

Molecular orbitals from group orbitals. IX. The problem of hybrid lone pairs

DANIEL KOST

Department of Chemistry, Ben Gurion University of the Negev, 84 120 Beersheva, Israel

H. BERNHARD SCHLEGEL

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA 15213, U.S.A.

AND

DAVID JOHN MITCHELL AND SAUL WOLFE

Department of Chemistry, Queen's University, Kingston, Ont., Canada K7L 3N6

Received August 14, 1978

DANIEL KOST, H. BERNHARD SCHLEGEL, DAVID JOHN MITCHELL, and SAUL WOLFE. *Can. J. Chem.* **57**, 729 (1979).

The quantitative PMO analysis of the *ab initio* wavefunction of a molecule A—B is based upon a partitioning of the Fock matrix elements of this wavefunction to obtain the fragments A and B, followed by computation of the stabilizing and destabilizing orbital interactions between the orbitals of these fragments that contribute to the HOMO of A—B. However, when one or both of the fragments is NH₂ or a congeneric species, neither the 3a₁ nor the 1b₁ orbital of this fragment is appropriate for overlap with the second fragment, and the PMO analysis cannot be performed. A solution to this problem is proposed, and has been tested by application to various conformational properties of methylamine.

DANIEL KOST, H. BERNHARD SCHLEGEL, DAVID JOHN MITCHELL et SAUL WOLFE. *Can. J. Chem.* **57**, 729 (1979).

L'analyse quantitative PMO de la fonction d'onde *ab initio* de la molécule A—B est basée sur une partition des éléments de la matrice de Fock de cette fonction d'onde en vue d'obtenir les fragments A et B suivie par une évaluation des interactions orbitales stabilisantes et déstabilisantes entre les orbitales de ces fragments qui contribuent à la OM haute occupée de A—B. Toutefois si l'un ou les deux fragment est NH₂ ou une espèce congénère, ni l'orbitale 3a₁ ni l'orbitale 1b₁ de ce fragment n'est appropriée pour un recouvrement avec le deuxième fragment et l'on ne peut pas réaliser une analyse PMO. On propose une solution à ce problème et on l'a vérifié en l'appliquant à diverses propriétés conformationnelles de la méthylamine.

[Traduit par le journal]

The concept of the functional group has long been a part of the language of organic chemistry. In terms of this concept, 'chemical intuition' might be described as the ability to predict the properties of a molecule from a knowledge of the number, location, and different kinds of functional groups that are present.

Molecular orbital calculations also lead to predictions concerning molecular properties, but the notion of functional groups does not emerge naturally from such work. This has made it difficult to convey the results of theory in a manner compatible with chemical intuition.

Significant progress on this communication problem has been made recently, as a result of the observation that molecular orbitals can often be expressed qualitatively as a linear combination of a small number of canonical 'group orbitals' which recur from molecule to molecule (1). Using the language of perturbational molecular orbital (PMO) theory (2) to estimate the stabilizing and/or destabilizing effects associated with these linear combinations (orbital

interactions) it has become possible, in principle (3), to treat the behaviour of every molecular orbital of a molecule in a manner that closely parallels the traditional conception of functional group interactions. For practical reasons, however, it has seemed desirable to focus attention upon the interactions that lead to certain specific molecular orbitals. In particular, it is of interest to consider the interactions in the highest occupied molecular orbital (HOMO), because trends in calculated total energies from one system to another are very often paralleled by trends in the energy of the HOMO (4).

The PMO interpretation of a molecular orbital calculation on the general system A—B, which contains the functional groups A and B, will, therefore, require the following information: (i) a knowledge of the nature, origin, and energies of the canonical orbitals of A and of B; (ii) a knowledge of the electron occupancies of these orbitals; (iii) a knowledge of which orbitals of A and of B contribute to the HOMO of A—B.

In several recent publications (5–9), we have de-

0008-4042/79/070729-04\$01.00/0

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scribed a quantitative PMO analysis of *ab initio* SCF-MO wavefunctions, in which the required information is obtained by a partitioning of the Fock matrix elements of these wavefunctions. The computer program for the analysis of A—B, with the fragmentation A··B, provides the orbitals of A and of B, their energies (e_i^0) and occupancies (i.e., gross populations), the interaction matrix elements, Δ_{ij} , the overlap integrals, S_{ij} , and an expansion of each of the molecular orbitals of A—B in terms of the fragment orbitals of A and of B. Equations [1] and [2] are then employed (5) to calculate, respectively, the stabilizing (i.e., doubly occupied with unoccupied) and destabilizing (i.e., doubly occupied with doubly occupied) interactions associated with the fragment orbitals that contribute to the HOMO of A—B.

$$[1] \quad \Delta e_{ij} = 2(\Delta_{ij} - S_{ij}e_i^0)^2/(e_i^0 - e_j^0)$$

$$[2] \quad \Delta e_{ij} = 2S_{ij}[-2\Delta_{ij} + (e_i^0 + e_j^0)S_{ij}]/(1 - S_{ij})^2$$

The molecules treated in this manner include ethane (5), propylene (5), $(\text{CH}_3)_2\text{X}$ (6), the dimethyl- (7) and difluoroethylenes (8), and XCH_2YH ($\text{X} = \text{CH}_3, \text{H}_2\text{N}, \text{HO}, \text{F}, \text{Cl}; \text{Y} = \text{O}, \text{S}$) (9). The results for these molecules have been characterized by the following general features: (i) the HOMO is comprised mainly of a linear combination of π -type and π^* -type group orbitals and (where applicable) p -type lone pairs; (ii) the electron occupancies of these orbitals are either very close to 2 or very close to 0; (iii) the energy differences, from conformation to conformation or from molecule to molecule, that are calculated by application of eqs. [1] and [2], are close to the calculated total energy differences.

It has now been found that this quantitative procedure requires modification when the HOMO of the molecule contains a significant contribution from a hybrid lone pair orbital, as is the case in amines and their congeners. The purpose of this paper is to explain why the problem exists, and to provide a solution to it which otherwise retains the features of the general method.

Consider a molecule of ammonia, oriented as in Fig. 1, with one hydrogen on the x -axis of the coordinate system. If the fragmentation $\text{H}_2\text{N}\cdots\text{H}_x$ is performed, the amino group that results has the set of canonical orbitals shown in Fig. 1 as σ , π , n_σ , and n_π , and 7 valence electrons. The lower lying σ and π orbitals are each doubly occupied, leaving three electrons to populate n_σ and n_π . Our intuition suggests that one of these orbitals should be doubly occupied, and the other should be singly occupied. Moreover, the doubly occupied orbital should point in the direction of the lone pair of ammonia; and the

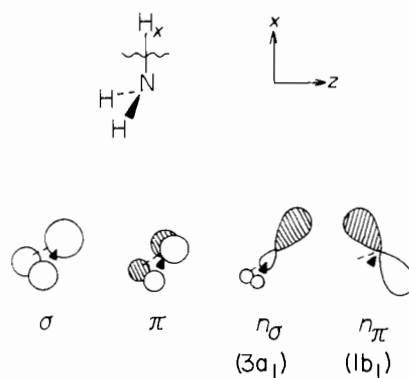


FIG. 1. The canonical orbitals of the NH_2 fragment of ammonia.

singly occupied orbital should be directed along the x -axis, because it will form the bond to H_x . It is clear, however, that neither n_σ nor n_π meets these latter requirements. The quantitative PMO treatment of ammonia in the manner just described¹ leads to NH_2 orbitals corresponding to σ , π , n_σ , and n_π , and the electron occupancies of n_σ and n_π are found to be approximately 1.5 in each case. Equations [1] and [2] are, therefore, not applicable.

The problem arises because the C_{2v} axis of the NH_2 fragment does not coincide with the $\text{H}_2\text{N}-\text{H}_x$ bond axis. This leads to significant overlap of H_x with both n_σ and n_π . As discussed in ref. 5, orbital occupancy depends upon the overlap between the fragment orbitals, because the gross population (Q_p) of an orbital ϕ_p^0 is defined as

$$[3] \quad Q_p = Q_{pp} + \sum_{i \neq p} Q_{pi}$$

where

$$[4] \quad Q_{pi} = 2 \sum_n^{\text{occ}} S_{pi} T_{pn} T_{in}$$

with T the matrix that expresses the molecular orbitals in the fragment orbital basis. Fragment orbitals with populations close to 1.5 might be regarded as linear combinations of filled (population close to 2) and half-filled (population close to 1) orbitals. Therefore, one solution to the problem might consist of 'unmixing' these orbitals manually by taking a linear combination to form two new fragment orbitals with populations ca. 1 and ca. 2.

Alternatively, such a linear combination might be based upon the overlap properties of the two fragment orbitals. For any 2×2 rotation of a pair of orbitals ϕ_p^0 and ϕ_q^0 of one fragment, one has the

¹All calculations were performed at the STO-3G level on a Burroughs B6700 computer, using a locally modified version of GAUSSIAN 70, and the optimized geometries reported in ref. 10.

result

$$[5] \quad S'_{ip} = S_{ip} \cos \theta - S_{iq} \sin \theta$$

$$[6] \quad S'_{iq} = S_{ip} \sin \theta + S_{iq} \cos \theta$$

where ϕ_i^0 is an orbital of the second fragment and S' is the overlap matrix after transformation. The sum of the squares of these overlap integrals with all n orbitals of the second fragment is invariant under the transformation, i.e.,

$$\sum_i^n (S'_{ip}{}^2 + S'_{iq}{}^2) = \sum_i^n \{(S_{ip} \cos \theta - S_{iq} \sin \theta)^2 + (S_{ip} \sin \theta + S_{iq} \cos \theta)^2\} = \sum_i^n (S_{ip}{}^2 + S_{iq}{}^2)$$

The angle θ should then be chosen so that $\sum_i^n S'_{ip}{}^2$ is maximized (while $\sum_i^n S'_{iq}{}^2$ is minimized), with the result that $\phi_p^{0'}$ more closely approximates the singly occupied σ -bonding orbital between the fragments, and $\phi_q^{0'}$ describes the lone pair orbital.

Application of this latter procedure to the $n_\sigma(3a_1)$ and $n_\pi(1b_1)$ orbitals of Fig. 1 leads to the hybrid fragment orbitals shown in Fig. 2. As can be seen, one of these is nearly aligned with the bond axis, and the other is nearly aligned with the C_{3v} symmetry axis of the molecule. In addition, the transformation has changed the electron occupancies, from 1.686 and 1.565 in n_σ and n_π , respectively, to 1.256 for the orbital on the bond axis and 1.996 for the orbital on the symmetry axis.

Methylamine

Figure 3 shows the effects of this transformation procedure upon the $3a_1$ and $1b_1$ fragment orbitals of the amino group of methylamine in its staggered conformation. As a result of the transformation, the computation of the destabilizing and stabilizing interactions between the nitrogen 'lone pair' ($4a'$)

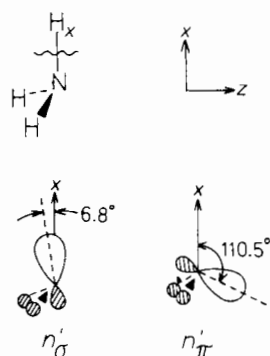


FIG. 2. Transformation of the n_σ and n_π canonical orbitals of the NH_2 fragment of ammonia based upon the criterion of maximization of the overlap of one of these orbitals with the fragmented H.

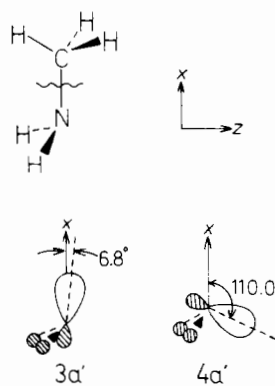


FIG. 3. The transformed n_σ and n_π orbitals of the NH_2 fragment of methylamine in its staggered conformation.

and the π_z and π_z^* methyl group orbitals becomes feasible. These are the only doubly occupied and unoccupied fragment orbitals that contribute to the HOMO. It is noteworthy that, since the axis of the methyl group coincides with the C—N bond axis, transformation of the orbitals of this fragment is not necessary, as is evident from the gross populations: π_z , 1.998; π_z^* , 0.019; π_x , 1.025.

The quantitative PMO analysis of methylamine will, therefore, be based upon the interaction diagram shown in Fig. 4, which contains a destabilizing interaction between N_{1p} and π_z , and a stabilizing interaction between N_{1p} and π_z^* . The energies of these fragment orbitals, and the calculated interaction energies in the staggered and eclipsed conformations, are collected in Table 1. In terms of this analysis, the staggered conformation is found to be less destabilized by 0.20 kcal/mol, and more stabilized by 0.34 kcal/mol, than the eclipsed conformation.

The (N_{1p} - π_z^*) interaction is shown in Fig. 5. As a result of this interaction, antibonding CH regions become populated, and the CH bonds are weakened.

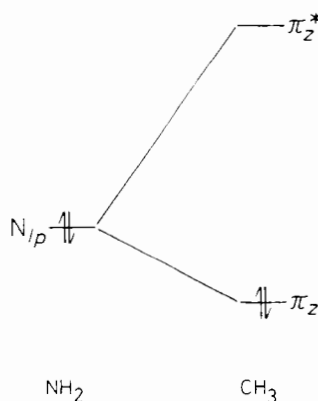


FIG. 4. Interaction diagram for the PMO analysis of methylamine.

TABLE I. Quantitative PMO analysis of methylamine

Conformation	Fragment orbital	e_i^0 (au)	Interaction energy (kcal/mol)	
			$N_{I_p-\pi}$	$N_{I_p-\pi^*}$
Staggered ^a	N_{I_p}	-0.3592	20.43	-4.95
	π_{CH_3}	-0.5314		
	$\pi_{CH_3}^*$	0.6801		
Eclipsed ^b	N_{I_p}	-0.3561	20.63	-4.61
	π_{CH_3}	-0.5274		
	$\pi_{CH_3}^*$	0.6780		

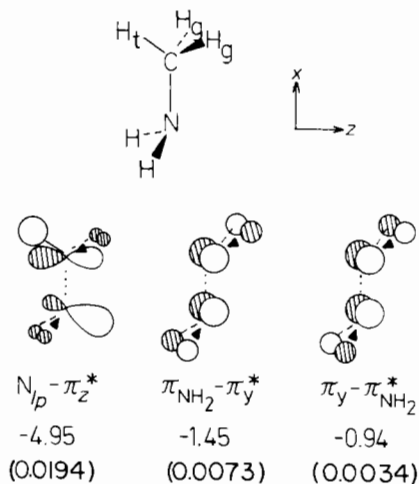
^aCalculated total energy, -94.03286 au.^bCalculated total energy, -94.02838 au.

FIG. 5. The ($N_{I_p-\pi_z^*}$), ($\pi_{NH_2}-\pi_y^*$), and ($\pi_y-\pi_{NH_2}^*$) orbital interactions in the staggered conformation of methylamine, and the values calculated for these interactions in kcal/mol. The numbers in parentheses are the gross populations of the π^* orbitals.

However, since H_t has a larger atomic orbital coefficient in π_z^* than does H_g , the C— H_t bond is weakened preferentially (11). An experimental manifestation of this effect is found in the Bohlmann bands (12), which appear in the infrared spectrum of methylamine (13).

Although they do not contribute to the HOMO, two other orbital interactions, shown in Fig. 5 as ($\pi_{NH_2}-\pi_y^*$) and ($\pi_y-\pi_{NH_2}^*$), also lead to weakening of CH bonds. In the ($\pi_{NH_2}-\pi_y^*$) interaction, the charge transfer is to antibonding C— H_g regions; this leads to preferential weakening of the C— H_g bonds. In the ($\pi_y-\pi_{NH_2}^*$) interaction, the charge transfer is from bonding C— H_g regions; this also weakens the C— H_g bonds preferentially. The values computed for the three orbital interactions are included in

Fig. 5, together with the gross populations of the three π^* orbitals. These populations reflect the amount of charge transfer which occurs in each case. As can be seen, the ($N_{I_p-\pi_z^*}$) interaction, which contributes to the HOMO, and weakens C— H_t preferentially, is significantly larger than the other two. This indicates that the Bohlmann band phenomenon has been predicted by a quantitative PMO analysis which is based upon examination of the interactions in the HOMO.

Acknowledgements

We thank the Advisory Research Committee of Queen's University and the National Research Council of Canada for financial support of this work.

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