

On Orbital Hybridization

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Abstract: A quantitative procedure is developed to determine the average hybridization and the degree of fluctuation from the average hybridization for an arbitrary orbital. The method is applied to the ab initio valence bond and localized Hartree-Fock molecular orbitals of H₂O with interesting results.

I. Introduction

Hybridization is one of the most important concepts of quantum chemistry since it provides a basis for correlating many physical properties of molecules with electronic structure.¹ This concept was originally introduced² by Pauling and Slater who suggested that a mixture of s and p atomic orbitals (AO's) would provide a better function for bond formation than either an s or p orbital alone. In their treatment the bond is described by a pair of electrons in atomic orbitals, one on each of the two centers involved. Thus, hybridization is a valence bond concept. Yet, because of its appeal, this concept has also been applied to localized molecular orbitals (LMO's) which are often truncated³ to remove contributions from AO's on all but one center. The LMO's, however, are not uniquely determined by an energy criterion⁴ as are their valence bond orbital (VBO) counterparts.

In this note we present a quantitative method for determining hybridization coefficients of orbitals obtained by ab initio calculations. The salient features of our method are: (1) truncation is avoided since it can lead to arbitrary results; (2) an average hybridization taken over all radial distances from the center of interest is defined; and (3) a measure is provided of how much the hybridization fluctuates from its average value. This latter quantity is related to how effective the hybridization is in altering the angular electron distribution of the orbital.

II. Definition of Hybridization Coefficients

Pauling's original treatment assumes that a normalized hybrid orbital can be expressed as the product of a *one-center* normalized radial function multiplied by a linear combination of normalized spherical harmonics, viz., $f(r)\sum_{l,m}\lambda_l^m Y_l^m(\theta,\phi)$. Such an orbital is characterized by the hybridization coefficients $\sum_m |\lambda_l^m|^2$ which describe the fraction of the total density found in each total angular momentum l . However, in modern ab initio calculations optimum orbitals $\chi(r,\theta,\phi)$ are obtained by letting the radial functions depend upon l (and sometimes m) and by taking linear combinations of AO's on more than one center. The optimum orbitals then do not have the simple Pauling form.

Generally, most of the density in a VBO or LMO can be associated with one principal nuclear center, with smaller contributions being found near some or all of the other nuclei in the molecule. The multicenter character could be removed by truncation,³ retaining only those contributions from AO's on the principal center. But this leads to arbitrary results. To give an extreme example, the exact orbital could be written alternatively as an expansion in a complete set of basis functions located only on a *truncated* center. In that case, nothing would be left after truncation! As a practical consequence, truncation will lead to results which are particularly sensitive to how the AO basis set is "balanced" among the various nuclear centers.

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It is better to retain all terms and to expand⁵ the entire orbital about the principal center giving the (unique) result

$$\chi(r,\theta,\phi) = \sum_{l,m} R_l^m(r) Y_l^m(\theta,\phi) \quad (1)$$

At a particular distance r from the principal center, the hybridization coefficient $h_l(r)$ is then the fraction of the radial density found in angular momentum l :

$$h_l(r) \equiv \rho_l(r)/\rho(r) \quad (2)$$

where

$$\rho_l(r) = \sum_m r^2 |R_l^m(r)|^2 \text{ and } \rho(r) = \sum_l \rho_l(r) \quad (3)$$

Since each spherical harmonic will, in general, be multiplied by a different radial function $R_l^m(r)$, it follows that *the hybridization coefficients vary with radial distance*.

A more useful description of the hybridization would be given by a set of coefficients that are suitably averaged over radial distances along with a measure of the deviation of each coefficient from its average value. One obvious way to proceed is by fitting the exact orbital as closely as possible to Pauling's simplified form. This approach is straightforward to implement computationally.⁶ But the fundamental significance of Pauling's form is questionable.⁷ It appears somewhat preferable, therefore, to construct the more conventional radial average

$$\bar{h}_l \equiv \frac{\int_0^\infty w(r) h_l(r) dr}{\int_0^\infty w(r) dr} \quad (4)$$

with $w(r)$ being an appropriate weight function. The choice of $w(r)$ is somewhat arbitrary, but it seems natural to select a function that weights most heavily those regions where the orbital has the largest total density. The simplest such choice,⁸ namely $w(r) = \rho(r)$, yields (assuming χ to be normalized)

$$\bar{h}_l = \int_0^\infty \rho_l(r) dr = \sum_m \int_0^\infty r^2 |R_l^m(r)|^2 dr \quad (5)$$

This definition has further appeal because the average hybridization coefficient, \bar{h}_l , becomes just that fraction of the total integrated radial density which is due to the angular momentum l .

In order to know how well the average hybridization describes the orbital we require information on the dispersion of the hybridization coefficients about their average values. For this purpose, it is most convenient to employ the ordinary standard deviation of \bar{h}_l which is given by ($w(r) = \rho(r)$)

$$\sigma_l = \left[\int_0^\infty \frac{\{\rho_l(r)\}^2}{\rho(r)} dr - \bar{h}_l^2 \right]^{1/2} \quad (6)$$

Note that the Pauling treatment mentioned earlier corresponds to having each radial function proportional to a single $f(r)$, i.e., $R_l^m(r) = \lambda_l^m f(r)$, so that $h_l(r) = \bar{h}_l$ for all r and $\sigma_l = 0$. In

Table I. Average Hybridization Coefficients ($sp^n d^m f^l$) for the Lone Pair and Bonding Orbitals of H_2O Calculated^a from (5) with $n = \bar{h}_p/\bar{h}_s$, $m = \bar{h}_d/\bar{h}_s$, etc.^b

Orbital	Valence-bond hybridization			Localized MO hybridization			
Bonding ^c	$s^{1.00 \pm 0.15}$	$p^{1.83 \pm 0.14}$	$d^{0.01 \pm 0.01}$	$s^{1.00 \pm 0.23}$	$p^{3.31 \pm 0.14}$	$d^{0.20 \pm 0.18}$	$f^{0.03 \pm 0.03}$
Lone pair ^d	$s^{1.00 \pm 0.14}$	$p^{1.38 \pm 0.13}$		$s^{1.00 \pm 0.32}$	$p^{2.50 \pm 0.30}$	$d^{0.01 \pm 0.01}$	
	$s^{1.00 \pm 0.21}$	$p^{0.56 \pm 0.20}$					
Truncated bonding ^c	$s^{1.00 \pm 0.15}$	$p^{1.77 \pm 0.13}$	$d^{0.02 \pm 0.03}$	$s^{1.00 \pm 0.27}$	$p^{3.93 \pm 0.22}$	$d^{0.05 \pm 0.07}$	
Truncated lone pair ^d	$s^{1.00 \pm 0.18}$	$p^{1.52 \pm 0.18}$		$s^{1.00 \pm 0.18}$	$p^{1.83 \pm 0.18}$	$d^{0.01 \pm 0.01}$	
	$s^{1.00 \pm 0.09}$	$p^{0.36 \pm 0.09}$					

^a Coefficients with values less than 0.005 are not listed. ^b The error limits represent one standard deviation as given by eq 6. For proper normalization σ_l has been divided by \bar{h}_s . ^c The second valence bond bonding orbital is not included since it is essentially an s orbital localized on the H atom. ^d Each valence bond lone pair consists of two distinct spatial orbitals, the second listed being more radially diffuse and angularly more parallel to the molecular plane than the first.

the general case, as long as σ_l is small compared to \bar{h}_l there are only small deviations of the hybridization about the average. If it turns out that σ_l is large compared to \bar{h}_l then the average hybridization is not a meaningful measure of the true point by point hybridization, at least for that particular angular momentum component.

For the hybridization to be effective at altering the angular electron distribution there must be substantial overlap between the radial functions of the important contributing angular momenta. This becomes clear if one considers the extreme case in which an orbital has an s component which drops off to essentially zero at some distance r_0 and a p component which is significant only at larger distances. In that case, the angular variation of the orbital function is entirely independent of the relative proportions of the s and p components! As a warning signal of such behavior, our procedure automatically produces a large standard deviation. For example, with an orbital of the extreme type just described, the value of σ_p ranges from 58% of \bar{h}_p for an sp^3 orbital to 100% for an sp orbital.

It should also be noted that the average hybridization coefficients do not uniquely determine the angles between the orbitals as they would in the Pauling formulation.⁹ In fact, the orbital axes must be found by a separate calculation, and often they will be curved, rather than straight lines, as they recede from the center of interest. In principle one can trace these axes by requiring that the first derivatives of the orbital function vanish in a plane perpendicular to the axis. This is the condition for local rotation symmetry about the axis. The defining equations that obtain are identical with those that determine the steepest ascent (descent) path from the nucleus of interest.

III. Application to H_2O

To illustrate our method we have calculated average hybridization coefficients for the lone pair and bonding orbitals on the oxygen atom in H_2O . Four sets of orbitals are presented: valence bond,¹⁰ truncated VB (with AO's centered on the H atoms deleted), localized molecular orbitals,⁴ and truncated LMO's. Each orbital was obtained in terms of a double ζ plus d basis set¹⁰ of Slater-type functions. For the nontruncated orbitals, the d and f terms were retained in the ζ -function expansions of the hydrogen atomic orbitals about oxygen although their inclusion has only a small effect.

The results are summarized in Table I. In general, the effect of truncation appears to be quite substantial for the LMO orbitals, but less so for the better localized VB ones. As indicated earlier the nontruncated orbitals are more satisfying on theoretical grounds.

The standard deviations indicate small fluctuations from the average in most cases; exceptions occur only if the hybridization coefficient itself is small. Furthermore, the average

coefficients obtained by the alternate fitting procedure of ref 6 differ little from those reported here. These results are in accord with the strong similarity between the s and p radial functions which one notices upon direct examination. We conclude that hybridization in H_2O very effectively redistributes the angular orbital electron density and that the calculated average hybridization coefficients will be insensitive to the choice of weighting function in eq 4.

On the basis of the usual bond angle prescription¹¹ the lone pairs on oxygen would be $sp^{2.33}$ and the bonding orbitals $sp^{4.01}$. The LMO's, which are constrained to be orthogonal, come closer to these values than their VB counterparts which were not so constrained. But the latter are preferred because they lead to a more accurate overall wave function.¹⁰ Note that the VB hybrids for H_2O have substantially more s character than the corresponding MO's and much more than one might have expected. Indeed, the diffuse outer VB orbital of each lone pair has a hybridization of $sp^{0.56}$!

Using the method given above we have also determined the angle between the axes of the bonding VBO's on oxygen which turns out to be 8.2° less than the corresponding internuclear angle. The resulting "bent bonds" are essentially linear all the way out to the region of large overlap with the hydrogen atomic orbitals. On the other hand, the lone pair VB orbitals are markedly curved. The more diffuse one, in particular, starts off on one side of the molecular plane and then rapidly crosses over to the other side where it has its maximum value.¹²

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References and Notes

- (1) (a) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960; (b) C. A. Coulson, "Valence", 2d ed, Oxford University Press, London, 1961.
- (2) (a) L. Pauling, *J. Am. Chem. Soc.*, **53**, 1367 (1931); (b) J. C. Slater, *Phys. Rev.*, **37**, 481 (1931).
- (3) See, for example, M. D. Newton, E. Switkes, and W. N. Lipscomb, *J. Chem. Phys.*, **53**, 2645 (1970).
- (4) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).
- (5) This can be accomplished by the ζ function technique for Slater functions [see M. P. Barnett, *Methods Computational Phys.*, **2**, 95 (1963)] and by a similar technique for Gaussian functions.
- (6) The basic equations are derived by minimizing the mean square deviation of the exact normalized orbital from one of Pauling's form, i.e.,

$$\int \left| \chi(r, \theta, \phi) - \sum_{lm} \lambda_l^m Y_l^m(\theta, \phi) \right|^2 dr$$

with respect to λ_l^m and the coefficients λ_l^m . This minimization condition leads to the matrix eigenvalue relation $\sum_b (A_{ab} - \epsilon \delta_{ab}) \lambda_b = 0$, where a (or b) stands for the (l, m) pair, $A_{ab} = \int R_a(r) R_b(r) r^2 dr$, and δ_{ab} is the Kronecker delta. Choose the eigenvalue ϵ closest to unity and its corresponding ei-

genvector λ to construct the best approximation to χ of Pauling's form as

$$\chi(r, \theta, \phi) \simeq \left[\epsilon \sum_a \lambda_a^2 \right]^{-1} \left[\sum_a \lambda_a P_a(r) \right] \left[\sum_a \lambda_a Y_a(\theta, \phi) \right]$$

The fitting parameter ϵ turns out to be the square of the overlap between χ and the optimum orbital of the form $f(r) \sum_{l,m} \lambda_l^m Y_l^m(\theta, \phi)$.

- (7) For example, in order to obtain 2s and 2p orbitals with identical radial functions Pauling used a nodeless 2s orbital which cannot be orthogonal to a 1s orbital.
- (8) Other choices of $w(r)$ might be made. For example, if one wishes to correlate hybridization with a particular physical property then $w(r)$ might be chosen to weight most heavily the radial regions of importance for that property.
- (9) In addition to assuming identical hybridization at all radial distances, the Pauling formulation also assumes that the axis of a bond orbital points directly at the nucleus to which the bond is formed and that hybrid orbitals

on the same center are orthogonal. These assumptions provide constraints on the relative orientation of the hybrid orbitals.

- (10) The valence bond orbitals were obtained by a self-consistent-field optimization of the wave function for a single perfect-pairing structure. See, D. M. Chipman, B. Kirtman, and W. E. Palke, *J. Chem. Phys.*, **65**, 2556 (1976).
- (11) According to the prescription we mix normalized s, p_x , p_y , and p_z orbitals to produce two equivalent bond hybrids pointing at the hydrogen atoms (which subtend an angle of 104.45° at the oxygen) and two equivalent lone pair hybrids above and below the molecular plane. Constraints of normalization and orthogonality then uniquely determine the hybrid orbitals leading to lone pairs forming an angle of 115.42° and giving the hybridization coefficients quoted in the text.
- (12) In practice we have found it difficult to follow this rapid crossover because of numerical roundoff errors. For the same reason the direction of the bonding VBO on oxygen becomes poorly determined as one enters the bonding overlap region.

Ab Initio Calculations of the Equilibrium Structure of Cyclobutane

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Abstract: The equilibrium structure of cyclobutane has been calculated by single determinant restricted Hartree-Fock theory using an extended basis set of Gaussian orbitals augmented by polarization functions. The molecule is found to be nonplanar with a degree of puckering of 0.23 Å and a barrier to planarity of 0.9 kcal mol⁻¹. Tilting of the methylene groups proves to be essential for relieving steric strain.

Cyclobutane¹ has been extensively investigated using electron diffraction^{2,3}, IR-Raman,⁴⁻¹⁰ and NMR.¹¹ All experimental results agree that the molecule possesses a puckered structure with a small surmountable barrier to planarity. As its degree of nonplanarity is determined by a single puckering amplitude q ¹² one would expect detailed experimental information on the equilibrium conformation and the inversion process. For a number of cyclobutane derivatives¹³⁻¹⁷ microwave and far-IR studies provide these data but for the parent molecule itself the corresponding details are less accurate, owing to the fact that it has no dipole moment and hence no microwave spectrum. Furthermore, the ring puckering vibration is IR inactive and no far-IR spectrum can be expected. Although the height of the inversion barrier has been determined quite accurately,^{8,9} several structural features are still not fully resolved: (a) Recent spectroscopic studies of the degree of puckering^{8,11} vary considerably. (b) The amount of bond staggering of the methylene groups remains unclear. (c) The CH bond lengths found by electron diffraction^{2,3} and high resolution proton resonance in a nematic solvent¹¹ are unexpectedly long compared with CH bond lengths of other cycloalkanes. (d) No experimental account of the difference between axial and equatorial hydrogens in puckered cyclobutane has been given.

Recent ab initio studies on cyclobutane¹⁸⁻²¹ were rather inconclusive with regard to these questions. With a minimal basis set of Slater-type orbitals the molecule was found to be rather flat with almost no barrier to inversion.¹⁸ A calculation employing floating spherical Gaussian orbitals was in reasonable accord with experimental structural data but gave a barrier value much too high.¹⁹ Therefore, we would like to report a thorough ab initio study of cyclobutane using elaborate basis sets in order to get reliable predictions of the various energetic and structural features of the four-membered ring.

Quantum Mechanical Method

Our investigation is based on single determinant restricted Hartree-Fock theory.²² A 6-31G split-valence basis set augmented by six d functions (6-31G* basis) for the description of the carbon atoms was used.²³ From previous studies it has become obvious that extended basis sets including polarization functions are sufficient to reproduce relative energies and geometries in good agreement with experiment.^{23,24} Therefore, our study was essentially aimed at determining these features of planar (D_{4h}) and puckered (D_{2d}) cyclobutane at the 6-31G* level. In order to obtain an initial guess of the theoretical structures, preliminary calculations with smaller basis sets were done, namely the minimal STO-3G basis²⁵ and the extended 4-31G basis.²⁶

As indicated in Figure 1 the equilibrium structure of the D_{4h} form was evaluated by optimizing the CC bond length, the CH bond length, and the HCH bond angle. In the puckered D_{2d} form axial and equatorial hydrogens were distinguished, thus giving two different CH bonds to be calculated. The degree of nonplanarity was determined by the puckering amplitude q .²⁷ An additional sixth degree of freedom arose from the fact that because of ring puckering the local C_{2v} symmetry of a C-CH₂-C fragment is relieved: the methylene groups tilt, which is quantitatively described by the tilting angle τ depicted in Figure 1.²⁸ The structure optimizations were done using an improved version of the complementary Davidson-Fletcher-Powell method.²⁹

Results and Discussions

Table I presents the RHF energies of the two cyclobutane forms obtained with the STO-3G, 4-31G, and 6-31G* basis sets. Also listed are theoretical and experimental barrier heights. Table II gives the computed structural data of planar and puckered cyclobutane. The latter are compared with the results of two experimental studies.