

Calculation and properties of non-orthogonal, strictly local molecular orbitals

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A general procedure to calculate non-orthogonal, strictly local molecular orbitals (NOLMOs) expanded using only a subset of the total basis set is presented. The energy of a single determinant wave function is minimised using a Newton-Raphson approach. Total energies and barriers to internal rotation for CH₄, NH₃, H₂O, CH₃CH₃, CH₃NH₂, CH₃OH, NH₂NH₂, NH₂OH and HOOH, and certain properties of the NOLMOs present in these molecules, are investigated using the 4-31G basis set.

Key words: Non-orthogonal local molecular orbitals—local basis sets—direct energy minimisation—*ab-initio* calculations

1. Introduction

Thanks to the general availability of efficient SCF-MO *ab-initio* programs [1, 2], quantum-mechanical calculations are nowadays readily performed by many chemists. Although these calculations can provide quantitative information in conformational and other problems, it is often not straightforward to explain the behavior of the observed system in terms of “classical” chemical concepts as, for instance, functional groups and their interactions [3, 4].

Localisation of canonical SCF-molecular orbitals is usually possible by a unitary transformation [5, 6]. The main problem with these orthogonal localised MOs is that they possess “tails” outside the localisation center which complicate the transfer of localised orbitals from one system to another [7].

However, as pointed out by several authors [8-12], it is not necessary to use orthogonal MOs, but instead one can use a single determinant of non-orthogonal, strictly local, molecular orbitals (NOLMOs).

In this paper a calculation scheme is outlined that leads to a description of bonds, lone pairs and inner shells in terms of properties that are more or less transferable from one molecule to another.

2. Variational optimisation of NOLMOs using local basis sets

In order to be able to analyse the potential usefulness of NOLMOs in the study of conformational problems, it is necessary to devise a procedure to determine NOLMOs in an unambiguous way. Furthermore, it is desirable to have NOLMOs which lead to the lowest energy upon being inserted into the Hartree-Fock energy expression. In the case of self-consistent NOLMOs singly excited configurations ($\phi_p \rightarrow \phi_p^*$) do not contribute to the total energy owing to a local Brillouin theorem [13, 14].

Procedures for variational optimisation of NOLMOs using local basis sets have been published by Payne [11] and by Stoll et al. [10]. It was shown by the latter group of authors that the equations given by Payne were incorrect [15].

The method of Stoll et al. consists of partitioning a set of basis functions into subsets Γ_p corresponding to certain localisation centers (atom, lone pair, bond). Each NOLMO is now expanded in the basis functions of the corresponding subset, which means that "tails" are explicitly excluded.

$$\phi_p = \sum_{i \in \Gamma_p} C_{ip} \eta_i \quad (1)$$

Defining reciprocal orbitals $\tilde{\phi}_p$ as

$$\tilde{\phi}_p = \sum_q^m \phi_q \cdot S_{qp}^{-1} \quad (2)$$

where S_{qp}^{-1} is an element of the matrix inverse to the matrix containing the non-orthogonality integrals $\langle \phi_p | \phi_q \rangle$ and m is the number of electron pairs, the partial derivatives of the electronic energy E^{elec} with respect to the non-zero orbital coefficients C_{ip} become [10]

$$dE^{\text{elec}}/dC_{ip} = 4\langle \eta_i | (1-\rho)F | \tilde{\phi}_p \rangle \quad (3)$$

and

$$\begin{aligned} dE^{\text{elec}}/dC_{ip} dC_{jq} \\ \approx 4(A(F)_{ij} \cdot S_{qp}^{-1} - A(1)_{ij} \cdot \langle \tilde{\phi}_q | F | \tilde{\phi}_p \rangle - \langle \eta_i | \tilde{\phi}_q \rangle \cdot B_{jp} \\ - \langle \eta_j | \tilde{\phi}_p \rangle \cdot B_{iq}) \end{aligned} \quad (4)$$

with

$$A(X)_{ij} = \langle \eta_i | (1-\rho)X(1-\rho) | \eta_j \rangle$$

and

$$B_{iq} = \langle \eta_i | (1-\rho)F | \tilde{\phi}_q \rangle$$

In the derivation of Eq. (4), the dependence of the Fock operator on ϕ_q was neglected. One of the variational procedures as suggested by Stoll et al. is to optimise the orbital coefficients by expanding E^{elec} in a Taylor series. This yields (using Eqs. (3) and (4)) a set of linear equations in ΔC_{ip} . The procedure is repeated until self-consistency is reached. This scheme works well for minimal basis sets. For larger basis sets (e.g. double zeta) however, it is no longer feasible to use the full hessian matrix since the solution of the set of linear equations becomes unstable because of the size of the matrix.

An alternative procedure suitable for large basis sets is to neglect the off-diagonal elements of the hessian matrix. In this case we can express ΔC_{ip} as:

$$\Delta C_{ip} = -\frac{dE^{\text{elec}}/dC_{ip}}{dE^{\text{elec}}/dC_{ip} dC_{ip}} \cdot \text{SCALE}(ip) \quad (5)$$

with

$$\text{SCALE}(ip) = \text{SCALE}(ip)^{\text{prev}} \cdot \frac{(dE^{\text{elec}}/dC_{ip})^{\text{prev}}}{(dE^{\text{elec}}/dC_{ip})^{\text{prev}} - dE^{\text{elec}}/dC_{ip}}$$

with the constraints

$$\text{SCALE}(ip) \leq 1$$

and

$$|\Delta C_{ip}| \leq \text{a maximum stepsize}$$

The superscript “prev” refers to the previous iteration.

3. Convergence acceleration

For the calculation of the various energy terms corresponding to NOLMOs (see Sect. 5) to be meaningful, it is necessary that the NOLMOs are calculated to a very high level of self-consistency. Since, in general, convergence is slow at the end of the SCF-procedure, a modified version of the direct inversion in the iterative subspace (DIIS) method of Pulay [16, 17] was implemented. With this method the convergence of Newton-Raphson type algorithms can be significantly improved. In each iteration step we define some error vector e_i which is required to vanish as convergence is reached. It is assumed that an improved parameter vector p can be obtained as a linear combination of a number of previous vectors p_i : $p = \sum_i w_i p_i$. The coefficients w_i are determined by requiring the error vector $e = \sum_i w_i e_i$ to approximate the zero vector in the least-squares sense under the constraint that $\sum_i w_i$ equals one. As shown by Pulay [16, 17], this leads to a small set of linear equations which, once solved, gives us the coefficients w_i .

In the original procedure [16], the Fock-matrix elements transformed to an orthonormal basis, i.e. $S^{-1/2}FS^{-1/2}$ (where S is the overlap matrix), were chosen as parameters. For the present purposes, however, one is not only interested in the density but also in the NOLMO-coefficients. Therefore it is more convenient

to adopt the following alternative definitions for p_i and e_i . Taking the NOLMO-coefficients of the i th iteration as the parameter vector p_i one can define the j th element of the corresponding error vector e_i as:

$$e_{ji} = \left[\frac{dE^{\text{elec}}/dC_j}{dE^{\text{elec}}/dC_j dC_j} \right]_i \quad (6)$$

In practice a number of standard iterations are performed until the quadratic region is reached. From this point onwards the DIIS extrapolation procedure is applied periodically after a predetermined (5-15) number of standard cycles. Results obtained from HF-SCF and NOLMO calculations on CH_4 , NH_3 and H_2O are shown in Table 1. From these examples it should be clear that the gain by even a single extrapolation step, which in this case lies between 7 and 15 iteration steps, can be quite significant. The convergence acceleration properties of the presently modified DIIS procedure are found to be comparable to those of the original method [16].

4. Transformations leading to unique NOLMOs

In the case of non-orthogonal molecular orbitals ϕ_p, ϕ_q the first-order density matrix can be written as:

$$\rho = \sum_{p,q}^m \phi_p S_{pq}^{-1} \phi_q^* \quad (7)$$

It can be shown [18] that the first-order density matrix is invariant with respect to a linear transformation of the molecular orbitals, i.e.:

$$\phi_p^t = \sum_q^m \phi_q a_{qp} \quad (8)$$

Because in the present procedure each NOLMO has been assigned its own local subset Γ_p of the total basis set, there exist only two cases where linear transformations among NOLMOs are still possible without violating the condition that each NOLMO is expanded solely in the atomic orbitals of its own local basis set.

(1) The first case occurs when some of the subsets assigned to different NOLMOs are equal i.e.: $\Gamma_p = \Gamma_q = \dots$. This happens, for instance, in the case of an inner shell and one or more lone pairs localised on the same atom. For this case the ambiguity between these NOLMOs can be resolved by orthogonalising all NOLMOs having the local basis set in common, and subsequently applying one of the known procedures [19] to localise orthogonal MOs. Examples of some of the known localisation procedures are: (i) The external uniform localisation method of Magnasco and Perico [6, 20] in which a sum of selected overlap populations is maximized. (ii) The maximum electron distance suggested by Boys [21] which uses the minimization of $I = \sum_p \langle \phi_p \phi_p | r_{12}^2 | \phi_p \phi_p \rangle$. (III) The maximum self-interaction criterion of Ruedenberg [5] which is based upon the maximization of the quantity $\sum_p \langle \phi_p \phi_p | 1/r_{12} | \phi_p \phi_p \rangle$. This method is slightly more general than the previous one, since also systems with coinciding centroids of charge can be localised.

Table 1. HF-SCF and NOLMO-convergence of CH₄, NH₃ and H₂O^a

cycle	CH ₄			NH ₃			H ₂ O				
	HF-SCF	NOLMO	convergence parameter ^b	cycle	HF-SCF	NOLMO	convergence parameter ^b	cycle	HF-SCF	NOLMO	convergence parameter ^b
1	8.58-2	1.60-2		1	1.11-1	2.58-2		1	2.48-1	2.73-2	
5	1.62-5	1.83-4		5	1.02-4	6.75-4		5	1.36-3	2.71-3	
10	1.90-9	9.90-6		10	9.34-8	6.51-5		10	5.69-6	3.68-4	
11	3.16-10	7.51-6		13	1.58-9	1.52-5		15	2.54-8	6.39-5	
15		2.14-6		14	4.07-10	9.37-6		17	2.94-9	3.02-5	
20		1.76-7		16		3.89-6		18	9.97-10	2.04-5	
24		2.18-8		21		3.99-7		22		4.63-6	
25		1.29-8		23		1.82-7		24		2.32-6	
29		1.74-9		26		5.49-8		27		7.94-7	
30		1.12-9		29		1.48-8		37		4.09-8	
31		7.43-10		34		1.72-9		42		6.75-9	
(39)		(1.60-11)		35		1.10-9		47		1.18-9	
10-term DIIS(5-14) ^c		2.03-8		36		6.87-10		48		8.08-10	
15-term DIIS(5-19)		2.13-9		10-term DIIS(6-15)		1.91-7		10-term DIIS(7-16)		2.73-6	
20-term DIIS(5-24)		1.50-11		15-term DIIS(6-20)		1.20-8		15-term DIIS(7-21)		4.17-8	
				20-term DIIS(6-25)		2.09-9		20-term DIIS(7-26)		6.23-9	

^a 4-31G basis set [22], standard geometry [23].

^b The convergence parameter equals the difference between the value of the total energy (a.u.) at the iteration cycle *i* and the converged value.

^c The error vectors utilized in the DIIS procedure are given in parentheses.

(2) A second case where linear transformations among NOLMOs are allowed occurs when a given local basis set turns out to be a subset of another one. This, for example, happens when the local basis set of an inner shell or lone pair on some atom is a subset of the local basis set of a bond involving the same atom. In this case the NOLMOs involved cannot be made orthogonal; therefore, none of the previous localisation schemes can be applied. What one needs is a localisation criterion which is intrinsic to a specified NOLMO (bond). Intrinsic means that the specified criterion should be a function of parameters which only depend upon the NOLMO at hand. One such intrinsic criterion, related to the procedure of Magnasco and Perico [6, 20], and suitable for linear transformations among NOLMOs, is the following:

If the local basis set of NOLMO q is a subset of the local basis set of NOLMO p , or $\Gamma_q \subset \Gamma_p$, then find α , where

$$\phi_p' = N^{-1/2}(\cos(\alpha) \cdot \phi_p + \sin(\alpha) \cdot \phi_q) \quad (9)$$

and

$$N = 1 + 2S_{pq} \cos(\alpha) \sin(\alpha) \quad (10)$$

such that

$$P = \sum_{i \in \Gamma_A} \sum_{j \in \Gamma_B} C_{ip} C_{jp} S_{ij} \quad (11)$$

is maximized. In these equations ϕ_p refers to a bond between atoms A and B . Γ_A , Γ_B are subsets of Γ_p , local to atoms A and B respectively. C_{ip} e.g. refers to an element of the NOLMO-coefficient matrix. Maximization of P in Eq. (11) implies a maximization of the overlap population between the hybrids on the atoms A and B for a bond $A-B$. In case the local basis sets of more than one NOLMO are subsets of some other local basis set, the procedure described above is applied in sequence for all subsets until convergence is reached. The optimization problem specified by Eqs. (9–11) can easily be solved by standard techniques.

5. Applications

In this section aspects concerning the practical use of NOLMOs will be discussed:

i) Each NOLMO has at its disposal only a subset of the full basis set and consequently the minimal energy that results from a single determinant of NOLMOs will be higher than the SCF energy calculated using the full basis set. One may now ask how closely the SCF energy actually is reproduced.

ii) It is well-known [4] that equilibrium geometries, as well as energy differences between conformations and barriers to internal rotation can be predicted quite well by standard HF-SCF calculations. Are such predictions also possible by NOLMO-determinant calculations?

iii) A third, and most interesting, question concerns the possible transferability of NOLMOs from one molecule to another. To what extent do various properties of NOLMOs remain conserved?

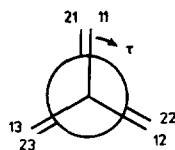


Fig. 1. Reference conformation ($\tau = 0^\circ$) τ = torsion angle

5.1. Total energy and barriers to internal rotation

Ab-initio calculations using the 4-31G basis set [22] were performed on CH_4 , NH_3 , H_2O , CH_3CH_3 , CH_3NH_2 , CH_3OH , NH_2NH_2 , NH_2OH , and HOOH using a modified version of the GAUSSIAN-80 program [2]. In all cases standard bond lengths and angles [23] were adopted. Barriers to internal rotation were calculated by varying torsion angles in steps of 30° . The reference conformation ($\tau = 0$) for those molecules having a barrier to internal rotation is defined in Fig. 1 and Table 2. Note that, in order to have a uniform labeling in all molecules, lone pairs were included as substituents.

Local basis sets for each NOLMO were chosen so as to correspond to bonds, inner shells and lone pairs. Local basis sets of bonds consisted of all atomic orbitals associated with the two bonded atoms, other basis functions were not included. Inner shell and lone pair local basis sets were restricted to all the atomic orbitals of a single atom. NOLMOs having an identical local basis set were made orthogonal and subsequently localised by maximising the sum of their self-repulsion energies according to the Edmiston-Ruedenberg procedure [5]. This localisation criterion leads to equivalent lone pairs on oxygen in all cases studied. In the cases that one or more local basis sets were subsets of another one, the overlap population between the two hybrids on the bonded atoms was maximised according to the procedure described in the previous section.

In Table 3 total energies obtained from standard HF-SCF and NOLMO calculations are compared. These results clearly demonstrate that the constraint imposed on the wave function by the use of NOLMOs leads to total energies which in all cases are very close to the standard SCF values. The maximum deviation found in the present series of molecules is about 0.03 a.u. (~ 20 kcal/mole). This is in

Table 2. Definition of substituent labels for CH_3CH_3 , CH_3NH_2 , CH_3OH , NH_2NH_2 , NH_2OH , and HOOH . Lone pairs are included as substituents

Label	Substituent					
1	C	C	C	N	N	O
11	H	H	H	H	H	H
12	H	H	H	H	H	lp
13	H	H	H	lp	lp	lp
2	C	N	O	N	O	O
21	H	H	H	H	H	H
22	H	H	lp	H	lp	lp
23	H	lp	lp	lp	lp	lp

Table 3. Comparison of total energies and barriers to internal rotation from standard SCF and NOLMO calculations. Basis set: 4-31G

Molecule/ r^*	(a.u.)			(kcal/mole)		
	Standard =	Total Energy (NOLMO)	+ Δ	Δ	Standard =	Barrier (NOLMO) + Delec
CH ₄	-40.1396	-40.1328	-0.0068	-4.24		
NH ₃	-56.1045	-56.0964	-0.0081	-5.10		
H ₂ O	-75.9084	-75.9010	-0.0074	-4.65		
CH ₃ CH ₃ / 0	-79.1096	-79.0899	-0.0197	-12.37	3.26	3.26
30	-79.1123	-79.0919	-0.0203	-12.76	1.62	2.01
60	-79.1148	-79.0939	-0.0210	-13.17	0.0	0.79
CH ₃ NH ₂ / 0	-95.0647	-95.0395	-0.0251	-15.76	2.13	2.13
30	-95.0663	-95.0408	-0.0255	-16.01	1.06	1.31
60	-95.0680	-95.0421	-0.0260	-16.29	0.0	0.53
CH ₃ OH/ 0	-114.8684	-114.8439	-0.0246	-15.41	1.12	1.12
30	-114.8693	-114.8445	-0.0248	-15.58	0.56	0.73
60	-114.8702	-114.8451	-0.0251	-15.74	0.0	0.34
NH ₂ NH ₂ / 0	-110.9825	-110.9565	-0.0260	-16.35	12.16	12.82
30	-110.9877	-110.9610	-0.0267	-16.77	8.94	10.03
60	-110.9970	-110.9695	-0.0275	-17.25	3.09	4.65

90	-111.0019	-110.9747	-0.0272	-17.08	0.0	1.40	-1.40
120	-111.0009	-110.9747	-0.0262	-16.45	0.65	1.42	-0.77
150	-110.9978	-110.9725	-0.0253	-15.89	2.59	2.79	-0.20
180	-110.9964	-110.9714	-0.0250	-15.68	3.47	3.47	0.0
NH ₂ OH/	-130.7745	-130.7457	-0.0288	-18.10	8.01	9.73	-1.71
-30	-130.7722	-130.7440	-0.0281	-17.66	9.49	10.76	-1.27
0	-130.7688	-130.7420	-0.0268	-16.80	11.61	12.04	-0.42
30	-130.7704	-130.7443	-0.0261	-16.38	10.59	10.59	0.0
60	-130.7772	-130.7509	-0.0263	-16.52	6.34	6.47	-0.13
90	-130.7843	-130.7576	-0.0267	-16.77	1.86	2.24	-0.38
120	-130.7873	-130.7604	-0.0269	-16.85	0.0	0.47	-0.47
HOOH/	-150.5412	-150.5259	-0.0153	-9.60	7.95	9.01	-1.06
0	-150.5436	-150.5281	-0.0155	-9.70	6.46	7.62	-1.16
30	-150.5486	-150.5329	-0.0156	-9.81	3.32	4.59	-1.26
60	-150.5526	-150.5372	-0.0154	-9.64	0.81	1.92	-1.10
90	-150.5539	-150.5392	-0.0147	-9.21	0.0	0.67	-0.67
120	-150.5539	-150.5394	-0.0139	-8.73	0.34	0.54	-0.19
150	-150.5533	-150.5392	-0.0136	-8.54	0.65	0.65	0.0
180	-150.5528	-150.5392	-0.0136	-8.54	0.65	0.65	0.0

^a τ denotes the torsion angle ($^{\circ}$) with respect to the reference conformation (see Table 1 and Fig. 1).

perfect agreement with the results previously obtained by Stoll et al. [10], who used a minimal basis set. Even more important is the finding that barrier potentials are reproduced correctly in all cases studied (see Table 3 and Fig. 2). These results show that the inclusion of electron delocalisation, which is explicitly excluded by the use of NOLMOs, is not a "conditio sine qua non" to obtain qualitatively correct barrier potentials, at least not in an *ab-initio* scheme. This finding is in contradiction with Weinhold's opinion [24]. A more extensive discussion on the weaknesses inherent to the interpretation by Weinhold of LCBO-MO calculations [24, 25] was given by Magnasco and Musso [26, 27]. The difference in total energies between the standard- and the NOLMO-calculations can be considered a measure of the afore-mentioned delocalisation effect, when second-order contributions are unimportant. These contributions indeed have been shown to be small [26, 27]. The influence of delocalisation on the barrier is listed in Table 3 under the heading deloc. It is clear that this contribution is small, although not negligible. It follows that delocalisation must be included in order to obtain a quantitatively correct barrier.

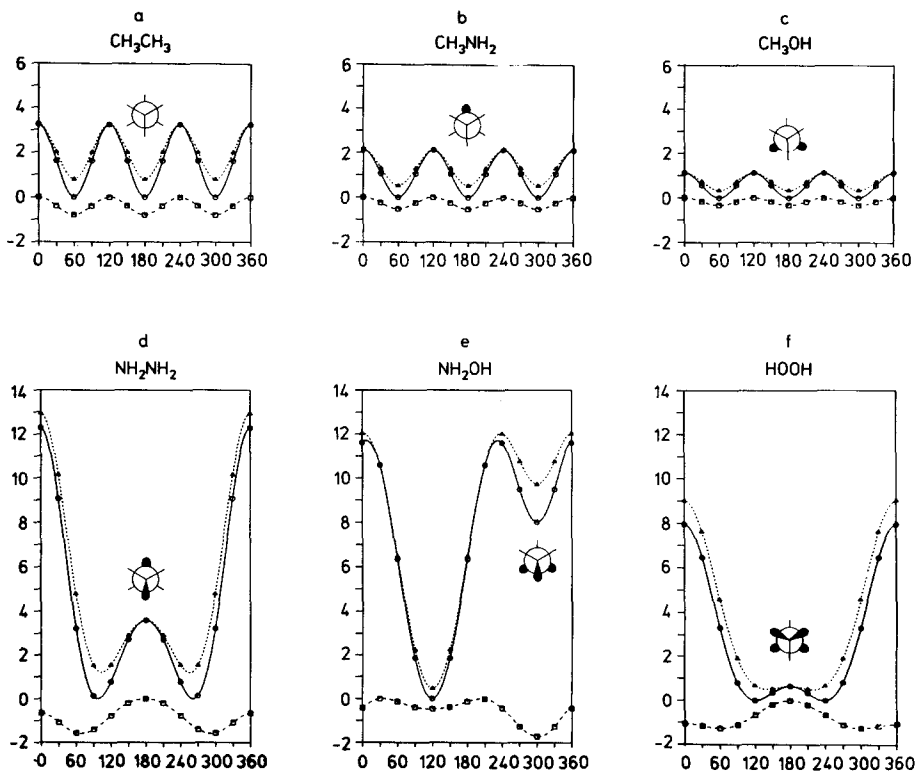


Fig. 2. Comparison of *ab-initio* (O) and NOLMO (Δ) SCF barriers to internal rotation for: (a) CH₃CH₃, (b) CH₃NH₂, (c) CH₃OH, (d) NH₂NH₂, (e) NH₂OH, (f) HOOH. Also shown (\square) is the effect of electron delocalisation on the barriers. The ordinates and abscissas represent the energy (in kcal/mole) and the torsional angle (0-360°) respectively

Table 4. Geometrical parameters in angstroms and degrees, optimised using the 4-31G basis set and the same basis set augmented with polarisation functions (1s- + 5 d-functions on the heavy atoms + 3 p-functions on the hydrogen atoms). Values in brackets represent the corresponding HF-SCF results

MOLECULE	4-31G		4-31G**	
	$r(X-H)$	$\angle(HXH)$	$r(X-H)$	$\angle(HXH)$
CH ₄	1.081 (1.081)		1.081 (1.083)	
NH ₃	0.990 (0.991)	118.8 (115.8)	1.000 (1.000)	109.3 (107.5)
H ₂ O	0.948 (0.950)	112.9 (111.2)	0.943 (0.943)	107.7 (105.8)

5.2. Transferability of certain properties of NOLMOs

From Table 4 one can compare the calculated equilibrium geometries for CH₄, NH₃ and H₂O using the 4-31G and 4-31G** basis sets [22]. Whereas bond lengths are almost unaffected in NOLMO-SCF calculations, bond angles are consistently calculated a few degrees larger than the corresponding HF-SCF values. However, considering the difference between the 4-31G and the 4-31G** HF-SCF results, one can say that equilibrium geometries are reproduced quite well by the NOLMO-SCF calculations.

Table 5. Statistics for the quasi-classical kinetic energy (a.u.) of some types of NOLMOs

NOLMO	Mean	Std ^a	Min	Max	Range
Cis ^b	32.0728	0.0132	32.0544	32.0864	0.0320
Nis	45.2189	0.0329	45.0915	45.2629	0.1714
Ois	61.2561	0.1051	61.0792	61.3985	0.3193
C—C	1.7808	0.0004	1.7803	1.7813	0.0010
C—N	2.3326	0.0000	2.3325	2.3326	0.0000
C—O	3.1998	0.0005	3.1991	3.2005	0.0014
N—N	2.4345	0.0072	2.4242	2.4439	0.0197
N—O	3.0453	0.0089	3.0366	3.0588	0.0222
O—O	3.3462	0.0082	3.3356	3.3578	0.0222
C—H	1.5909	0.0241	1.5623	1.6528	0.0906
N—H	2.3293	0.0421	2.2801	2.4199	0.1398
O—H	3.2738	0.0763	3.1717	3.3857	0.2140
Nlp ^c	2.7413	0.0304	2.7005	2.8134	0.1129
Olp	3.8302	0.0428	3.7629	3.8791	0.1163

^a Standard deviation.

^b Inner shell.

^c Lone pair.

Table 6. Statistics for the quasi-classical one-electron potential energy (a.u.) of some types of NOLMOs

NOLMO	Mean	Std ^a	Min	Max	Range
Cis ^b	-22.6335	0.0047	-22.6383	-22.6268	0.0115
Nis	-26.8143	0.0069	-26.8245	-26.7860	0.0385
Ois	-31.1199	0.0204	-31.1477	-31.0866	0.0610
C—C	-2.5487	0.0001	-2.5488	-2.5485	0.0002
C—N	-2.7760	0.0000	-2.7760	-2.7759	0.0001
C—O	-3.0147	0.0002	-3.0150	-3.0145	0.0005
N—N	-2.8289	0.0028	-2.8326	-2.8252	0.0074
N—O	-3.0677	0.0036	-3.0721	-3.0636	0.0085
O—O	-3.0110	0.0049	-3.0178	-3.0047	0.0131
C—H	-3.1749	0.0109	-3.1983	-3.1656	0.0327
N—H	-3.4709	0.0131	-3.4979	-3.4548	0.0431
O—H	-3.7663	0.0184	-3.7888	-3.7399	0.0489
Nlp ^c	-3.5958	0.0287	-3.6404	-3.5473	0.0932
Olp	-4.2823	0.0348	-4.3245	-4.2338	0.0907

^a Standard deviation.^b Inner shell.^c Lone pair.**Table 7.** Statistics for the quasi-classical two-electron potential energy (a.u.) of some types of NOLMOs

NOLMO	Mean	Std ^a	Min	Max	Range
Cis ^b	3.5111	0.0010	3.5097	3.5122	0.0025
Nis	4.1691	0.0012	4.1643	4.1709	0.0065
Ois	4.8477	0.0036	4.8423	4.8527	0.0103
C—C	0.6796	0.0000	0.6796	0.6797	0.0001
C—N	0.7311	0.0000	0.7311	0.7312	0.0001
C—O	0.7908	0.0000	0.7908	0.7909	0.0001
N—N	0.7343	0.0016	0.7320	0.7365	0.0045
N—O	0.7944	0.0019	0.7926	0.7973	0.0047
O—O	0.7619	0.0012	0.7604	0.7637	0.0033
C—H	0.6873	0.0035	0.6843	0.6949	0.0106
N—H	0.7648	0.0044	0.7594	0.7738	0.0145
O—H	0.8485	0.0059	0.8402	0.8563	0.0161
Nlp ^c	0.7752	0.0089	0.7548	0.7876	0.0329
Olp	0.9252	0.0097	0.9109	0.9372	0.0262

^a Standard deviation.^b Inner shell.^c Lone pair.

To estimate the degree to which NOLMOs can be considered as more or less transferable units, the following characteristics for a specified NOLMO ϕ_p are compared:

1) The energy components associated with the quasi-classical density $\phi_p\phi_p^*$ corresponding to NOLMO ϕ_p

a) The kinetic energy: $2\langle\phi_p|-\frac{1}{2}\nabla^2|\phi_p\rangle$ (see Table 5).

b) The one electron potential energy: $2\langle\phi_p|\sum_A^{Na} Z_p(A)/R_A|\phi_p\rangle$, where $Z_p(A)$ refers to that part of the nuclear charge of atom A assigned to ϕ_p^1 , and Na is the number of atoms. (See Table 6).

c) The two electron potential energy: $\langle\phi_p\phi_p|1/r_{12}|\phi_p\phi_p\rangle$. (See Table 7).

2) Mulliken populations in the basis of atomic hybrids for those cases where NOLMO ϕ_p corresponds to a bond. (See Table 8).

Table 8. Statistics for the hybrid populations of those NOLMOs corresponding to bonds

NOLMO	Population	Mean	Std ^a	Min	Max	Range
C—C	Hybrid-C	0.6095	0.0000	0.6095	0.6095	0.0001
	Hybrid-C	0.6095	0.0000	0.6095	0.6095	0.0001
	Overlap	0.7810	0.0000	0.7810	0.7811	0.0001
C—N	Hybrid-C	0.3759	0.0002	0.3756	0.3762	0.0007
	Hybrid-N	0.9238	0.0004	0.9233	0.9243	0.0010
	Overlap	0.7003	0.0001	0.7001	0.7004	0.0003
C—O	Hybrid-C	0.2997	0.0002	0.2994	0.3000	0.0006
	Hybrid-O	1.0900	0.0004	1.0894	1.0905	0.0011
	Overlap	0.6103	0.0002	0.6100	0.6106	0.0006
N—N	Hybrid-N	0.6344	0.0002	0.6342	0.6346	0.0004
	Hybrid-N	0.6344	0.0002	0.6342	0.6346	0.0004
	Overlap	0.7312	0.0003	0.7309	0.7317	0.0008
N—O	Hybrid-N	0.4883	0.0136	0.4693	0.5041	0.0348
	Hybrid-O	0.8262	0.0164	0.8072	0.8489	0.0417
	Overlap	0.6856	0.0028	0.6818	0.6888	0.0070
O—O	Hybrid-O	0.6808	0.0006	0.6799	0.6814	0.0015
	Hybrid-O	0.6808	0.0006	0.6799	0.6814	0.0015
	Overlap	0.6385	0.0011	0.6372	0.6403	0.0031
C—H	Hybrid-C	0.7211	0.0129	0.6895	0.7516	0.0621
	Hybrid-H	0.4798	0.0110	0.4596	0.5075	0.0479
	Overlap	0.7990	0.0040	0.7888	0.8030	0.0142
N—H	Hybrid-N	0.9656	0.0155	0.9430	0.9970	0.0540
	Hybrid-H	0.3175	0.0087	0.3022	0.3342	0.0320
	Overlap	0.7168	0.0074	0.7009	0.7251	0.0243
O—H	Hybrid-O	1.0833	0.0151	1.0591	1.1131	0.0539
	Hybrid-H	0.2708	0.0076	0.2573	0.2833	0.0260
	Overlap	0.6459	0.0085	0.6297	0.6576	0.0279

^a Standard deviation.

¹ $Z_p(A) = 2$ if ϕ_p corresponds to an inner shell or a lone pair on atom A . $Z_p(A) = Z_p(B) = 1$ if ϕ_p corresponds to a bond between atoms A and B .

In Tables 5, 6 and 7, for each type of NOLMO present in the molecules studied, the mean value, the standard deviation, the minimum and maximum value and the range of the kinetic energy, the one-electron potential energy and the two-electron potential energy, respectively are given. From these Tables it is clear that the three energy components are remarkably constant, as witnessed by the relatively small standard deviations. The kinetic energy (Table 5), which is related to the shape of the NOLMOs is seen to be the most sensitive parameter, whereas the self-repulsion energy (Table 7), is least sensitive to the chemical environment; the standard deviation of the latter is almost an order of magnitude smaller than the standard deviation in the kinetic energy. It is seen that standard deviations associated with NOLMOs corresponding to bonds between carbon, nitrogen and oxygen are small compared to the remainder of the NOLMOs. It should be realized, however, that in the present set of calculations each of these bonds is represented by a single molecule and has been influenced only by internal rotation.

Table 8 shows some statistics for the Mulliken populations, in the basis of their constituent hybrids, for all NOLMOs corresponding to bonds. Again one observes low standard deviations suggesting the transferability of NOLMOs. Note that all overlap populations, regardless of the particular bond they originate from, are calculated in the rather limited range of 0.6 to 0.8 electrons. This could mean that, in order to have a stable bond, the overlap population is limited to a narrow range of values.

6. Conclusions

The calculation scheme outlined in the previous sections leads to a description of bonds, lone pairs and inner shells in terms of properties that are well transferable from one molecule to another. When the wave function is written as a single determinant of NOLMOs, the energy calculated is very close to the energy obtained by a standard HF-SCF calculation. Furthermore, qualitatively correct barrier potentials are reproduced in all cases studied. This means that the influence of electron delocalisation is relatively small, contrary to what might be concluded from a number of semi-empirical calculations [24, 25].

The transferability of NOLMOs, as well as the qualitatively correct prediction of barrier potentials, suggest that NOLMOs can be used as a basis for the analysis of conformational problems by means of an energy decomposition scheme which will be presented in a number of subsequent papers.

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Note added in proof. The signs of the torsion angles, as used throughout this paper, are inverted with respect to the usual convention. Klyne, W. and Prelog, V.: *Experientia* **16**, 521 (1960).

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