

Are Bonds Bent? To What Extent Do Bond Orbitals Follow Nuclear Motions?

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Abstract: In order to make definitive statements about bent bonds and orbital following accurate ab initio self-consistent valence bond orbitals have been obtained for CH₄, NH₃, H₂O, and H₂S as a function of nuclear geometry. The directions of the orbitals are uniquely determined by the energy minimization criterion. It is found that the bonding orbitals on the central atoms are normally bent a small amount at equilibrium unless constrained to be otherwise by symmetry. More striking is the fact that in almost all cases these orbitals remain nearly stationary as the nuclei undergo bending motions about equilibrium. At the same time there are changes in hybridization which occur in a direction in accord with chemical intuition. Localized molecular orbital calculations were also carried out for comparison purposes. They lead to the same qualitative conclusion that, in general, orbital stasis is a much better approximation than complete orbital following.

Introduction

In theories of valence, it is often assumed that σ bonds can be described by orbitals that are localized in the region between the bonded nuclei and that have approximate cylindrical symmetry about the internuclear axis. Thus, each OH bond in H₂O is taken to point from the oxygen toward the appropriate hydrogen. Closely related to this is the concept of orbital following, in which it is assumed that the bonding orbitals reorient so as to remain along the internuclear axes as the nuclear framework bends during vibrational motions. Much of our intuitive understanding of molecular structure is based on the bonding picture that emerges from these models. However, evidence has accumulated from a variety of sources to cast doubt on both assumptions.

The earliest indications that equilibrium bond densities might be bent away from the corresponding internuclear axes came from semiempirical valence bond studies of strained hydrocarbons.² Subsequently, experimental results on the nuclear spin^{3,4} and quadrupole⁵ coupling constants of halo-methanes and on the magnetic hyperfine structure of triplet carbenes⁶ were interpreted to indicate the presence of bent bonds. More recent ab initio localized molecular orbital calculations predict bent bonds for a variety of molecules, including both strained⁷ and unstrained⁸⁻¹¹ hydrocarbons, electron-deficient boron hydrides,¹² free radicals,¹³ ammonia,^{8,9} and water.^{8,14} Total electron density maps,¹⁵ obtained from X-ray diffraction measurements and from molecular orbital calculations, directly show the bent electron density in several molecules. Finally, it has been claimed¹⁶ that bent bonds are actually to be expected in free radicals and carbenes on the basis of Pauling's principle of maximum overlap.¹⁷

The concept of orbital following has been less well investigated, but there are indications that directed valence orbitals can lag well behind the nuclei during bending vibrational motions. The idea of incomplete orbital following was first postulated in empirical analyses of the infrared frequencies in methane¹⁸ and ammonia¹⁹ and has also been invoked in studies of infrared intensities²⁰⁻²² in a variety of molecules. Semiempirical molecular orbital calculations²³⁻²⁵ on the out-of-plane vibrational motion of methyl radical commonly allow for the possibility of incomplete orbital following. It has also been found for this radical that the observed deuterium isotope effect on the magnetic hyperfine coupling constants can be rationalized within a semiempirical valence bond model only if substantial orbital lag is invoked.^{26,27} Ab initio calculations utilizing localized molecular orbitals have indicated only a small degree of orbital following in water,^{28,29} and this result

has been confirmed by valence-bond treatments.^{30,31} The latter procedure leads to a similar result for methylene.³² Finally, it has recently been shown³³ that incomplete electron cloud following is a natural consequence of the Hellmann-Feynman and integral Hellmann-Feynman theorems. Ab initio molecular orbital computations³⁴ have been made which support this contention.

The aforementioned studies suggest that bent bonds and incomplete orbital following may, in fact, be quite common. However, the degree to which they occur is still an open question. Interpretations of experimental results based on only one physical property should be viewed with caution, particularly when they rely on crude semiempirical electronic structure theories. The same is true of conclusions based on any calculations that employ minimal basis sets and/or strong orthogonality constraints. Such restricted wave functions can artificially force changes in orbital direction to accompany changes in hybridization. In reality, these two properties may or may not be strongly coupled—only studies utilizing extended basis sets without constraints will tell. The localized molecular orbital treatment is suspect, in addition, since the localization condition is not unique and different criteria could lead to significantly different bonding pictures.

In order to make definitive statements about bent bonds and orbital following, an orbital method free of the defects mentioned above is required. The perfect-pairing valence bond model is ideally (though not uniquely) suited for this purpose. It is used here to determine energy localized orbitals for the first-row hydrides CH₄, NH₃, and H₂O, and for H₂S as well, in order to provide a comparison with the second row. An outline of the computational procedure is provided in the next section. Suffice it to say here that the orbitals are optimized within an extended basis set by an ab initio self-consistent-field method without orthogonality constraints. Thus, hybridization changes are possible with or without orbital movement and vice versa. Furthermore, the self-consistent feature allows for proper account of charge-transfer effects that can be important in polar covalent bonds.

It is found that the equilibrium bonding orbitals on the central atom are bent in all the molecules except for the highly symmetric case of methane. Furthermore, in nearly every case the central atom bonding orbitals move only very slightly as the hydrogen nuclei undergo bending motions of up to 20° or more from equilibrium. It appears that orbital stasis (i.e., no change in direction) is closer to the truth than is complete orbital following!

A unique type of orbital movement is found in the umbrella (inversion) vibrational mode of ammonia. There, as the ge-

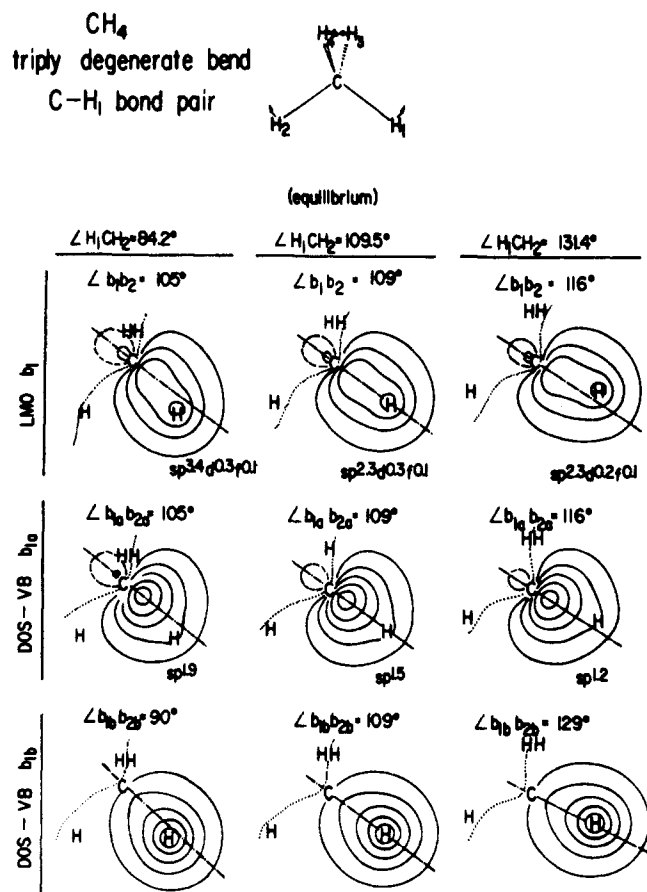


Figure 1. Contour plot of the C-H₁ bond pair in a triply degenerate bend of CH₄.

ometry gets very close to planar, the nitrogen bonding orbitals rapidly change direction (i.e., begin to move) so that they point straight toward the protons when the nuclei are planar. In this case, then, there is a tendency to form highly symmetrical orbitals in a highly symmetrical nuclear configuration.

It is also of interest to see how well the localized molecular orbital (LMO) model can reproduce the basic features of a true valence-bond (VB) calculation. To this end, the same basis sets were used to obtain self-consistent molecular orbitals which were then localized by the Edmiston-Ruedenberg³⁵ criterion. Qualitatively the results are similar but quantitative differences are found. In particular, for the inversion mode of ammonia the bonding LMOs are bent at the planar geometry in contrast with the VB result.

Computational Procedures

In the perfect-pairing valence bond (VB) model a covalent bond is described by two distinct spatial orbitals. In general, each of these orbitals turns out to be localized near one of the bonded atoms. The spins of the two electrons in the bond are paired to form a singlet. In a similar way, the two electrons in a lone or inner-shell pair also occupy different spatial orbitals. Thus, for example, the VB wave function for ammonia with an inner shell,³⁶ three bond pairs, and a lone pair would be written as

$$\psi_{\text{VB}} = A(1s_a 1s_b)(b_{1a} b_{1b})(b_{2a} b_{2b})(b_{3a} b_{3b})(l_a l_b)\chi$$

where A is the antisymmetrizer, the subscripts a and b distinguish the two spatial orbitals in a pair (which are constrained to be identical in the LMO model), and χ is an overall singlet spin function consisting of a product of singlet-coupled two-electron spin functions.

Optimization of the VB orbitals by means of the energy variation condition normally leads to well-localized orbitals

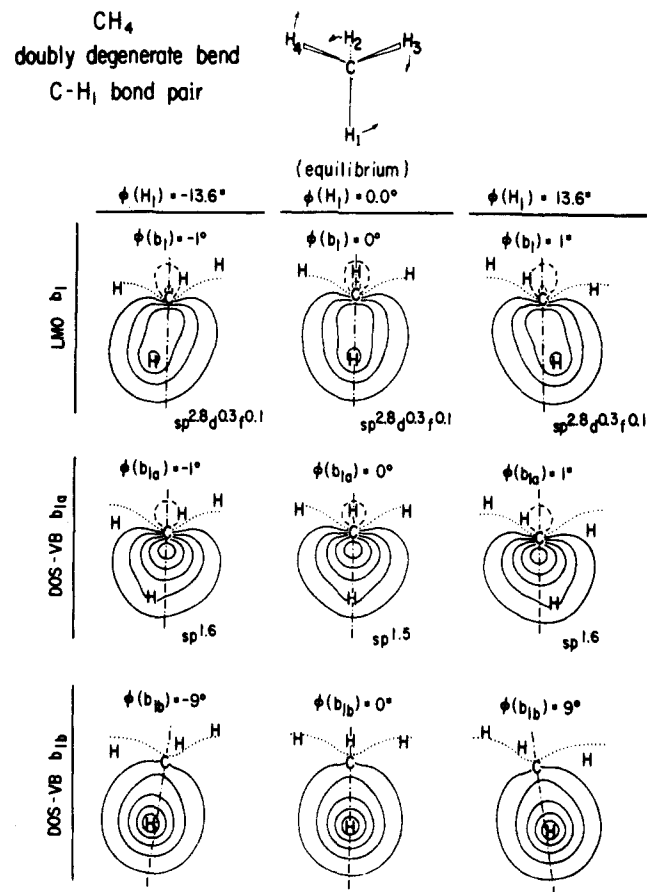


Figure 2. Contour plot of the C-H₁ bond pair in a doubly degenerate bend of CH₄.

that are easily recognized as core, bond, or lone pairs. Nevertheless, the orbitals from different pairs often overlap to a considerable extent. The doubly occupied orbitals of the molecular orbital wave function, in contrast, can always be taken as orthogonal because the antisymmetrizer will cancel all terms due to nonorthogonality. In the VB model the overlap terms complicate the energy expression and make a straightforward optimization of the orbitals prohibitively expensive for more than just a few electrons. One possible simplification is to force the orbitals of different pairs to be orthogonal to one another.³⁷ This constraint raises the energy, often produces artificial nodes in the orbitals, and, most seriously from the present viewpoint, alters their shape and direction.

We have developed³⁸ an alternative method to obtain the optimum VB orbitals without imposing any orthogonality restrictions. In this procedure, each VB pair is optimized separately in the field due to the nuclei and the remaining electrons. The distribution of the remaining electrons is approximated by that set of doubly occupied orbitals which best reproduces their actual VB density. This determines the pair of interest except for its overlap with all the other pairs. Each such overlap is then optimized while holding everything else constant. The two-step sequence is carried out successively for all the VB pairs and repeated until overall convergence is obtained. Detailed working equations for our doubly occupied orbital sea (DOS) method have been given previously.³⁸ In trial calculations on small systems,³⁹ it was found to yield essentially the same results as a complete optimization. Furthermore, for larger systems virtually the same convergence point is reached regardless of the initial guess.

The DOS-VB calculations reported in this work were carried out with a double ζ basis set of Slater-type functions augmented by d functions on the central atom.⁴⁰ The molecular integrals and canonical Hartree-Fock orbitals were obtained

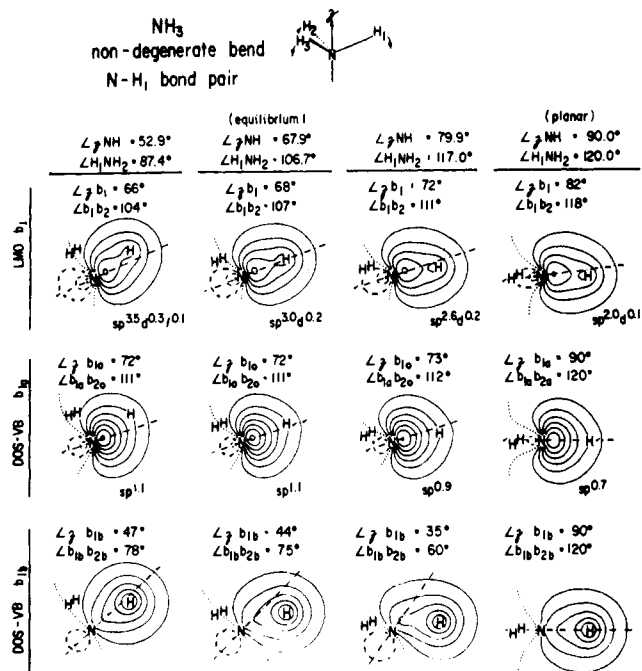


Figure 3. Contour plot of the N-H bond pair in a nondegenerate bend of NH₃.

from Stevens' POLYCAL program package.⁴¹ All bond lengths were held fixed at their equilibrium values,⁴² and bond angles were allowed to vary.

For quantitative discussion of bent bonds and orbital following, a precise definition of the orbital "direction" is required. This direction is determined by the relative coefficients of the p_x , p_y , and p_z functions in the orbital. The p-function contributions can be written in the general form $f_x(r)x + f_y(r)y + f_z(r)z$, where x , y , z , and $r = (x^2 + y^2 + z^2)^{1/2}$ are measured with respect to Cartesian axes located at the central atom. Then the orbital path is defined as that curve which passes through the points $f_x(r)\hat{i} + f_y(r)\hat{j} + f_z(r)\hat{k}$, and the orbital direction at any radial distance r is the tangent to this curve. For a minimal basis set the orbital path is a straight line, but this need not be true for an extended basis. In most of the cases examined here the curvature turned out to be small, the orbital directions fluctuating by at most a few degrees over a wide range of radial distances. Thus, it was meaningful to assign a single value for the orbital direction by averaging over all radial distances from the central atom out to somewhat beyond the distance of the bonded hydrogen atoms.

The average orbital direction determined as described above is reported in the next section. For comparison, however, orbital paths in H₂O were also obtained by two other means. The first was simply a straight line drawn from the central atom to the nearest point of maximum orbital amplitude, while the second was the path of steepest descent (or ascent) away from the central atom. These methods typically gave average directions differing by up to 2-3° and consequently the values reported herein should be taken as meaningful only to that extent. It is important to note, however, that the amount of orbital following, i.e., the change in orbital direction as the nuclei move, is much more accurately determined than the direction itself. The three methods all agreed on the extent of orbital following to well within 1°. This observation also applies to comparisons between the valence bond and the localized molecular orbital results at any particular geometry.

An appropriate generalization is also required to define orbital hybridization for extended basis calculations. The hybridization coefficients reported here were found by the weighted averaging procedure described previously.⁴³ In this

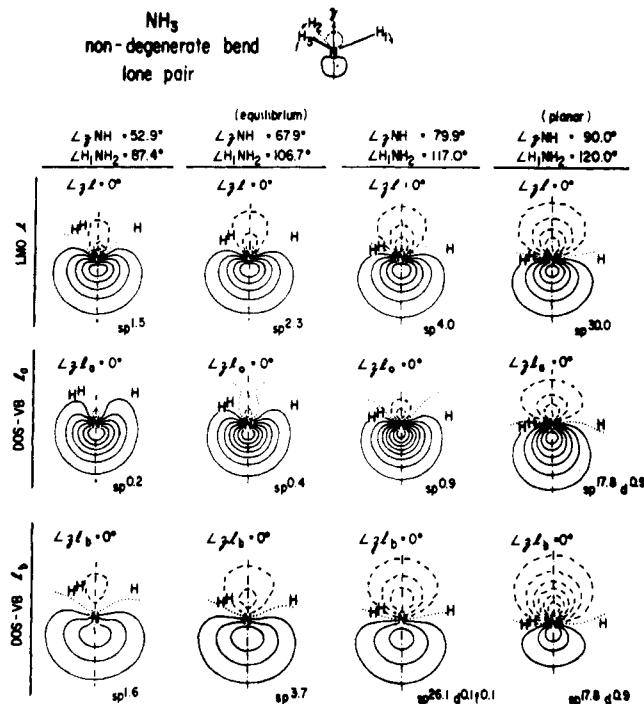


Figure 4. Contour plot of the lone pair in a nondegenerate bend of NH₃.

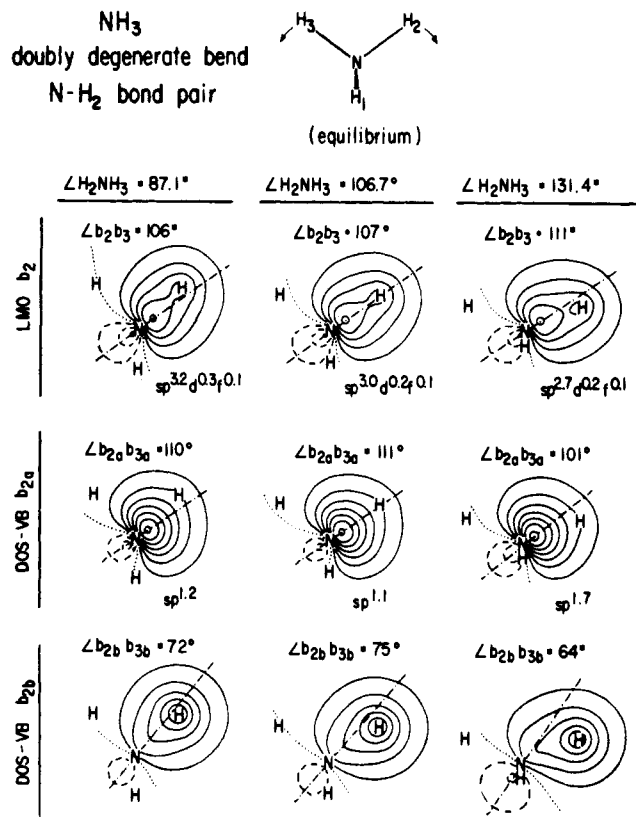


Figure 5. Contour plot of the N-H₂ bond pair in a doubly degenerate bend of NH₃.

method, contributions from functions located on peripheral atoms are included by expansion in spherical harmonics about the central atom.

Results

Figures 1-11 show contour plots of orbital amplitude in appropriate slices of the bonding (b) and lone-pair (l) orbitals

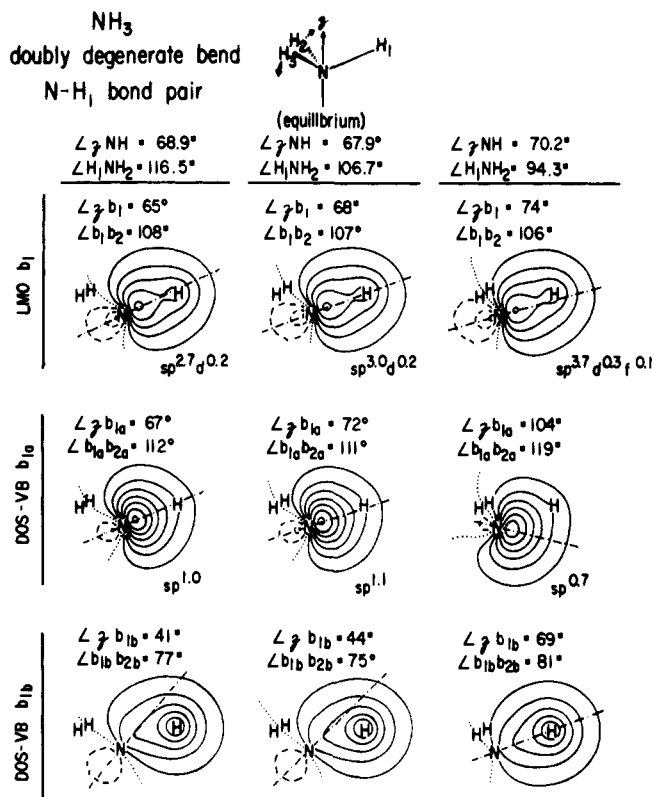


Figure 6. Contour plot of the N-H₁ bond pair in a doubly degenerate bend of NH₃.

for CH₄, NH₃, H₂O, and H₂S at equilibrium and at a variety of bent molecular geometries. The subscripts 1, 2, . . . , on b and l identify the particular bond or lone pair being depicted. In the VB case, additional subscripts a and b are used to distinguish between the two members of a pair. Thus, b_a denotes a bonding orbital localized primarily on the central atom, whereas b_b is localized primarily on one of the hydrogens. For each lone pair, one member is more diffuse (l_b) and the other more compact (l_a).

Methane and ammonia each have two independent bending vibrations. In methane, there is a triply degenerate scissors mode (Figure 1) and a doubly degenerate twist (Figure 2). In ammonia one vibration is the nondegenerate totally symmetric umbrella (or inversion) mode (Figures 3 and 4) and the other is a doubly degenerate wag (Figures 5, 6, and 7). Both H₂O (Figures 8 and 9) and H₂S (Figures 10 and 11) each have just the one totally symmetric bend. Movements of the nuclei in each bending motion are indicated by arrows in the inset at the top of the figure. These arrows show the reflection symmetry for the scissors mode of CH₄ and the degenerate bend of NH₃.

In methane (Figures 1 and 2) the equilibrium bonding orbitals are found to point directly at the hydrogens. This is required if the four bonds are to be equivalent to one another and if the wave function is to be totally symmetric under the point group T_d . In the other molecules, however, symmetry requirements are less stringent and the central atom VB bonding orbitals (b_a) are found to point several degrees away from the hydrogens. In NH₃ (Figures 3, 5, and 6) the angles between these orbitals are larger than the corresponding internuclear angles, whereas in H₂O (Figure 8) and H₂S (Figure 10) the angles are smaller.

The valence bond b_b orbitals, which are primarily localized on the hydrogens, contain small charge-transfer contributions that are delocalized onto the central atom. The relative amount of delocalization is in accord with expectations based on electronegativities—it is greatest in H₂O, less in NH₃, and very

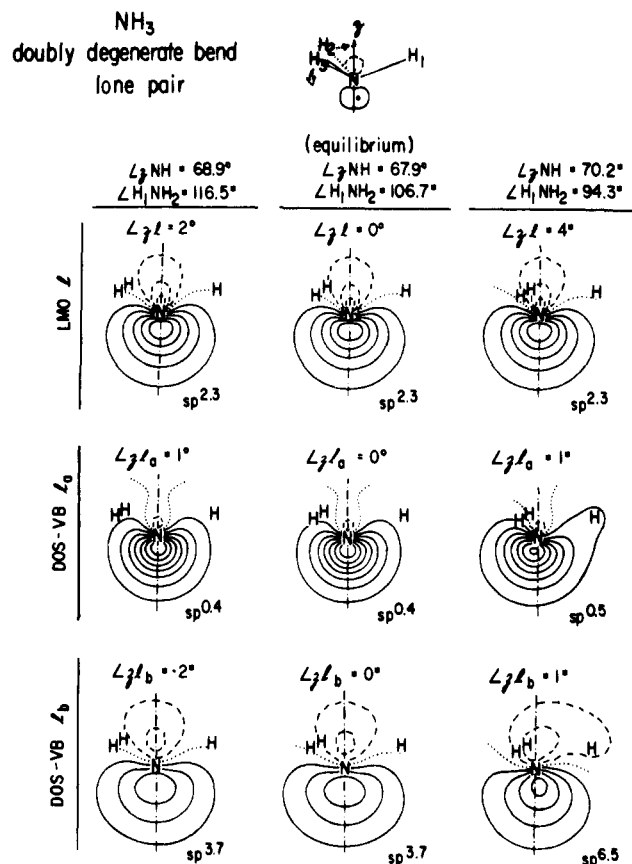


Figure 7. Contour plot of the lone pair in a doubly degenerate bend of NH₃.

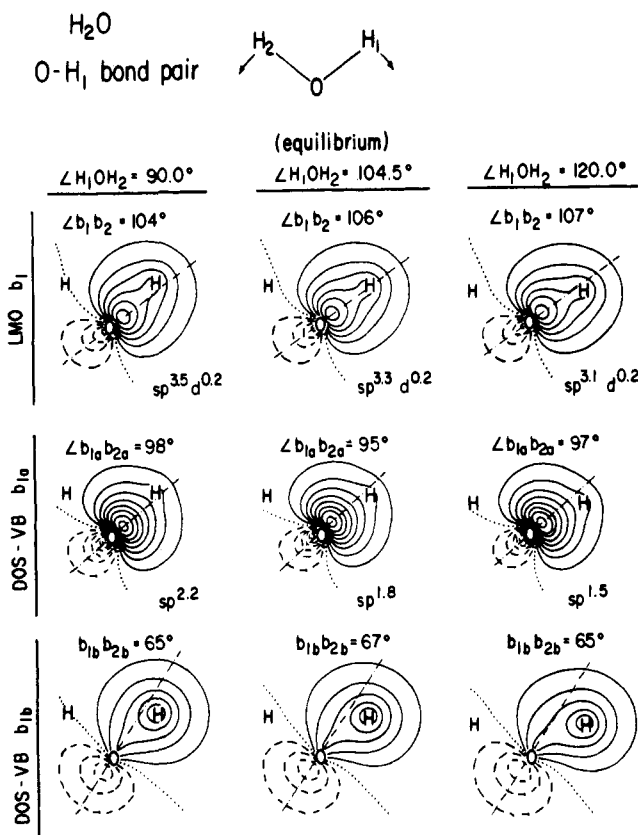
slight in H₂S and CH₄. These small charge-transfer components are generally highly bent even at equilibrium.

Equilibrium LMO bonding orbitals show no bending in CH₄ (again for symmetry reasons) and insignificant bending in NH₃ and H₂O. The bending in H₂S, however, is substantial, being greater in magnitude and opposite in direction to the bending of VB b_a.

Much more striking than the slightly bent equilibrium bonds is the behavior as the hydrogen nuclei vibrate away from their equilibrium positions. In almost every case the central atom VB bonding orbitals (b_a) are seen to lag far behind the nuclear motions. For example, consider the triply degenerate bend of methane (Figure 1), where the lowered symmetry away from equilibrium does not prevent orbital bending. As the H₁CH₂ angle varies by 47°, the angle between the equivalent b_{1a} and b_{2a} orbitals changes by only 11°. Similar results for the doubly degenerate bend of CH₄ and the bends in H₂O and H₂S are shown in Figures 2, 8, and 10. The highest degree of following in these figures occurs for H₂S on the large-angle side of equilibrium (Figure 10). Even there the orbitals remain closer to their equilibrium directions than to the directions of the bonded hydrogens. Thus, in most cases orbital stasis is a better assumption than complete orbital following.

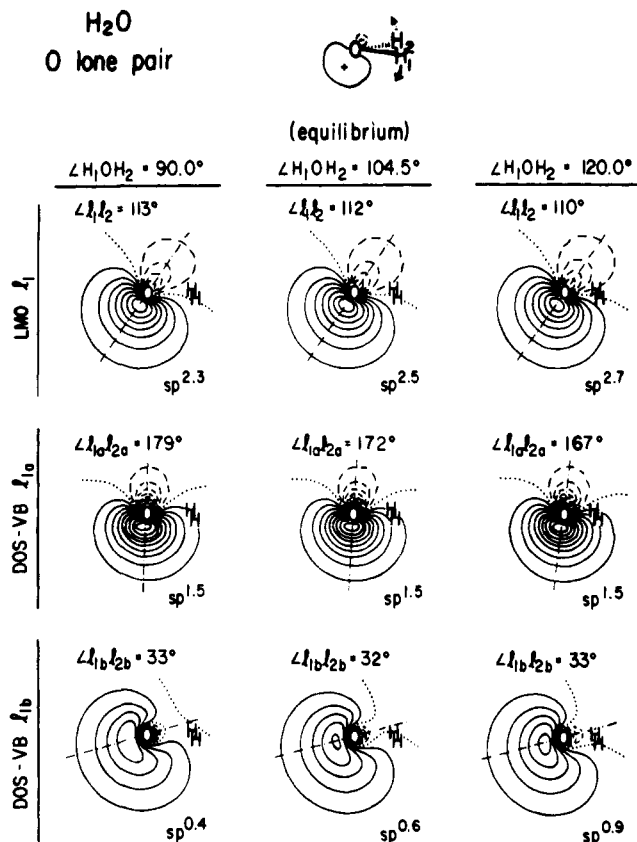
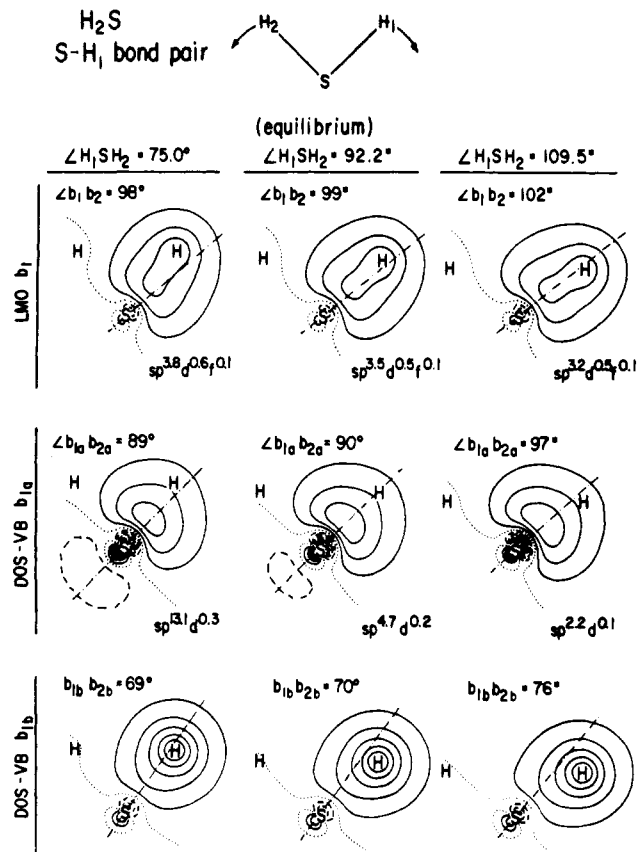
Rapid movement of VB b_a orbitals is seen in the nondegenerate bend of NH₃ (Figure 3) as the nuclei approach the planar configuration, at which point the orbitals point directly at the hydrogens. However, it is clear from Figure 3 that the onset of this exceptional behavior does not occur until the nuclei are well displaced from equilibrium. In order to investigate this region of rapid change an additional calculation (not illustrated) was made with a zNH angle of 88.5°. Here $\angle z b_a$ turned out to be 93°, showing that the VB b_a orbitals actually overshoot the mark and then back up to planar.

An unusual situation arises for the doubly degenerate bend of ammonia (Figures 5 and 6). In this vibration H₂ and H₃

Figure 8. Contour plot of the O-H₁ bond pair in the bend of H₂O.

“wag” and remain equivalent while H₁ remains nearly fixed. Here the equivalent b_{2a} and b_{3a} orbitals (Figure 5)⁴⁴ move much less than the corresponding nuclei, in accord with the behavior noted above for other cases. However, as $\angle \text{H}_2\text{NH}_3$ increases by 25° from equilibrium, b_{2a} and b_{3a} move in the opposite direction with $\angle b_{2a} b_{3a}$ decreasing by 10°. Even more unusual is the behavior of b_{1a} seen in Figure 6, where a reference body-fixed z axis is defined as the locus of all points equidistant from H₁, H₂, and H₃. Although H₁ moves by only 1–2° with respect to the z axis, $\angle z b_{1a}$ decreases by 5° as the H₂NH₃ angle closes down from equilibrium and it increases by 32° as H₂NH₃ is opened up! In the former instance, the movement of b_{2a} compensates the movement of b_{1a} , leaving $\angle b_{1a} b_{2a}$ nearly the same as at equilibrium. Thus, this movement can be described mainly as an overall rotation of the bond orbitals with respect to the nuclei. In the latter instance there is a significant change of $\angle b_{1a} b_{2a}$ indicating a movement of the bond orbitals with respect to one another in addition to their overall rotation. The deviation of b_{1a} from NH₁ by 34° is by far the greatest bending of any b_a orbital studied in this work. This unusual behavior of the bonding orbitals for an increase in $\angle \text{H}_2\text{NH}_3$ is accompanied by partial bonding (see below) between the lone pair and each of the hydrogens, especially H₁ (see Figure 7). Thus, the surprising direction changes in this case are probably best interpreted in terms of a bonding rearrangement rather than orbital following.

The central atom components of the valence bond b_b orbitals are generally small and considerably bent. This component is largest in H₂O, where very little movement occurs with nuclear vibration. The component is smaller in NH₃ and shows more considerable movement, which surprisingly is most often in a direction opposite to that of the nuclei. The component is quite small in H₂S, where little following is seen, and in CH₄, where substantial (but not complete) following is observed. Thus, the charge-transfer components of the b_b orbitals exhibit erratic orbital following behavior. However, these components are

Figure 9. Contour plot of a lone pair in the bend of H₂O.Figure 10. Contour plot of the S-H₁ bond pair in the bend of H₂S.

typically bent toward the symmetry axis even at the equilibrium geometry.

The LMO bonding orbitals, like their VB counterparts, are

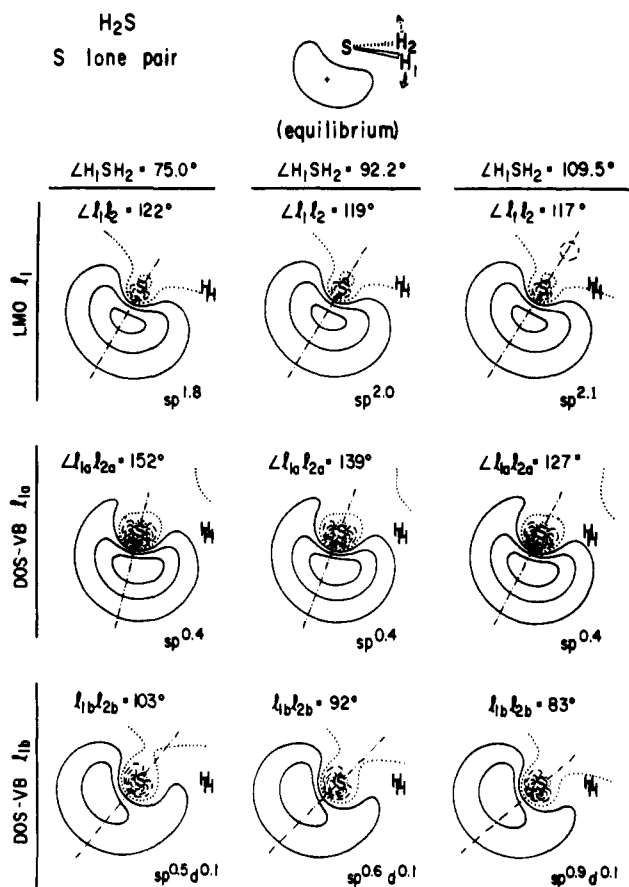


Figure 11. Contour plot of a lone pair in the bend of H_2S .

also found to be insensitive to nuclear vibrations. They move to roughly the same extent as the b_a VB orbitals in CH_4 and H_2O and even less in H_2S and in the doubly degenerate bend of NH_3 . They move to a greater extent only in the nondegenerate bend of NH_3 near equilibrium, although the movement is still small. Further away from equilibrium the situation reverses, so that at the planar configuration the LMO orbitals remain bent. This behavior of the planar NH_3 LMO orbitals has been noted previously.⁹ In general, one can say that the LMO and VB models give much the same qualitative picture of orbital following, although quantitative differences are found.

The directional behavior of the lone pairs varies considerably from molecule to molecule. Little movement occurs in either vibrational mode of NH_3 . For the nondegenerate mode (Figure 4) movement is prohibited by symmetry (assuming equivalent bonds and a totally symmetric wave function) but in the doubly degenerate mode (Figure 7) it is allowed. In the latter vibration the lone pair tends to remain nearly equidistant from the three hydrogens even though, as discussed above, there is considerable movement of the VB b_a bonding orbitals. When the H_2NH_3 angle increases from equilibrium, the VB lone pair orbitals acquire partial bonding character to the hydrogens, particularly to H_1 . This gives l_a , and especially l_b , a highly twisted shape which means that the average directions reported in the figures are not too meaningful. The lone pairs in H_2O (Figure 9) are nearly stationary as the nuclei vibrate, and so are the LMO lone pairs in H_2S (Figure 10). However, the angle between the two equivalent VB l_a (or l_b) orbitals in H_2S decreases significantly as the angle between the hydrogens opens up, a situation analogous to substantial orbital following.

No necessary connection exists between hybridization and orbital direction in calculations using extended basis sets and no orthogonality constraints. Indeed, the VB orbitals are found

in all cases to have less p character than conventional wisdom (or the corresponding LMOs) would have it. However, the changes of hybridization with internuclear angle do go in the direction indicated by chemical intuition. Thus, for example, as the bond angle in H_2O goes from 90 to 120°, the p character of b_{1a} decreases from $sp^{2.2}$ to $sp^{1.5}$ and that of l_{1b} increases from $sp^{0.4}$ to $sp^{0.9}$. The more diffuse l_b lone pair orbitals generally change hybridization more easily than the corresponding l_a orbitals. The only drastic changes in hybridization occur for the lone-pair orbitals in the nondegenerate bend of NH_3 and for the VB b_a orbitals of H_2S . Both of these cases correspond to little or no change in the orbital directions, which reinforces our previous statement that hybridization and orbital direction are independent parameters.

Conclusion

Central atom bonding orbitals are normally bent a small amount at equilibrium, although the bending shows no simple trend in either magnitude or direction. A more significant point is that the orbitals usually move little as the nuclei vibrate. With some qualification in the case of NH_3 , it is found that orbital stasis is a much better approximation than complete orbital following.

References and Notes

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A Poly-*p*-nitrostyrene on Platinum Electrode. Polymer Charging Kinetics and Electrocatalysis of Organic Dihalide Reductions

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Abstract: Platinum electrodes were modified by dip coating them with poly-*p*-nitrostyrene from a *N,N*-dimethylformamide solution. The coated electrodes were dried and then used for electrochemical studies in dry acetonitrile containing tetraalkylammonium fluoroborate electrolytes. Cyclic voltammetry showed that cycling the potential of these electrodes from -1.0 to -1.8 V vs. a Ag/AgNO₃ reference produced some initial desorption and formation of a stable polymer layer which was charged and discharged with peak potentials of -1.6 V. The peak shapes and the dependence of the voltammograms on the sweep rate, electrolyte cation, and amount of adsorbed polymer provided evidence about the structure and about the kinetics and thermodynamics of charging. The catalyzed reduction of 1,2-dibromo-1,2-diphenylethane to stilbene was investigated using cyclic voltammetry and preparative electrolysis. It was shown that the efficiency of catalysis increased to a limiting value as the amount of chargeable polymer increased. High efficiencies for reduction of this dihalide (3 mm) in acetonitrile could be obtained with layers corresponding to a surface charge of 4 nM cm⁻². The turnover number for catalyst sites was estimated to be 10⁴.

Considerable attention has recently accrued to "chemically modified electrodes".¹ These devices are constructed by binding organic or organometallic species to the surfaces of conductors. The *molecular* structure of the modified surface endows these electrodes with specific physical and chemical properties not otherwise attainable. Our research in this area has emphasized the invention of techniques for synthesizing useful electrode surfaces, provided tests for surface structure and stability under electrochemical conditions, and demonstrated that such devices could be used to achieve greater selectivity in preparative reactions. Although our initial studies demonstrated the feasibility of producing and using surfaces modified by covalent binding, our attention has since moved to polymer modified electrodes. It was anticipated that such surfaces would have unique properties and some advantages over covalently modified materials. This anticipation has begun to be realized and there are now a number of research groups pursuing this approach.²⁻⁹ The goal of all this work, and the present study in particular, is generalizable as selective electrocatalysis.

Electrocatalysis with chemically modified electrodes can occur by several (somewhat arbitrarily defined) mechanisms. An electroinactive modifier, which is not capable of accepting or donating electrons, can interact with incoming substrate molecules to alter their chemical reactions or electrochemical reaction rates. Alternatively, an electroactive modifier can act to relay charge from the underlying conductor to a solution species. This is a two-step process first involving (for reductions) electron transfer from the conductor to the modifier. The reductions of solution species can then take place either by an outer-sphere electron transfer from the modifier to the substrate or by an inner-sphere reaction in which nuclei as well as

electrons move between modifier and substrate. The latter seems most interesting from the viewpoint of selectivity, but it also seems difficult to accomplish because of the greater mechanistic complexity. We have, therefore, chosen to test some ideas concerning the preparation, structure, stability, and catalytic efficiency of polymer modified electrodes using materials and a process which are chemically more simple. In this report we detail and amplify a preliminary communication concerning the use of a Pt/poly-*p*-nitrostyrene surface.⁴ Evidence is provided concerning the charging of the polymer and the first example of preparative-scale electrocatalysis by an electroactive modifier is described.

Results and Discussion

Electrode Preparation and Voltammetric Characterization. Poly-*p*-nitrostyrene/Pt electrodes, as previously described,⁴ were prepared from solutions of the polymer in *N,N*-dimethylformamide (DMF). Unless otherwise noted, the concentration was 1% w/v. These solutions were sufficiently stable to be used over a period of 1 week. Platinum disk electrodes (3 × 10⁻³ cm²) set in soft glass were dipped in the solution for 10 min. The electrodes were then removed, shaken to remove the excess solution droplet, and dried in an oven at 130 °C for 30 min. Electrodes so prepared are referred to as electrode I. As shown below, the quantitative reproducibility of this dip-coating procedure as determined voltammetrically is usually obscured by the complexity of the electrochemistry. A few X-ray photoelectron spectra (X-ray PES) were obtained for electrodes which had not received any electrochemical treatment, but these are insufficient to provide any quantitative assessment. We have, therefore, reserved spectroscopic studies from this paper. In studies with other polymers² we have found