Localized Molecular Orbital Description of Nitrogen Lone Pairs (peptide bond/tau bond)

DANIEL A. KLEIER, JOHN H. HALL, JR., THOMAS A. HALGREN, AND WILLIAM N. LIPSCOMB

Department of Chemistry, Harvard University, Cambridge Massachusetts 02138

Contributed by William N. Lipscomb, March 25, 1974

ABSTRACT The Boys localization procedure is applied to several molecules possessing nitrogen lone pairs. The Boys structures show a tendency for the N lone pairs to participate in bonding to nearby electron sinks. For example, the Boys structure for planar formamide has two equivalent τ -bond orbitals between the carbonyl carbon and nitrogen atoms. The change in this description with variation of geometry at nitrogen is treated, and analogous Edmiston-Ruedenberg localizations on formamide are included for comparison.

Electron pair bonds, *per se*, are not observable. However, they do provide a consistent framework for organizing a large and diverse array of phenomena. As such, the electron pair bond is an extremely useful model. However, it is not always possible to write objectively a single Lewis structure for a molecule, especially if it is electron rich or electron deficient. Several localized molecular orbital procedures (see below) are available, however, for obtaining valence structures objectively. For a molecule where there is little ambiguity in writing a Lewis structure, the localized structure is essentially identical. Where several Lewis structures may be written, localization procedures objectively choose the best such structure or a weighted hybrid.

The Hartree-Fock self-consistent field-wave function for a closed-shell molecule is invariant to any unitary transformation of its constituent molecular orbitals (MOs). A unitary transformation combines these orthonormal MOs to yield a new set of orthonormal MOs that leave the total wave function unchanged. In addition, the one-electron density is invariant to such a transformation even though the partitioning of the density among the MOs is altered. The unitary transformation simply slices the electron-density pie in a different fashion. If judiciously chosen, a unitary transformation partitions the density to MOs localized in regions of space corresponding closely to two- and three-center bonds, lone pairs, and inner shells. In a procedure suggested by Boys (1), the partitioning is accomplished by separating the MO centroids to the greatest possible extent. Edmiston and Ruedenberg have developed the method of Lennard-Jones *et al.* (2) into a procedure whereby localized molecular orbitals (LMOs) are obtained by maximizing the intraorbital coulomb repulsion energy (self-energy) or, equivalently, by minimizing the nonclassical exchange energy (3). We note, however, that the total energy is unchanged in the Edmiston-

Ruedenberg (ER) procedure. Only the partitioning between various energy contributors (i.e., self-energy, interorbital coulomb energy, exchange energy) is altered, reflecting the reallocation of density to the LMOs. The implementation of the ER procedure is computationally much less efficient than the implementation of the Boys procedure and, hence, we use the latter method almost exclusively for large molecules.

While the Boys procedure is not based on an energy criterion, it indirectly accomplishes nearly the same task as the ER procedure and, hence, in many cases the localized structures are nearly identical. A detailed comparison of the two methods is now in preparation. From our experience to date, we tend to favor the ER procedure because of the chemically unreasonable tendency for the Boys procedure to mix inner shell with valence shell orbitals in metastable species.

The Boys procedure (1) has been used to obtain the localized molecular orbitals for the molecules in Fig. 1. Canonical molecular orbitals (CMOs) were obtained by solving the self-consistent field equations in the approximation of partial retention of diatomic differential overlap (PRDDO) (4). The LMOs were then generated by subjecting the CMOs to a unitary transformation which maximized the sum of squares of distances between centroids of MOs. In this article we focus attention on the LMO description of lone pairs of nitrogen.

As noted above, when applied to molecules having unique Lewis valence structures, the Boys LMOs are in conformity with traditional ideas of bonding. However, when applied to molecules with several nearly degenerate valence structures, Boys LMOs are often appropriately not in conformity with any single "classical" structure. Consider the valence bond and LMO descriptions of formamide as a function of the dihedral angle, χ ,

where $\chi = \phi_1 + \phi_2$, and for simplicity we take $\phi_1 = \phi_2$. The valence bond structure is a resonance hybrid dominated by A and B:

The contribution of B to the hybrid increases as the molecule approaches planarity. Similarly, in the LMO description,

Abbreviations: MO, molecular orbital; LMO, localized molecular orbital; CMO, canonical molecular orbital; PRDDO, partial retention of diatomic differential overlap; ER, Edmiston-Ruedenberg.

FIG. 1. Boys localized structures for (A) formamide, (B) urea, (C) aminodifluoroborane, (D) a "tripeptide," (E) aniline, (F) nitrobenzene, (G) guanine, and (H) cytosine. All geometries are planar except for that of the "tripeptide," which is fully extended.

we expect a greater participation of the nitrogen lone pair in bonding as the molecule approaches planarity.

In Fig. 2 atomic populations (5), $P(i,k)^*$, are plotted as a function of χ for the formamide LMOs, ψ and ψ' , which describe the nitrogen lone pair and $C'-N$ bonding, respectively. Experimental (6) bond lengths and bond angles at C' were maintained throughout the geometry variation, while the angle $\alpha = \angle C'-N-H_3 = \angle C'-N-H_2 = \angle H_2-N-H_3$ was varied from 120° to 108° (χ variation, 0° to 64°). At $\chi = 60^\circ$ (tetrahedral bond angles at N), ψ is a lone pair on N with negligible delocalization towards C' , while ψ' is a two-center $C'-N$ bond slightly polarized towards N. For small χ , Boys LMOs ψ and ψ' change rapidly so that at $\chi = 0^\circ$, they become equivalent τ -like $C'-N$ bonding orbitals highly polarized towards N. Boys localizations as a function of χ were also performed on conformations in which the amide group was rotated by an angle $\tau = \pm 90^\circ$ about the $C'-N$ axis. These localizations consistently describe a nitrogen lone pair and a single $C'-N$ bond.

ER localizations were also performed on formamide as a function of χ . Since the ER and Boys structures are practically indistinguishable for all but small χ values, we include for simplicity only the results for $\chi = 0^\circ$ in Fig. 2. The ER structure for planar formamide has a N lone pair slightly delocalized towards C' [$P(\psi, N) = 1.75$; $P(\psi, C') = 0.22$] and a $C'-N$ two-center σ -bond slightly polarized towards N [$P(\psi', N) = 1.27$; $P(\psi', C') = 0.77$]. Thus the ER structure shows σ - π separation in the LMOs in contrast to the Boys equivalent τ -bond description.

For comparison we include in Fig. 2 results from Boys' procedure for an analogous χ variation in ethylene. At $\chi =$

FIG. 2. LMO atomic populations, $P(i,k)$ (electrons), plotted against dihedral angle, χ (degrees), for Boys LMOs ψ and ψ' of formamide and ξ and ξ' of ethylene. (—) $P(\psi, N)$, $P(\psi, C')$, $P(\xi, C_1)$, and $P(\xi, C_2)$; (---) $P(\psi', N)$, $P(\psi', C')$, $P(\xi', C_2)$, and $P(\xi', C_1)$; (X) atomic populations for the experimental geometry ($\chi = 19^\circ$); (●) populations in ER lone pair LMO, ψ ; (○) populations in ER $C'-N$ bond LMO, ψ' .

0° there are two equivalent unpolarized bonding orbitals, and here the equivalent τ -bond description is insensitive to χ variations. In ethylene the double bond forms between two identical C atoms, each supplying an electron pair to the LMOs, while in planar formamide a double bond is formed between a C' atom supplying one electron [$P(\psi', C') + P(\psi, C') = 1.0$] and a more electronegative N atom supplying three electrons [$P(\psi', N) + P(\psi, N) = 3.0$]. For planar ethylene, both Boys' and ER's procedures give equivalent bonds.

All molecules of Fig. 1 contain $X-N$ where X is an electron sink, i.e., any group having an affinity for the nitrogen lone pair due to resonance interactions, inductive interactions, a general electron deficiency, or any combination of these. These molecules show participation of the "lone pairs" in bonding to the electron sinks, indicated by a line, half solid and half dotted. Special attention is called to the three-center bond occupied by one of the nitrogen "lone pairs" in the imidazole ring of guanine, where there is a demand for the "lone pair" in two directions. The "lone pair" is thus shared with both "electron sinks." A similar situation prevails at the nitro group of nitrobenzene. Here, however, the polarizing O atoms each have an electron pair to share so that double bonds are formed between N and each oxygen.

Perhaps the participation of lone pairs of N in bonding is very common. The equivalent Boys LMOs found here may be used as an alternative to σ - π descriptions of restricted rotation in peptide linkages, low basicity of aniline, etc. However, the amount of participation of lone pairs does depend critically on the geometry at nitrogen.

We are grateful to the Office of Naval Research for support. D.A.K. thanks the National Science Foundation for a postdoctoral fellowship.

* $P(i,k)$ is the gross atomic population on atom k in MO i .

1. (a) Boys, S. F. (1960) *Rev. Mod. Phys.* **32**, 296-299; (b) Foster, J. M. & Boys, S. F. (1960) *Rev. Mod. Phys.*, **32**, 300-302; (c) Boys, S. F. (1966) in *Quantum Theory of Atoms, Molecules, and the Solid State*, ed. Löwdin, P. (Academic Press, New York), pp. 253-262.
2. (a) Lennard-Jones, J. E. (1949) *Proc. Roy. Soc. Ser. A* **198**, 1-13, 14-26; (b) Hall, G. G. & Lennard-Jones, J. E. (1950) *Proc. Roy. Soc. Ser. A* **202**, 155-165; (c) Lennard-Jones, J. E. & Pople, J. A. (1950) *Proc. Roy. Soc. Ser. A* **202**, 166-180; (d) Lennard-Jones, J. E. & Pople, J. A. (1951) *Proc. Roy. Soc. Ser. A* **210**, 190-206.
3. Edmiston, C. & Ruedenberg, K. (1963) *Rev. Mod. Phys.* **35**, 457-465.
4. Halgren, T. A. & Lipscomb, W. N. (1972) *Proc. Nat. Acad. Sci. USA* **69**, 652-656; (b) Halgren, T. A. & Lipscomb, W. N. (1973) *J. Chem. Phys.* **58**, 1569-1591.
5. Mulliken, R. S. (1955) *J. Chem. Phys.* **23**, 1833-1840
6. Costain, C. C. & Dowling, J. M. (1960) *J. Chem. Phys.* **32**, 158-165.