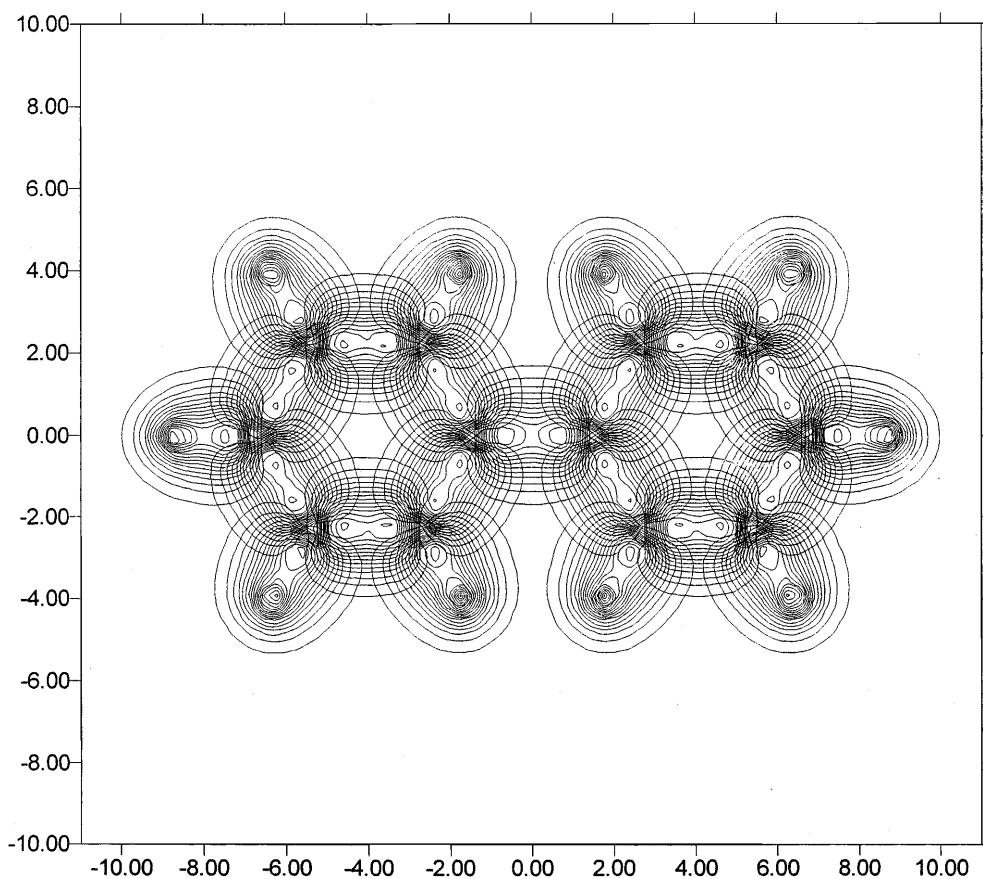
**Table 4.** Results for the biphenyl system. Calculated total energies (atomic units) are reported for planar, minimum and orthogonal conformations. Standard SCF and ELMO rotational barriers are in kilocalori/mole

Conformation	ELMO	SCF	Experimental [23]
Planar ( $\theta = 0^\circ$ )	-459.998980	-460.090703	
Minimum ( $\theta = 44.4^\circ$ )	-460.006410	-460.095861	
Orthogonal ( $\theta = 90^\circ$ )	-460.008138	-460.093215	
Barrier of rotation			
$\theta = 0^\circ$	4.66	3.24	1.43
$\theta = 90^\circ$	1.08	1.66	1.55

**Table 3.** Results for the ethane system. The total energy (atomic units) is reported for staggered and eclipsed conformations. Standard SCF and ELMO rotational barriers are reported in kilocalorie/mole

Conformation	$E/\Delta E$ ELMO	$E/\Delta E$ SCF
Eclipsed	-79.234734	-79.252485
Staggered	-79.238201	-79.257283
Barrier of rotation	2.87	3.70

**Fig. 2.** Superimposed contour plots of the extremely localised molecular orbitals corresponding to the  $\sigma$  C—C and C—H bonds of biphenyl (see text)



that extremely localised MOs do not have any tails on the regions adjacent to the localisation centres. This feature is essential to the possibility to transfer MOs from one molecule to another or in order to implement rigorous buffer regions in the QM/MM methodol.

Unfortunately, the deletion of the tails introduces a nonorthogonality of the orbitals which results in mathematical and computational difficulties. In this paper we have proposed an algorithm based on a generalisation of the SCF-MI wavefunction [15, 16] which permits an orthogonal formalism to be used while maintaining an extreme localisation.

In order to test the implemented algorithm, geometry optimisation of water and ammonia molecules was accomplished within the framework of extremely localised MOs. Benzene and naphthalene molecules were also investigated to analyse different localisation schemes and to provide an example of the application to larger molecules.

The preliminary calculations reported for ethane and biphenyl molecular systems are interesting. In particular the recognition of rotational strain effects in biphenyl is pivotal to the study of axial chirality in biaryls. Such investigation would be of great significance for the rationalisation of atropisomerism and of the role of chiral biaryl catalysts in asymmetric reactions [24].

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