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# On Determining Orbital Hybridization

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A simple method is presented for calculating the hybridization of any orbital. The dependence of the hybridization upon radial distance from a nucleus is discussed, and a procedure for determining the average hybridization is suggested with special consideration for doubly occupied orbitals.

### INTRODUCTION

Since its introduction by Pauling[1] and Slater[2], the concept of hybridization has proven to be useful in all areas of chemistry. Pauling's original paper is a thorough exposition on covalent bonds from the valence bond (VB) point of view. He begins with the proposition that a chemical bond is formed by the overlapping of two orbitals on different atoms each of which contains one electron whose spin is paired with the other. He then argues that the strongest bonds can be formed from orbitals with large overlaps and shows very clearly that the superposition of orbitals with different angular behavior can generate hybrids that are localized in specific directions and therefore should be particularly effective at bonding. The angular arrangements of hybrids that can form in different circumstances have formed very useful guidelines for the discussion of the geometry of molecules[3] ever since Pauling's work.

The development of computers has fostered a different viewpoint in the theory of molecular structure, however. Most modern *ab initio* methods of describing the electron distribution in molecules do not constrain the orbitals to be of a specific atomic form, but solve for those self-consistent field orbitals which minimize the energy of a certain approximate form for a total wavefunction. Thus, the »best« (in the sense of lowest energy) orbitals are obtained as linear combinations of basis functions situated on many atoms or even as numerical tabulations. Because the concept of hybridization has been so useful, it is desirable to determine the hybridizations of the orbitals that result from such calculations. Valence bond orbitals are easiest to analyze because hybridization was developed with them in mind. The optimum VB orbitals[4,5] turn out to be primarily localized on one atom and are spin-paired into bonds, lone pairs and inner shells. A typical VB orbital can be expressed in terms of functions on one atom, and its angular composition can be evaluated readily.

The case for Hartree-Fock (or any other doubly occupied) orbitals is not so simple. First of all, the (canonical) orbitals that satisfy the Fock equation[6]

are delocalized throughout the molecule, but this can be changed by a unitary transformation to localized orbitals. Various criteria have been proposed to define the most localized orbitals. The resulting sets of localized orbitals are all similar to one another, so the choice of methods is arbitrary, but we have used the Edmiston-Ruedenberg[7] method because it is widely accepted and easy to apply. The resulting localized Hartree-Fock (LHF) orbitals do correspond nicely to electron pair bonds, lone pairs and inner shells.

However, the LHF bond orbitals are usually concentrated around two nuclei and therefore present a problem in the determination of their hybridization about one of those centers. The usual solution to this difficulty has been to truncate the orbital, discarding all basis functions not centered on the nucleus of interest[8]. There are several reasons that truncation should be avoided. First of all it is arbitrary. Consideration of a numerical bond orbital illustrates that there is not an obvious unique way to divide an orbital between two atoms. If an orbital expressed in terms of a basis set is truncated, one should worry about whether the basis is balanced between the two centers. That is, do the basis functions on each center have the same flexibility of describing a wavefunction near it. Regions of rapid orbital fluctuation caused by the core electrons close to one nucleus ought not be considered in the hybridization of another center as we shall see. Yet valence and diffuse basis functions on a center can contribute significantly to the orbital amplitude and hence to the hybridization in the bonding region and in regions near a second atom. Such portions of an orbital should not be discarded.

In the next section, a method for determining the hybridization of any orbital without truncation is presented and discussed.

### COMPUTATIONAL METHOD

In a general orbital such as an optimum VB or LHF orbital, it is quite common that different angular momentum components predominate at different distances from a nucleus. Thus the relative proportions of $s$, $p$, $d$ etc. character of the orbital, that is its hybridization, are functions of the distance from the origin. It is of interest to investigate this radial hybridization behavior and to consider what sort of an average might show sufficient significance to be called »the hybridization« in a particular orbital. First a method is described by which any orbital can be decomposed into angular momentum components at a sequence of radii from the nucleus of interest. Then plots of hybridization *vs.* radius are presented, and the important considerations in determining an average hybridization are discussed.

We desire the fractional angular composition of an orbital a given distance from a nucleus. In other words, we want to determine its $s$, $p$, and $d$ etc. character on a spherical surface of a certain radius. For an orbital expressed in terms of a basis set, it is possible to expand every basis function onto the center of interest[9,10] But we prefer a more simple minded and more general approach which will work even for a numerical orbital. One can successively project the orbital onto normalized $s$, $p_x$, $p_y$, etc. angular functions on the surface of a sphere, giving the amplitude coefficients $a_{lm}(r)$

$$a_{lm}(r) = \int \psi(r, \vartheta, \varphi) \, Y_{lm}(\vartheta, \varphi) \, r^2 \sin(\vartheta) \, \mathrm{d}\vartheta \, \mathrm{d}\varphi$$

The relative contributions of angular momentum components are given by the squares of the $a_{lm}$'s. The p-hybridization, for example, would then be

$$h_1(r) = \sum_{m=x,y,z} \frac{[a_{1m}(r)]^2}{[a_{00}(r)]^2}$$

The average hybridization is then given by

$$h_l = \int_{r_{\min}}^{r_{\max}} h_l(r)\, w(r)\, r^2\, \mathrm{d}r$$

where $w(r)$ is a weighting function to be chosen. This procedure can be conveniently carried out numerically. The minimal number of integration points in $\vartheta, \varphi$ space that can determine all angular momentum components through $l = 2$ with acceptable accuracy seems to be a set of 26 points given by Abramowitz and Stegun[11].

The C—C bond of ethane will be used as a typical example. Pitzer's[12] localization of the original Pitzer-Lipscomb staggered ethane calculation[13] was reproduced, and the p-hybridization $(sp^h)$ of the carbon-carbon LHF orbital versus distance from one of the carbon nuclei is shown in Figure 1. Remember
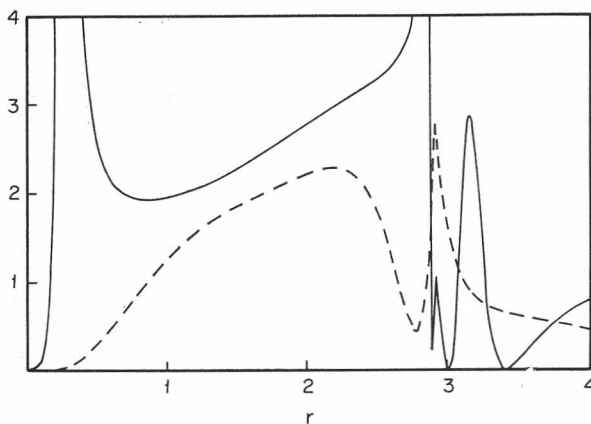


Figure 1. p-hybridization and radial density (dashed line) of ethane's C—C orbital; its average hybridization is $sp^{2.45}d^{0.23}$. The bondlength is 2.9 a. u.

that the abscissa of the figure is the radial distance from the carbon at the origin; hence, the plot is not symmetric about a radius equal to half the bond distance. The most important feature of this plot is that the hybridization varies slowly in the central portion of the bond. The radial electron density in the CC orbital is also plotted in Figure 1 in order to illustrate that the hybridization is relatively constant in the region where the CC orbital density is largest. If this were not true, an average hybridization would not seem meaningful. The large fluctuation in hybridization near $r = 0.25$ a. u. is near a node in the s portion of the orbital which is caused by the requirement that the C—C bond orbital be orthogonal to the doubly occupied inner shell orbital. A similar fluctuation is apparent near the carbon-carbon distance and is caused by the same effect. It is generally believed that such regions are not intimately associated with the C—C bond, so they should not be included in determining

the average hybridization. At large distances from the nucleus, not only do orbitals on the atom bonded cause rapid changes in hybridization, but contributions from other atoms add their effect. These contributions are largest in the high angular momentum terms because an extensive sum over angular momentum functions is required to expand even an s orbital onto a different center. Consequently, the region over which the hybridization is averaged should begin at some radius greater than zero and should end before the core region of the other nucleus is reached.

Because the importance and effectiveness of hybridization is greatest in regions of large electron density, it seems reasonable to use the electron density as a radial weighting factor in determining the averaged hybridizations. Such a procedure was also followed in reference 10. The electron density in the C—C bond LHF orbital is very small within 0.5 a. u. of the carbon nucleus, so using the orbital's electron density in a thin spherical shell as a weight function will effectively eliminate the contribution of the region near the node at $r = 0.25$ a. u. to an average hybridization.

The radial density does not die off at a radius near the bondlength; instead it fluctuates rapidly near the bonded nucleus and then tends smoothly to zero. Using the density as a weight function will not eliminate the hybridization fluctuations at large radii. Instead, the averaging process must be truncated at some point. It turns out that the resultant average hybridization is not very sensitive to the choice of a cutoff radius as long as it is short of the core region of the bonded nucleus. One might be tempted to average only to the bond midpoint, arguing with an attitude similar to that of truncation, that the portion of the orbital in the range $0 < r < 0.5 R$ »belongs« to the atom at the origin. Inspection of the plots, however, shows smooth hybridization versus $r$ behavior, and there seems to be no reason to stop the average at 0.5 R. Certainly the atom's orbitals extend past the bond midpoint, and it seems reasonable to average over as much of the orbital as is bonding in nature rather than core--like or rapidly fluctuating because of the orthogonality constraints. Based on ones indoctrination that ethane's bond orbitals should be $sp^3$ hybrids, one might be inclined to weight the outer region of the orbital more heavily, because all of the schemes suggested here yield less than 75% $p$-character. But that argument can not be taken seriously.

An array of results is listed in Table I. For comparison, the hybridization of the truncated C—C bond orbital in ethane is $sp^{1.92}$. Reducing the maximum

TABLE I

*Average Hybridization of the C—C Orbital in Ethane*

|  |  | Hybridization | |
| --- | --- | --- | --- |
| $r_{min}$ | $r_{max}$ | $p$ | $d$ |
| a. u. | a. u. |  |  |
| 0. | 10. | 2.44 | 0.54 |
| 0. | 5. | 2.46 | 0.53 |
| 0. | 2.75 | 2.51 | 0.26 |
| 0. | 2.5 | 2.45 | 0.23 |
| 0. | 2.0 | 2.27 | 0.11 |
| 0.5 | 2.75 | 2.50 | 0.26 |
| 0.5 | 2.5 | 2.44 | 0.24 |
| 0.5 | 2.0 | 2.25 | 0.11 |

cutoff to exclude the region near the second nucleus greatly reduces the $d$-hybridization for reasons already mentioned. The $p$-hybridization is fairly insensitive to the region averaged over. Also notice that beginning the average at 0.5 a. u. instead of zero has a negligible effect. So a reasonable rule of thumb seems to be to use the orbital electron density as a weight function and to average from the origin to about 0.5 a. u. short of the bonded atom. That is out to a radius of about 80% of the bondlength.

### EXAMPLES

The C—C bond of ethane shows somewhat more variation of hybridization with distance than do the ethylene or acetylene C—C bonds. C—H bonds in hydrocarbons have about the same amount of variation of hybridization with distance as the ethane C—C bond. Figures 2—4 display the hybridization in the C—H bonds of ethane, ethylene, and acetylene. (The computations of reference 8 were reproduced). The $p$-hybridization in each of the bonds shows
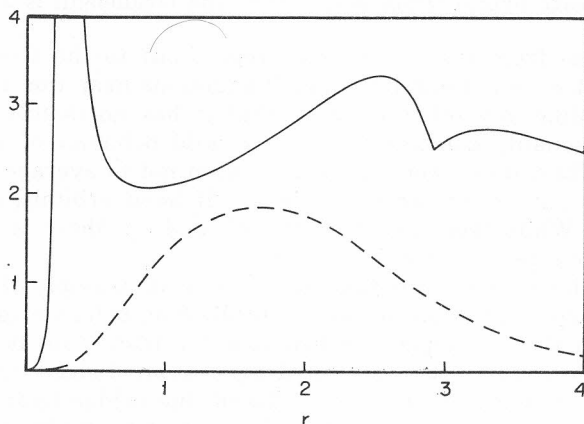


Figure 2. $p$-hybridization and radial density (dashed line) of ethane's C—H orbital; its average hybridization is $sp^{2.40}d^{0.08}$. The bondlength is 2.1 a. u.
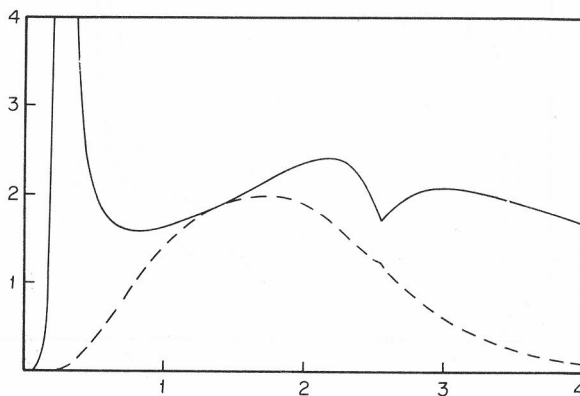


Figure 3. $p$-hybridization and radial density (dashed line) of ethylene's C—H orbital; its average hybridization is $sp^{1.90}d^{0.07}$. The bondlength is 2.0 a. u.
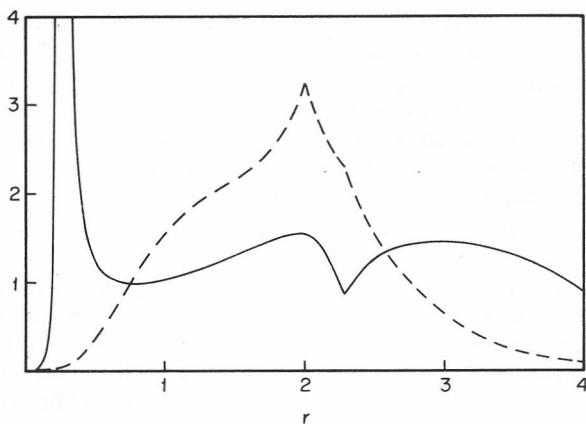
Figure 4. $p$-hybridization and radial density (dashed line) of acetylene's C—H orbital; its average hybridization is $sp^{1.25}d^{0.08}$. The bondlength is 2.0 a. u.

a steady increase from the carbon core region out to the C—H bond length (2.1 a. u.), and it does not exhibit rapid fluctuations near the hydrogen nuclei. Hydrogen is unlike any other atom in that it has no doubly occupied core, hence no orthogonality constraints, to force wild behavior of valence orbitals in its vicinity. Thus, there seems to be no reason not to average the hybridization all the way out to the proton in the C—H bond orbitals, so that is what has been done. While these are not $sp^3$, $sp^2$, and $sp$, there is a very distinct difference in their $p$-character.

The bridge bond in the diborane molecule is an example of an orbital that might be expected to have an unusual hybridization behavior (about the boron atom). This orbital is an especially bad case for truncation because it has so much contribution from the bridge hydrogen atom. Indeed, in the minimum basis calculation[14], which we have reproduced, the bridge hydrogen coefficient is more than twice as large as any other. Truncation to one boron atom actually eliminates 90% of the electron density in the B—H—B orbital. Figures 5 and 6
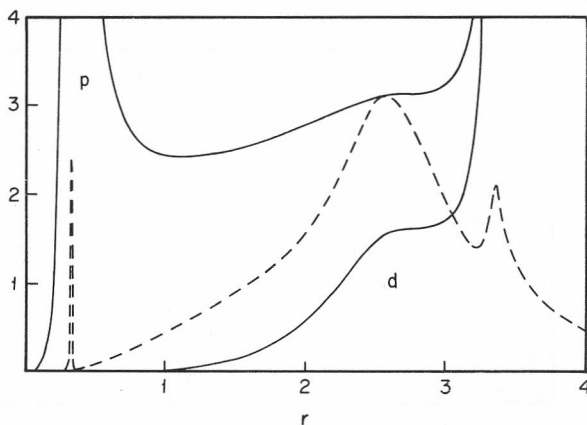


Figure 5. $p$- and $d$-hybridization and radial density (dashed line) of diborane's bridge bond orbital; its average hybridization is $sp^{2.86}d^{0.85}$, but see the text. The B—B distance is 3.4 a. u.
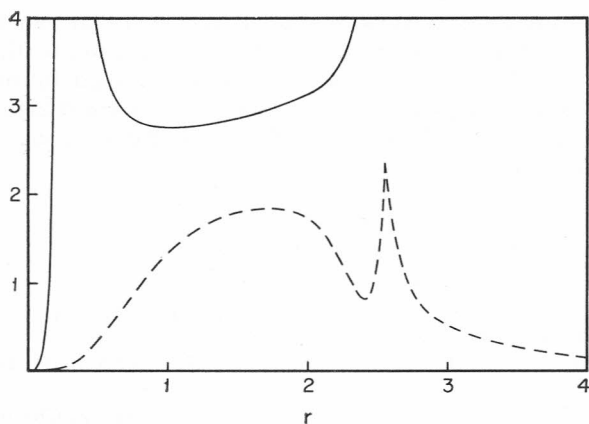
Figure 6. $p$-hybridization and radial density (dashed line) of ethylene's C—C orbital; its average hybridization is $sp^{2.91} d^{0.11}$. The bondlength is 2.6 a. u.

show plots of the hybridization of one of diborane's bridge bonds and one of ethylene's double bonds. (Localization produces two equivalent banana C—C bonds in $C_2H_4$.) They are quite similar with each showing only a modest change in $p$-hybridization outside of core regions. The contribution of the bridge hydrogen is far more evident in the density plot than in the hybridization itself. The $p$-hybridization in the bridge bond is quite well behaved, and from that point of view, it seems quite similar to one of the ethylene double bonds. See, however, the discussion in reference 14.

The bridge bond does have a significant amount of $d$-hybridization. This arises from the region near the bridge proton and from the second boron's core region. As a result, the average $d$-character of the B—H—B orbital, shown in Table II, is sensitive to the averaging cutoff radius. If a value for $r_{max}$ of 3.0 a. u.

TABLE II

*Average Hybridization of the Bridge Bond in Diborane*

| | | Hybridization | |
|---|---|---|---|
| $r_{min}$ | $r_{max}$ | $p$ | $d$ |
| a. u. | a. u. | | |
| 0. | 10. | 3.17 | 1.28 |
| 0. | 5. | 3.11 | 1.25 |
| 0. | 4. | 3.06 | 1.16 |
| 0. | 3. | 2.86 | 0.85 |
| 0. | 2.5 | 2.75 | 0.55 |
| 0. | 2.0 | 2.60 | 0.21 |
| 0.5 | 3.0 | 2.85 | 0.86 |
| 0.5 | 2.0 | 2.58 | 0.21 |

is used, the boron core is excluded, and the bridge hydrogen is included. This is a rather arbitrary choice, however, and it is perhaps better to say that the $d$-hybridization in the bridge bond is sizeable but not very well defined. None of the hydrocarbon orbitals has any significant $d$ or higher angular momentum character, and so those terms have not been discussed in detail.

The main result of this work is that a hybridization can be defined and readily computed for doubly occupied orbitals. Truncation of the orbitals need not be invoked, and the hybridization can be determined by methods that do not depend on having a balanced basis set. The hybridization of localized Hartree-Fock orbitals should be a useful tool in categorizing and comparing different calculations.

## REFERENCES

1. L. Pauling, *J. Amer. Chem. Soc.* **53** (1931) 1367.
2. J. C. Slater, *Phys. Rev.* **37** (1931) 481.
3. See, for example, *Chem One,* J. Waser, K. K. Trueblood, and C. M. Knobler, McGraw-Hill, New York, 1976.
4. D. M. Chipman, B. Kirtman, and W. E. Palke, *J. Amer. Chem. Soc.* **65** (1976) 2556.
5. W. J. Hunt, P. J. Hay, and W. A. Goddard III, *J. Chem. Phys.* **57** (1972) 738.
6. C. C. J. Roothaan, *Rev. Mod. Phys.* **23** (1951) 69.
7. C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.* **35** (1963) 457.
8. M. D. Newton, E. Switkes, and W. N. Lipscomb, *J. Chem. Phys.* **53** (1970) 2645.
9. M. P. Barnett, *Methods of Computational Physics,* **2** (1963) 95.
10. B. Kirtman, D. M. Chipman, and W. E. Palke, *J. Amer. Chem. Soc.* **99** (1977) 1305.
11. *Handbook of Mathematical Functions,* M. Abramowitz and I. A. Stegun, Dover Inc., New York, 1965.
12. R. M. Pitzer, *J. Chem. Phys.* **41** (1964) 2216.
13. R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.* **39** (1963) 1995.
14. E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.* **51** (1969) 2085.

## SAŽETAK

### O određivanju orbitalne hibridizacije

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Prikazana je jednostavna metoda računanja hibridizacije atomskih orbitala. Prodiskutirana je ovisnost hibridizacije o radijalnoj udaljenosti od jezgre i dan je postupak određivanja prosječne hibridizacije. Posebno su razmotrene dvostruko zaposjednute orbitale.