(3) At arbitrary fields (any β and γ), for both prolate ($\gamma > 0$) and oblate ($\gamma < 0$)

$$\frac{I_9}{I_8} = \frac{e^\gamma}{\gamma I_8} \sinh \beta - \frac{\beta}{2\gamma}$$

$$\frac{I_7}{I_8} = \frac{e^\gamma}{\gamma I_8}\left[\cosh \beta - \frac{\beta}{2\gamma} \sinh \beta\right] + \left(\frac{\beta}{2\gamma}\right)^2 - \frac{1}{2\gamma}$$

$$\frac{I_5}{I_8} = \left(1 - \frac{1}{\gamma}\right)\frac{I_9}{I_8} + \frac{\beta}{2\gamma}\left(1 - \frac{I_7}{I_8}\right),$$

$$\frac{I_3}{I_8} = \frac{\beta}{2\gamma^2}\frac{I_9}{I_8} + \frac{1}{2\gamma}\left(1 - \frac{\beta^2}{2\gamma}\right) + \left(1 - \frac{3}{2\gamma} + \frac{\beta^2}{4\gamma^2}\right)\frac{I_7}{I_8}$$

where I_8 is given by eq 23 for $\gamma > 0$ and by eq 24 for $\gamma < 0$

On the Shapes and Energetics of Polyatomic Molecules[1,2]

Gary W. Schnuelle[3] and Robert G. Parr*

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. *Received April 11, 1972*

Abstract: A model is presented for the prediction of shapes and energetics of the low-lying electronic states of small polyatomic molecules. Molecules are considered which have one or two central atoms and which involve coordination numbers two or three. The following assumptions are made. (1) *Simple valence bond structures are adequate to describe the bonding.* (2) *Structures with completed shells on terminal atoms are preferred. Between alternative such structures, the one for which all atoms are neutral is preferred.* (3) *Crude models of these localized structures can be used to determine molecular shapes with classical electrostatics.* (4) *The proper disposition of lone pairs on central atoms is obtained by using the crystal field theory to describe the interaction between them and the closed shells on terminal atoms.* The qualitative ideas and predictions largely conform with those of Pauling, Walsh, Gillespie, and others. Successful quantitative predictions are made of many bond angles and bending force constants for excited as well as ground states and several barriers to internal rotation. The use of an electrostatic model is justified from the polyatomic virial theorem, and a method of localizing canonical self-consistent-field molecular orbitals is proposed which brings conventional molecular orbital theory into coincidence with the model.

In the 1930's it became clear that the *number* of valence electrons determines the shapes of small polyatomic molecules.[4] In 1952, Walsh gave the first unified explanation of this essential chemical fact.[5] His arguments were a comprehensive modification, extension, and reinterpretation of the molecular orbital approach introduced by Mulliken for AB_2 molecules.[6] In addition to rationalizing the shapes of a great variety of molecules in their ground states, Walsh gave a detailed discussion of the spectra of the molecules and of their excited-state geometries. His work has enormously aided the interpretation and analysis of molecular electronic spectra; it is a triumph of the molecular orbital method.

Comprehensive discussions of geometry have also been given in terms of localized descriptions of the bonding. The valence-shell electron pair repulsion theory (VSEPR) gives a good description of the ground states of a great many molecules by focusing on the effects of repulsions between lone pair and bonding electrons.[4c,7] The classical valence bond theory (VB) concentrates on the nature of the hybridization at central atoms.[8] With both of these methods, the geometry of a molecule can be rationalized *if* an appropriate localized description is displayed. They both suffer from not providing a clear way to decide between alternative localized pictures. Also, neither method gives a satisfactory way of interpreting the observed electronic spectra or explaining the geometry in excited states.

Since we will be using concepts in our discussion which have been clearly stated in one or more of these earlier discussions, it is important to identify these at the outset. Our considerable indebtedness to earlier authors should then be clear throughout the rest of our analysis.

Both the VB and the VSEPR theories have demonstrated that *simple localized pictures are adequate to describe geometry.* In both theories, the role of lone pair electrons on central atoms is of paramount importance in fixing geometry. Walsh's MO discussion can be rigorously transformed into a localized picture in which central-atom lone pairs are emphasized. Indeed, Walsh gave a very explicit discussion of the bending process which is equivalent to that which we will give.[9] Walsh stated the assumptions underlying his

---

(1) Aided by research grants to The Johns Hopkins University from the National Science Foundation and the National Institutes of Health.

(2) Based on part of a thesis submitted by Gary W. Schnuelle in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The Johns Hopkins University, 1972.

(3) National Science Foundation Trainee, 1967–1971.

(4) (a) J. Cassie, *Nature (London)*, 131, 438 (1933); (b) W. G. Penney and G. B. Sutherland, *Proc. Roy. Soc., Ser. A*, 156, 654 (1936); (c) N. V. Sidgwick and H. M. Powell, *ibid.*, 176, 153 (1940).

(5) (a) A. D. Walsh, *J. Chem. Soc.*, 2260–2317 (1953); (b) A. D. Walsh, *Advan. Mol. Spectrosc., Proc. Int. Meet. Mol., 4th*, 159 (1962).

(6) R. S. Mulliken, *Rev. Mod. Phys.*, 14, 204 (1942).

(7) (a) J. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc., Ser. A*, 202, 166 (1950); (b) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, 11, 339 (1957); R. J. Gillespie, *J. Chem. Educ.*, 40, 259 (1963); R. J. Gillespie, *Angew. Chem.*, 6, 819 (1967); (c) A. W. Searcy, *J. Chem. Phys.*, 28, 1237 (1958); *ibid.*, 31, 1 (1959); A. E. Parsons and A. W. Searcy, *ibid.*, 30, 1635 (1959); (d) H. B. Thompson, *J. Amer. Chem. Soc.*, 93, 4609 (1971).

(8) (a) G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalogue Co., Inc., New York, N. Y., 1923; (b) I. Langmuir, *J. Amer. Chem. Soc.*, 41, 868 (1919); (c) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(9) Reference 5a, pp 2271–2272.

treatment in terms of delocalized orbitals, however, and our postulates are not a simple transformation of his.

That *classical electrostatic interactions are important* has been emphasized in the VSEPR approach, and simple classical models for determining geometry *via* this method have been given by Searcy[7c] and by Thompson.[7d] We will make extensive use of this idea.

Finally, it has only more recently been recognized that *closed shells on terminal atoms play an important role in the bending process.*[7c,10] A preliminary account of our own work which emphasizes this feature already has appeared.[10c]

Our discussion comprises a localized orbital model for determining geometry, capable of quantitative prediction. Localized descriptions have obvious advantages when they are appropriate. They are easy to apply to systems with low symmetry, and they are applicable to sections of very large systems. In our model, we are able to retain a picture of excited states and spectra which usually contains no less detail than that given by Walsh. The molecular orbital description is often the best starting point for understanding spectra, but there are many instances where it is helpful to retain the localized picture.[11] Our discussion maintains the simplicity of the VSEPR approach, in that the same effects are operative for a specific coordination number, no matter what the nature of the ligands. We will also be able to understand why the simplest molecular orbital approach fails in some cases. Our model can give quantitative predictions regarding molecular shapes, bending force constants, and even barriers to internal rotation.

Electrostatic Models for Molecular Shape

We assume that *crude classical models of the charge distributions will be adequate for discussion of molecular shapes.* Classical models may arise from different rigorous quantum mechanical treatments, and so it is important to give the specific form of the theory upon which the model is based. We do that first.

Our discussion derives from a version of the polyatomic virial theorem given by Nelander.[12] If the total Born–Oppenheimer energy is W, the total electronic kinetic energy T, and the total potential energy V, then

$$2T + V + \sum_i R_i(\partial W/\partial R_i) = 0 \text{ or}$$

$$W = {}^1\!/_2V - {}^1\!/_2\sum_i R_i(\partial W/\partial R_i) \quad (1)$$

The sums in eq 1 can run over *any* set of internuclear distances which, together with a set of angular coordinates, uniquely determine the structure. Thus we can let the sums be over bond lengths only, and the derivatives of W with respect to bond angles and torsional angles will not appear at all. As Nelander points out, this means that when bond lengths are at their equilibrium values for any set of angles, we have exactly the simplest form of the virial theorem

$$W = {}^1\!/_2V \quad (2)$$

Equation 2 is our justification for using a model which includes the potential energy only. If we locate the minimum in the total potential energy, along a path where bond lengths are optimized, eq 2 shows that we will have found the minimum in the total energy as well.

It is important to realize that this formula includes all potential interactions, including nuclear–nuclear repulsions. This is not the same picture as is generated from the Hellmann–Feynman theorem.[13] Discussions concerning the need to use very accurate charge densities in Hellmann–Feynman approaches[14] do not apply to our model.

Since we wish to use classical models for the electronic potential interactions, we must choose a description of the charge distribution which minimizes the exchange terms appearing in the total potential energy. This leads us to select an appropriate localized description of the bonding in which the orbitals involved nearly obey zero differential overlap.[15]

A Localized Description of Bonding

We assume that *one simple valence bond structure will suffice to describe bonding,* without including resonance with structures of different ionicity. Resonance between geometrically equivalent structures may be needed, of course. This means that the structure we write will usually involve only neutral atoms, with ionic effects regarded as implicit in the inherent polarities of the individual bonds.

One bond is always drawn to hydrogen and at least one bond to all other atoms. Only the valence orbitals of the same principal quantum number are employed. Thus no more than four electron pairs are assigned to second-row atoms, while more than this can be assigned to third-row central atoms to avoid extremely ionic structures.

We must next give a procedure for selecting the appropriate valence bond structure. In particular, we need to determine the location of the lone pairs. We assume that *those structures in which octets are filled on terminal atoms are preferred.* This will produce as many bonds as possible between central atoms and terminal atoms, and a maximum number of electrons shared between them. It will also have the effect of preferentially placing lone pairs on terminal atoms.

In most recent discussions of geometry, it is evident that the presence of lone pair electrons on central atoms is the factor responsible for distortions from the structures of highest symmetry. Any reasonable model of the charge distributions for molecules with no lone pairs on central atoms will have a minimum energy in the most symmetrical conformation. By a mechanism we will discuss below in more detail, a central-atom lone pair electron can lead to a distortion. We will see that this picture, together with our rules for choosing a valence bond structure, is sufficient to generate all the "critical numbers" of Walsh's discussion.[5] These are the maximum number of valence electrons which allow the molecule to remain in its most symmetric configuration. Molecules with less

---

[10] (a) R. D. Gillard, *Rev. Port. Quim.*, 11, 70 (1969); (b) Y. Takahata, Thesis, The Johns Hopkins University, Baltimore, 1970; (c) Y. Takahata, G. Schnuelle, and R. G. Parr, *J. Amer. Chem. Soc.*, **93**, 734 (1971).

[11] See p 2273 of ref 5a, where the difference between the lowest transitions in N_2O and CO_2 is interpreted this way.

[12] B. Nelander, *J. Chem. Phys.*, **51**, 469 (1970).

[13] H. Hellmann, "Einführung in die Quantenchemie," Franz Deuticke and Co., Leipzig, 1937; R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939).

[14] L. Salem and M. Alexander, *J. Chem. Phys.*, **39**, 2994 (1963); R. F. W. Bader, *Can. J. Chem.*, **86**, 5070 (1964).

[15] R. G. Parr, *J. Chem. Phys.*, 20, 1499 (1952).

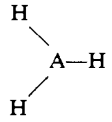
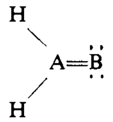
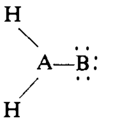
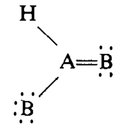
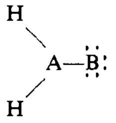
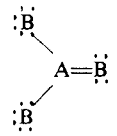
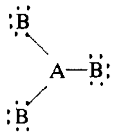
than the critical numbers of valence electrons generally take the most symmetric configurations.

To determine the maximum number of electrons possible to accommodate without placing lone pairs on central atoms, we should display those structures which have completed octets on terminal atoms. We can often find more than one structure which satisfies this requirement.

For molecules containing only one central atom, the various structures all lead to the same critical numbers. These are seen in Table I. For a particular molecule, we choose that structure which makes the constituent atoms most nearly neutral. For example, in the series HBeF, HBO, and HCN, all with ten electrons and therefore predicted to be linear, we select these

HBeF: HB=O HC≡N:

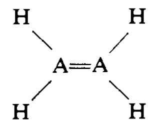
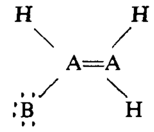
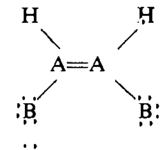
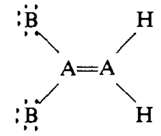
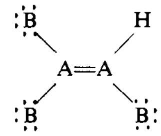
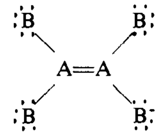
Table I. Critical Numbers from Valence Bond Structures for Molecules with One Central Atom

Molecular type	Structures[a]	Critical no.[b]
AH_2	H—A—H	4
HAB	H—A≡B: H—A=B H—A—B:	10
BAB	:B—A≡B: B=A=B :B—A—B:	16
AH_3		6
H_2AB	 	12
HAB_2	 	18
AB_3	 	24

[a] B may represent different atoms in the same molecule. [b] Molecules with more than these numbers of valence electrons distort to lower symmetries.

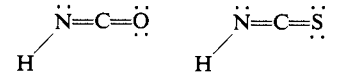
For molecules with more than one central atom, the various possibilities can lead to different critical numbers. In Table II we display only those which generate the maximum critical numbers. For some molecules, selecting a structure which is most nearly neutral at all atoms will lead to a geometry of lowered symmetry, even though the "maximum" critical number of valence electrons has not been reached.

Table II. *Maximum* Critical Numbers from Valence Bond Structures for Molecules with Two Central Atoms

Molecular type	Structures[a]	Max critical no.[b]
A_2H_2	H—A≡A—H	10
HAAB	H—A≡A—B:	16
BAAB	:B—A≡A—B:	22
H_2AAH_2		12
$HBAAH_2$		18
HBAABH		24
B_2AAH_2		24
B_2AABH		30
B_2AAB_2		36

[a] A's and B's may represent different atoms in the same molecule. [b] Critical numbers will be less when above structures are ionic. For the linear examples, one or two electrons over critical number gives double-bonded planar structure; three or four electrons over give skewed nonplanar structure.

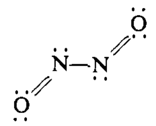
For example, the isocyanate and thiocyanate molecules should prefer the structures



and be bent at nitrogen. The alternative forms

$H{-}\overset{-}{N}{\equiv}C{-}O{:}^{-}$ $H{-}\overset{-}{N}{\equiv}C{-}S{:}^{-}$

are rejected because they have completed shells on the terminal atoms; they require a charge on N and O (or S). Similarly, the N_2O_2 molecule is described by the structure



and is bent at both nitrogen atoms.[16] The linear ionic structure

$^{-}{:}O{-}\overset{+}{N}{\equiv}\overset{+}{N}{-}O{:}^{-}$

is rejected. Gimarc discusses this example on the basis of extended Hückel calculations.[17]

It is important to note the order in which our selection of structures is performed. We *first* identify

---

(16) W. G. Fateley, H. A. Bent, and B. Crawford, *J. Chem. Phys.*, 31, 204 (1959); W. A. Guillory and C. E. Hunter, *ibid.*, 50, 3516 (1969).

(17) B. Gimarc, *J. Amer. Chem. Soc.*, 92, 266 (1970); *ibid.*, 93, 593 (1971); *ibid.*, 93, 815 (1971).

these structures which have closed shells on terminal atoms, and *then* we choose among these on the basis of the electroneutrality principle. Other things being equal, we follow the usual practice of VB theory of forming the maximum number of bonds.

We note that our critical numbers completely agree with Walsh's in those cases where comparison is possible.[18]

We can now also set a lower limit on the number of electrons that can be handled by the most simple discussion. If we do not have enough electrons to form at least one pair bond to each ligand, then a modification of our treatment will *certainly* have to be made. For example, if we have less than four electrons for AH_2 molecules, or less than six electrons for AH_3, then the bonding is obviously of a different nature. It is precisely for these cases that Gimarc found exceptions to Walsh's original rules.[17]

Closed Shells on Terminal Atoms

Since we imagine the critical numbers as arising from structures which have closed shells on the terminal atoms, these structures justify generating the Walsh critical numbers for molecules with one central atom by simply determining the number of valence electrons needed to fill all terminal octets. This was observed independently by Gillard[10a] and Takahata,[10b] and our preliminary account of this work made use of this idea.[10c]

The requirement that terminal atoms be assigned electrons ahead of central atoms suggests that terminal atoms will usually have the highest electronegativity in a molecule. Although this does not apply to hydrides, it is a remarkably correct generalization for other molecules. Walsh noted the applicability of the rule to the AB_2 series.[19] For choosing between isomeric structures, Pauling and Hendricks gave a related explanation in terms of "kernel repulsions" before the concept of electronegativity had been introduced.[20]

This rule explains, for example, the change in structure observed from ONF to NSF (electronegativities in parentheses)

$$\begin{array}{ccc} (3.4)(3.0)(4.0) & \qquad & (3.0)(2.6)(4.0) \\ \mathrm{O{-}N{-}F} & & \mathrm{N{-}S{-}F} \end{array}$$

It also suggests why the compounds N_2O_2 and N_2S_2 have different structures. The structure of N_2O_2 has already been mentioned above. To describe N_2S_2 in the same way would mean putting the more electronegative atom (nitrogen) in a central position. Placing the sulfur atoms in the center would result in a charged species when the closed shells on nitrogen are formed, so that this is also unfavorable. In fact, both these alternatives are abandoned and N_2S_2 exists as a ring of four atoms.[21]

Some violations are understood by noting that an alternative structure, which follows the rule, is either ionic or requires expansion of the octet on the central atom. Examples of this are HOBr, HCP, and ONBr. In other cases where exceptions to the rule exist, usually both forms are known. Thus both ClOCl and OClO exist, as do CCN and CNC.

Application of Crystal Field Theory

We now turn to a unique aspect of our model, the consideration of the disposition of lone pairs on central atoms for those cases in which the critical number of valence electrons is exceeded. Treated as a unit, we presume that the bonding electrons, lone pairs, and nuclei for terminal atoms can be thought of simply as appropriate net negative charges placed roughly at the bond distance. As a first approximation, *we consider the lone pairs on the central atoms as formed in such a way as to minimize their interaction with these net negative charges.* The procedure is analogous to that followed in the crystal field theory.[22]

We consider a molecule in its most symmetrical configuration and discuss the change in the total potential energy as a distortion to lower symmetry occurs. We attempt to form a hybrid on the central atom localized in a region of space away from that into which the terminal atoms are moving. Placing the lone pair electrons in such a hybrid will result in decreased repulsions between the lone pairs and terminal atoms and therefore provides a driving force for the distortion. This acts in competition with the repulsions between the terminal closed shells, which always are minimized in the most symmetrical conformation.

Alternatively, we can say that the hybridization at the central atom results in an atomic finite dipole, whose interaction with terminal-atom closed shells is minimized in a distorted conformation. Note that the increase in energy from terminal repulsions increases only in second order with the distortion, while the decrease in energy due to the interaction with the dipole is a first-order effect. Thus a minimum in the total repulsion energy is realized at some nonzero value of the distortion.

Coordination Number Two. We now give a detailed description of the lone pairs in this picture. Consider first a central atom with a coordination number of two. The most symmetrical conformation is a linear arrangement, and the only possible distortion is to a bent structure. Let the y axis be the symmetry axis in the linear case and consider the bend to occur in the yz plane toward positive z. The most favorable hybrid is a digonal sp_z hybrid directed toward negative z, which we label sp_z^-. A lone pair in the p_x orbital has the same energy throughout the bend, while one in the p_y orbital is of a much higher energy than either the p_x or the sp_z^+ hybrid. Since bond angles for these compounds are always greater than 90°, interactions with the p_y orbital are more unfavorable than with the sp_z^+ hybrid, and this determines their ordering. The designations "s" and "p" are *not* meant to imply pure central-atom atomic orbitals. Rather they are orbitals of s and p symmetry which have been orthogonalized to bonding orbitals, so that they are appropriate for a localized description of a lone pair. This means that the s and lowest two p orbitals in the linear conforma-

---

[18] See also P. J. Wheatley, *J. Chem. Soc.*, 4514 (1956), for the extension of Walsh's arguments to molecules of the type B_2AAB_2, H_2AAB_2, and H_2AAH_2.

[19] Reference 5a, p 2267.

[20] L. Pauling and S. B. Hendricks, *J. Amer. Chem. Soc.*, **48**, 641 (1926).

[21] J. R. W. Warn and D. Chapman, *Spectrochim. Acta*, 22, 1371 (1966).

[22] (a) H. Bethe, *Ann. Phys.* (Leipzig), 3, 133 (1929); (b) J. H. Van Vleck, *J. Chem. Phys.*, 3, 803, 807 (1935); (c) L. E. Orgel, "An Introduction to Transition-Metal Chemistry," Wiley, New York, N. Y., 1960.

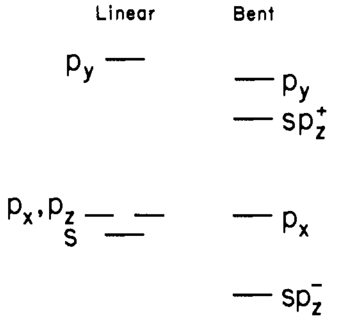


Figure 1. Lone pair orbitals on central atoms for two coordination. Bend in *yz* plane toward positive *z*. The s and p orbitals are *not* pure central-atom orbitals; see text. The notation sp_z^+ represents a digonal hybrid directed toward positive *z*.

tion may be nearly degenerate. A schematic correlation diagram is shown in Figure 1.

Considering the total repulsion energy, the distortion described here is formally a Renner, or second-order Jahn–Teller effect.[23] As the bend occurs, the near degeneracy in the linear conformation is lifted and two states arise depending on where the lone pair is placed. If it is in the hybrid, the total potential energy is initially lowered with the bend, while if it is in the p_x orbital, the total potential energy immediately rises due to the terminal closed shell repulsions.

We claim that Figure 1 contains the essence of the Walsh diagrams for all molecules considered here with coordination two, that is, HAH, HAB, HAAH, BAB, and BAAB. In one of these molecules, when the localized structure requires a single lone pair electron on a central atom, it is placed in the sp_z^- orbital, and a bend occurs. With two lone pair electrons, the sp_z^- hybrid is doubly occupied and the bend continues to a smaller equilibrium bond angle. With three or four lone pair electrons, the p_x orbital is filled, and there should be no change in the bond angle. This explains the remarkable constancy of the bond angle in the series $^1A_1$ CH_2 (102°), $^2A_1$ NH_2 (104°), and $^1A_1$ H_2O (105°).[24] Note also that the lowest triplet state of CH_2 would have one electron in the two lowest orbitals and should therefore be bent.[25] With five or six lone pair electrons, we must consider the possibility of using the orbitals sp_z^+ and p_y whose energy is above that of the p functions in the linear case. Since these orbitals are pointing toward the ligands, their interactions with them will be extremely unfavorable.

With only five lone pair electrons, the molecule should revert to near linearity to reduce the interaction with the sp_z^+ hybrid. Such molecules should be relatively unstable.

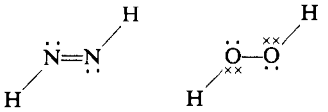
With six lone pair electrons, the repulsions are minimized in the linear conformation. The degeneracy present in the linear form *cannot* be removed by a distortion, because the *filled* s and two pure p orbitals are cylindrically symmetric regardless of the exact hybridization. The mechanism allowing a lowering of repulsions has been effectively blocked.

Assigning three lone pairs to the central atom and still imagining a pair bond to each terminal atom gives a total of five pairs on the central atom. Thus, for the AH_2 case, the bonding is better described as the resonance between the geometrically equivalent structures

$$^-H\ {:}\underset{\cdot\cdot}{\ddot{A}}{-}H \quad \text{and} \quad H{-}\underset{\cdot\cdot}{\ddot{A}}{:}\ H^-$$

The bonds are therefore expected to be very weak; no examples of this case are known. For the HAB types, the same kind of resonance is better for the AHB isomeric form, since the negative charge will be localized on an atom of higher electronegativity than hydrogen. Thus BHB^- molecules exist, and not HBB^-, where B is F, Cl, or Br.[26] Other examples of this case for AB_2 types are the negative trihalide ions, all linear. Very weak bonds with long bond distances are found in these molecules, as expected from the "no bond" resonance structures similar to the above.[27]

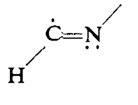
We will not consider all the examples of two coordination, but the HAAH molecules are particularly interesting. For acetylene we have exactly the critical number of electrons, ten, and the molecule is linear with the structure H—C≡C–H. The ground state of N_2H_2 is given by i and should be planar but bent. We



i ii

expect cis and trans isomers. With HOOH, the double bond must be broken, and we have ii where the X's represent electrons in the second orbital in Figure 1, that is, a pure p_x hybrid out of the plane of the trans conformation. Now there is no longer any multiple bond to hold the system planar. Furthermore, the repulsions between the two pure p_x pairs will be minimized when the dihedral HOOH angle is 90°. Finally, note that the cis–cis repulsions between the hydrogens and the electrons in the lone pair hybrids will give use to unfavorable interactions in *both* the cis and the trans forms. Thus the ground state should be skewed, with both cis and trans barriers to internal rotation, as observed. Walsh's molecular orbital diagram for HAAH molecules allows an equivalent interpretation.[5]

The case of intermediate compounds is of interest. The 11-electron molecule HCNH should have the structure



---

[23] (a) R. J. W. Bader, *Can. J. Chem.*, **40**, 1164 (1962); (b) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968); (c) R. G. Pearson, *Chem. Phys. Lett.*, **10**, 31 (1971); R. G. Pearson, *J. Chem. Phys.*, **52**, 2167 (1970); *ibid.*, **53**, 2986 (1970); R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

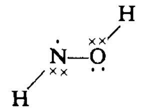
[24] G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1966.

[25] G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2277 (1971); E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yeager, *J. Amer. Chem. Soc.*, **92**, 7491 (1970); R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **53**, 1280 (1970); see also J. F. Harrison, *J. Amer. Chem. Soc.*, **93**, 4112 (1971).

[26] J. A. Ibers, *J. Chem. Phys.*, **40**, 402 (1964); J. C. Evans and G. Y. S. Lo, *J. Phys. Chem.*, **70**, 11 (1966); *ibid.*, **71**, 3697 (1967); *ibid.*, **73**, 448 (1969).

[27] R. W. G. Wyckoff, *J. Amer. Chem. Soc.*, **42**, 1100 (1920); R. C. L. Mooney, *Z. Kristallogr. Kristallgeometrie, Kristallphys. Kristallchem.*, **100**, 519 (1939); *ibid.*, **90**, 143 (1935); R. C. L. Mooney, *Phys. Rev.*, **47**, 807 (1935).

so that the bend at the nitrogen atom would be much larger than the bend at carbon. Cis and trans planar isomers should exist. The 13-electron molecule HNOH would be described as



The molecule should have bond angles near those in H_2O and NH_2 ($^2A_1$). There should be hindered rotation with a skewed conformation most stable and cis and trans barriers only slightly less than those in H_2O_2. Of course, both of these molecules would contain an unpaired electron and might be very unstable.

Coordination Number Three. Now consider the lone pairs for coordination number three. Here there are two kinds of distortion which can occur from the most stable planar conformation. The molecule may distort to a pyramidal structure, or it may bend entirely in the plane to a T-shaped form.

Let the z axis be out of the plane, through the central atom in the planar structure. Then a sp$_z$ hybrid in the negative z direction, sp$_z^-$, will have lower energy if the pyramidal distortion occurs toward positive z values. Hybrids in the x or y directions point toward the ligands and are thus not favorable. For a distortion to a T-shaped structure, a low-energy lone pair can be formed by a sp hybrid directed in the plane and out of the "top" of the T. If we let this be the x direction, then lone pair electrons in a p$_y$ hybrid would have high energy, while those in the pure p$_z$ hybrid out of the plane have constant energy throughout the bend. In this case the sp$_z^-$ hybrid points precisely in a bond direction, and therefore has the most unfavorable repulsions. The caution given earlier regarding the exact form of the s and p orbitals applies here as well. The complete diagram is given in Figure 2.

For one or two lone pair electrons, a distortion to the pyramidal structure is preferred, with the doubly occupied hybrid producing a smaller bond angle. With three or four electrons, the T-shaped structure should be realized, with the pure p$_z$ orbital occupied. The molecules CF_3, NF_3, and ClF_3 are examples with one, two, and four lone pair electrons, respectively.

The case of three coordination provides one classic exception to Walsh's rules: CH_3 is planar although it has a lone pair electron. However, even accurate SCF methods do not always predict planarity in this case.[28] We will return to this example later.

To indicate the power and the simplicity of our discussion, we consider finally the H_2AAH compounds. Gimarc has discussed these with a more extensive molecular orbital treatment,[17] and gives the same predictions as we do for the cases of 10 to 14 electrons. The valence bond structures and the predicted shapes are given in Table III. The 15- and 16-electron molecules probably do not exist since the AH bond lengths would not be long enough to allow room for so many pairs about the A atom. However, the corresponding B_2AAH compound may exist; for 28 valence electrons it would have a structure like that described in the table. A possibility is F_2ClOH.

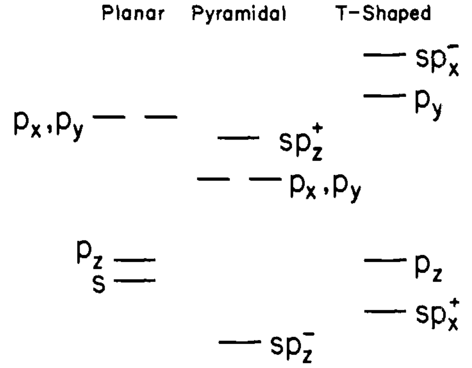


Figure 2. Lone pair orbitals on central atoms for three coordination. Distortion to pyramidal structure occurs symmetrically about z axis toward positive z. Planar bend to T-shape in xy plane, with x axis directed out of the top of the T.

Excited States

In our picture electronic transitions may arise in several ways. There may be various possibilities for assigning the central-atom lone pair electrons to the lower-lying orbitals. This is sufficient to explain the existence of the lowest observed states of the first-row hydrides. The appropriate descriptions are indicated in Table IV. The observed bond angles correlate nicely with the number of lone pair electrons in the sp$_z^-$ hybrid of Figure 1. This same diagram can be used to discuss the low-lying states of all molecules with two coordination.

Other excited states arise from the promotion of electrons from a bond to locations on central atoms. Since the lowest available hybrid on the central atom will be one which leads to a distortion, this gives a clear picture of how an electronic excitation leads to a change of shape.[5] That changes of shape on excitation are so common is also clear: molecules with exactly the magic number of electrons are unusually stable (and hence common) since they involve completed shells on all the terminal atoms.

One well-known example is the acetylene molecule. The first excited state corresponds to the breaking of one of the triple bonds, with an electron reorganization leaving a lone pair electron localized at each carbon, $H{-}\dot{C}{=}\underset{\cdot}{C}{-}H$. These electrons must go into the sp$_z^-$ orbital shown in Figure 1, which has the lowest energy when the CCH segment is bent. So the first excited state is bent, although the molecule is still held planar by the remaining double bond.

Transitions to the highest orbitals in Figures 1 and 2 should result in very unstable states, with large changes in shape required to minimize the unfavorable interactions of electrons in these orbitals. Transitions to Rydberg levels are often preferred instead, and the geometry is determined mainly by the remaining electrons in the lower orbitals.[5b]

Note that the excited states are described in as natural a way as the ground states are described. No modification of the model is necessary.

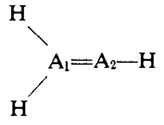
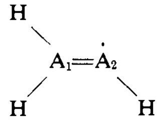
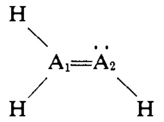
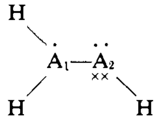
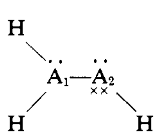
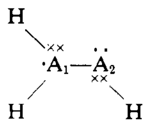
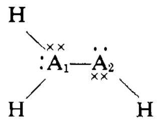
Quantitative Results

So far our discussion has been restricted to qualitative statements concerning bond angles. We now show that quantitative results can be obtained using precisely the same model. Our earlier communication contained some of these results.[10c]

---

[28] S. Y. Chang, E. R. Davidson, and G. Vincow, *J. Chem. Phys.*, **52**, 5597 (1970).

Table III. Shapes of H_2AAH from Valence Bond Structures

No. of valence electrons	Structure	Predicted shape[a]	Example
10		Planar, C_{2v}	H_2CCH^+ [b]
11		Planar, bent at A_2	H_2CCH[c]
12		Planar, more bend at A_2	H_2CNH[d]
13		Pyramidal at A_1, bend at A_2 similar to 12 electron case, restricted rotation about A_1A_2 bond	H_2COH[e]
14		Same as 13 electron case, but more pyramidal at A_1	H_2NOH[f]
15		Planar T-shape at A_1, restricted rotation about A_1A_2 bond	*g*
16		Same as 15 electron case, but more T-shaped at A_1	*g*

[a] Gimarc gives similar predictions for 10 to 14 electrons.[17] x's are electrons in pure p orbitals. [b] D. R. Kelsey and R.G. Bergman, *J. Amer. Chem. Soc.*, **92**, 228 (1970), give indirect evidence favoring the planar form. [c] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964); F. J. Adrian and M. Karplus, *ibid.*, **41**, 56 (1964); G. A. Peterson and A. D. McLachlan, *ibid.*, **45**, 628 (1966); T. Yonezawa, H. Nakatsuji, and H. Kato, *Bull. Chem. Soc. Jap.*, **40**, 2211 (1967). [d] D. E. Milligan, *J. Chem. Phys.*, **35**, 1491 (1961); C. B. Moore, G. C. Pimentel, and T. D. Goldfarb, *ibid.*, **43**, 63 (1965); J. M. Lehn and B. Mimseh, *Theor. Chim. Acta*, **12**, 91 (1968). [e] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963); P. Ros, *J. Chem. Phys.*, **49**, 4902 (1968). [f] L. Pedersen and K. Morokuma, *ibid.*, **46**, 3941 (1967); W. H. Fink, D. C. Pan, and L. C. Allen, *ibid.*, **47**, 895 (1967). [g] See text for a discussion of these cases.

Table IV. Low-Lying States of AH_2 Molecules

Molecule	Lone pair electrons	Orbital description[a,b]	
BH_2	1	$^2\Pi(180)\ p_x$	$^2A_1(131)\ sp_z^-$
CH_2	2	$^1A_1\ (104)\ (sp_z^-)^2$	$^1B_1(140)\ (sp_z^-)(p_x)$
		$^1A_1(180)\ (p_x)^2$	$^3B_1(136)\ (sp_z^-)(p_x)$
NH_2	3	$^2B_1(103)\ (sp_z^-)^2(p_x)$	$^2A_1(144)\ (sp_z^-)(p_x)^2$
OH_2	4	$^1A_1(105)\ (sp_z^-)^2(p_x)^2$	

[a] Experimental angles (deg) in parentheses, mainly from ref 24. Note the correlation between bond angle and occupation of the sp_z^- orbital. [b] Orbitals used are described in the text and Figure 1. Note that the correct symmetry of the states can be inferred from the localized orbital description.

Bond Angles. To model the closed shells on terminal atoms, we imagine all the bonding and lone pair electrons on each terminal nucleus to yield a net negative integral point charge located precisely at the terminal nucleus. For the sp lone pair hybrids, we place point charges at the center of charge of analytical sp hybrids formed from Slater-type orbitals. We use the Slater exponents for the positively charged central atoms remaining after all the bonding electrons have been assigned to the terminal atoms. Experimental bond lengths or suitable estimates using ionic radii[8c] are employed and are held constant as the angles are varied to locate the minimum electrostatic energy. The predictions are quite insensitive to the exact values of the bond lengths. This procedure is not the same as that envisioned in producing eq 2, in that the bond lengths are not at their equilibrium values for all bond angles. We assume that the model used will correctly describe the angular variation of potential energy along the path where $W = {}^1/_2V$ exactly.

Results are given in Table V for triatomics, and in Table VI for tetratomics. We emphasize that there are no adjustable parameters in this treatment. The calculations are no more difficult for excited states than they are for ground states. Notice that even where there are large deviations from the experimental results, the trends are well reproduced.

Table V. Bond Angles (deg) for Triatomic Molecules HAB, AH_2, and AB_2

Molecule[a]	Exptl[b]	Calcd[c]	Molecule[a]	Exptl[b]	Calcd[c]
BH_2	131	118	OCl_2	111	110
CH_2 $^1A_1$	102[d]	100	SiF_2	101	99
$^3B_1$	136[d]	120	SO_2 $^1A_1$	120	120
$^1B_1$	140[d]	119	$^3B_1$	126	140
NH_2 $^2B_1$	103	101	ClO_2	118	122
$^2A_1$	144	120	ClO_2^-	118	110
NH_2^-	105[e]	100	HCF $^1A'$	102[h]	101
OH_2	105	102	$^1A''$	127	120
AlH_2	119	117	HCO	120	131
PH_2 $^2B_1$	92	99	HCCl	103	101
$^2A_1$	123	118	HNO $^1A'$	114[i]	113
SH_2	92	99	$^1A''$	116	132
CF_2 $^1A_1$	105[f]	102	ONF	110	119
$^3B_1$		122	ClNO	116[g]	125
$^1B_1$	122[f]	122	OOH	108[j]	113
NO_2	134	144	HOCl	113[g]	103
NF_2	104	105	HSiCl $^1A'$	103	99
O_3	117	128	$^3A''$	116	118
OF_2	103[g]	107	HPO	105	110
			SSO	118	122

[a] Ground states unless otherwise indicated. [b] Experimental data from ref 24 unless otherwise indicated. [c] Calculated from point charge model described in the text. [d] Reference 25. [e] J. W. Nibler and G. C. Pimentel, *Spectrochim. Acta*, 21, 877 (1965). [f] C. W. Mathews, *Can. J. Phys.*, **45**, 2355 (1967); for $^1A_1$ see: F. X. Powell and D. R. Lide, *J. Chem. Phys.*, **45**, 1067 (1966). [g] L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11, M67 (1958). [h] A. J. Merer and D. N. Travis, *Can. J. Phys.*, **44**, 1541 (1966). [i] J. L. Bancroft, *et al.*, *ibid.*, **40**, 322 (1962). [j] T. T. Paukert and H. S. Johnson, University of California Radiation Laboratory Report No. UCRL-19109, Nov. 1969, quoted by D. H. Liskow, H. F. Schaefer, III, and C. F. Bender, *J. Amer. Chem. Soc.*, 93, 6734 (1971).

Bending Force Constants. We may differentiate eq 1 twice to obtain

$$(\partial^2W/\partial\theta^2) = {}^1/_2(\partial^2V/\partial\theta^2) - {}^1/_2\sum_i R_i(\partial^3W/\partial\theta^2\partial R_i) \quad (3)$$

Table VI. Bond Angles (deg) for Tetratomic Molecules, AB_3

Molecule[a]	Exptl	Calcd[b]	Molecule[a]	Exptl	Calcd[b]
CH_3	120[c]	110	PI_3	100[d]	100
NH_3	107[c]	101	ClO_3	112[c]	116
PH_3	93[d]	97	NO_3^{2-}	116[e]	117
NF_3	102[d]	104	PO_3^{2-}	110[e]	115
PF_3	102[d]	98	SO_3^-	111[e]	116
PCl_3	100[d]	99	SO_3^{2-}	107[f]	109
PBr_3	101[d]	99	ClO_3^-	109[g]	110

[a] All ground states. [b] Calculated from point charge models described in text. [c] Reference 24. Doubt about the geometry of CH_3 remains. [d] S. Mizushima and T. Shimanouchi, *Annu. Rev. Phys. Chem.*, 7, 445 (1956). [e] P. W. Atkins and M. C. R. Symons, "The Structures of Inorganic Radicals," Elsevier, Amsterdam, 1967. Angles determined from esr spectra. [f] R. W. G. Wyckoff, "Crystal Structures," Interscience, New York, N. Y., 1951. [g] W. H. Zachariasen, *Z. Kristallogr. Kristallgeometrie, Kristallphys. Kristallchem.*, **71**, 517 (1929).

Simons has suggested the neglect of the mixed partial derivatives in eq 3 and has used the resulting purely potential energy formula to obtain force constants, although with a classical model different from that given here.[29] We use the same approximation, so that

$$k_{\theta\theta} = (1/R_e^2)(\partial^2 W/\partial\theta^2) = (1/2R_e^2)(\partial^2 V/\partial\theta^2) \qquad (4)$$

We use exactly the same classical model that we employed to calculate bond angles. Results are given in Table VII.

Table VII. Bending Force Constants for Triatomic Molecules AH_2 and AB_2

Molecule[a]	Exptl[b]	Calcd[c]	Molecule[a]	Exptl[b]	Calcd[c]
H_2O	0.762	0.81	NF_2	1.076	0.24
H_2S	0.429	0.45	OF_2	0.719	0.20
CO_2	0.583	0.37	O_3	0.816	0.63
CS_2	0.237	0.15	SO_2	0.820	0.76
CF_2	1.396	0.31	BO_2	0.30	0.29
SiF_2	0.440	0.31	NO_2	1.137	0.56
			ClO_2	0.626	0.62

[a] Ground states. [b] Units are mdyn/Å. Data from ref 29. [c] Calculated from eq 4, using point charge model, as described in text.

Except for the fluorides and NO_2, the results are surprisingly good. The fluorides are known to have unusually high values for the interaction force constants,[29] so we should expect the approximation leading to eq 4 to be worst here. Again, calculations could be done for excited states with no increase in difficulty.

Instead of neglecting the interaction terms, we could employ eq 3 to generate a sum rule for the force constants.

Barriers to Internal Rotation. If we assume that bond lengths are not changed significantly during internal rotation, we can use our model to calculate the height of a barrier from eq 2. We will consider the application to C_2H_6 and H_2O_2.

We first find the bond angles by treating each end of a molecule independently of the other. That is, we find the CCH angles in ethane by treating C_2H_6 as FCH_3 and the OOH angles in hydrogen peroxide by treating H_2O_2 as FOH. These angles are fixed, and we then vary only the dihedral angles.

For ethane the model has negative point charges at each H location; the calculated barrier is 2.6 kcal/mol *vs.* the experimental value 2.9 kcal/mol.[30] If we use the experimental CCH angle, we obtain 2.4 kcal/mol.

For H_2O_2, we have negative point charges at the H positions, and sp hybrid charges projecting at each oxygen. In addition, we place a charge of −1 in each lobe of the filled pure p orbital on the oxygens, located at the calculated center of charge for the lobe. The experimental data are the following: $\sphericalangle$ OOH = 94.8, $\sphericalangle$ HOOH = 111.5°; cis barrier = 7.0, trans barrier = 1.0 kcal/mol.[31] We find the following: $\sphericalangle$ OOH = 103, $\sphericalangle$ HOOH = 102°; cis barrier = 5.6, trans barrier = 1.8 kcal/mol. If we use the experimental $\sphericalangle$ OOH = 94.8°, we obtain $\sphericalangle$ HOOH = 120°, cis barrier = 11 kcal/mol, and trans barrier = 0.7 kcal/mol. Veillard has performed an extensive SCF calculation which gives cis and trans barriers of 10.9 and 0.6 kcal/mol, respectively, and a dihedral angle of 120°, while most other *ab initio* calculations on H_2O_2 give essentially no trans barrier at all.[32] Earlier models which emphasized electrostatic interactions have correctly predicted a trans barrier.[33]

Justification from Molecular Orbital Theory

Consider a molecule AB_2 of the kind we have been discussing, which has two electrons in a central atom lone pair orbital F and an even number of other electrons in other orbitals i. Using eq 2 and the Hartree–Fock formula for potential energy, we will have

$$2W = \Big[V_{nn} + 2\sum_{i \neq F} V_i + 2V_F^0 + J_{FF} + \sum_{i,j \neq F}(2J_{ij} - K_{ij})\Big] + \Big[2V_F' + \sum_{i \neq F}(4J_{iF} - 2K_{iF})\Big] \qquad (5)$$

where V_{nn} is the nuclear–nuclear repulsion energy, and V_i and V_F are orbital-core potential energy interactions, with V_F^0 the interaction of F with core A, V_F' the interaction of F with the cores B. The J's and K's have their usual meaning. Nonvalence electrons are incorporated in the cores.

Consider the behavior of the bracketed terms *along the path where 2W = V exactly*, so that eq 5 always holds. Our scheme requires that, to within an additive constant on this path, the first bracketed term is estimable as an end–end octet–octet interaction. Namely, it requires that

$$V_{nn} + 2\sum_{i \neq F} V_i + 2V_F^0 + \sum_{i,j \neq F}(2J_{ij} - K_{ij}) + J_{FF} \approx \frac{(8 - Z_B)(8 - Z_B)}{R_{BB}} + \text{constant} \qquad (6)$$

The correlation diagram of Figure 1 describes the second bracketed term, again to within an additive constant.

Our numerical results show that eq 6 is reasonably accurate. And that this must be so becomes highly plausible when one realizes that *one may require the validity (or approximate validity) of eq 6 as a criterion for determining the localized orbitals in the Hartree–Fock description.* This is a point of much interest.

---

(29) G. Simons, *J. Chem. Phys.*, **56**, 4310 (1972).

(30) D. R. Lide, *ibid.*, **29**, 1426 (1958).

(31) R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *ibid.*, **42**, 1931 (1965).

(32) A. Veillard, *Theor. Chim. Acta*, **18**, 21 (1970).

(33) J. P. Lowe and R. G. Parr, *J. Chem. Phys.*, **43**, 2565 (1965).

Discussion

As we have said, our model has many features in common with the molecular orbital, the VSEPR, and the valence bond theories. Indeed, we believe that we have retained the best features of all three pictures. However, our method is the only one of which we are aware that allows a simple quantitative calculation of bond angles and force constants for ground and excited states.

There are no adjustable parameters in our calculations. Searcy's success with an empirical model[7c] gives us reason to be optimistic that introducing a single parameter to empirically monitor one feature of our model may dramatically improve the results.

We should note that a similar discussion can certainly be given for coordination numbers of 4, 5, 6, etc. A direct extension of our scheme, without the use of d orbitals, may in fact suffice. For these molecules the kind of arguments we have used are routinely employed in the discussion of the spectra of transition metal complexes with the crystal field theory.[22] Ordinarily, the geometry is assumed to be known, and the interaction with the central-atom orbitals is used to generate spectral information. Our use of this type of discussion for determining geometry suggests that it may also yield quantitative structural information for transition metal complexes. Alternatively, we may hope that diagrams of hybrid levels will be useful in a quantitative way for spectral predictions. Walsh has given some discussion to show that the corresponding parts of the molecular orbital diagrams are of quantitative use in this regard.[5b]

We have concentrated our discussion on bond angles and ignored bond lengths. Certainly many of the structures we display are inappropriate for estimating bond lengths in the usual way from valence bond structures.[8c] This does not mean that the structures are unreasonable, only that the usual methods of assigning fixed values to bonds between the same atoms cannot be employed within our framework. To get reasonable correlations with bond lengths with our scheme, the influence of the neighboring atoms on the polarity of a bond would have to be included in the discussion. Walsh in fact has already shown that in many cases this concept of bond polarity can be substituted for the consideration of resonance among ionic structures.[34]

In those cases where nonhydrogenic atoms of very low electronegativity occupy terminal positions, the structures we give may seem quite severe. For example, Li_2O and LiOH are correctly predicted to be linear with the structures $^{-}\text{Li}{=}\text{O}^{2+}{=}\text{Li}^{-}$ and $\text{Li}^{2-}{\equiv}\text{O}^{+2}{-}\text{H}$. In these cases, the bonds are extremely polar, and composed almost entirely of the oxygen valence atomic orbitals, so that there is not in fact a net migration of charges to the terminal atoms.[35] Similarly, the highly charged models which we have employed are *not* expected to give reasonable values for dipole moments.

One effect which we have neglected is the influence of the sp promotion energy in forming the lone pair hybrids. If the s and p functions are not strictly degenerate, placing an electron in an sp hybrid instead of a pure s orbital results in an energy loss which is not included in our model. Explanations for the apparently anomalous behavior of CH_3 have been offered in terms of this promotion requirement.[36]

The elucidation of Walsh's molecular orbital approach on the basis of more sophisticated SCF methods is far from complete, although much progress has been made.[17,23a,37] Other important discussions of quite different character have been given,[38] but there has been little or no work of a more theoretical nature directly relating to the valence bond approach. Since our model is so closely connected with classical valence bond structures, we hope it will stimulate more investigations of Walsh's rules along these lines. In this connection we should note that our formulation avoids the two main stumbling blocks of molecular orbital models: it does not regard the total energy as a sum of one-electron orbital energies, and the nuclear–nuclear repulsion terms are included throughout the discussion rather than ignored or added in at the end.

One may inquire whether there is something fundamental about the choice of sp hybridization for our crystal field model. The answer to this question requires an analysis of actual Hartree–Fock wave functions along the lines outlined in Justification from Molecular Orbital Theory. An accurate analysis of the contributions to the things we label "sp" and so on is going to involve all the functions on the central *and* terminal atoms of the correct symmetry; in this sense our scheme includes more than any hybrid scheme at the central atom can ever do. It is the *symmetry* of the orbitals we are constructing, rather than the detailed composition to them, that is important.

Similarly, our use of point-charge interactions going as a reciprocal distance is not an essential part of our model. One could use a weaker interaction, going as the reciprocal of some power of the distance, and the results would not be much affected.

The quintessence of the Walsh diagrams and the Walsh numbers, we have argued, is contained in the central-atom lone pair orbital energy diagrams of Figures 1 and 2. Calculations of bond angles can be made by elementary application of crystal field theory. The structural postulates which lead to these diagrams, and to this method of calculation, are simple and clear.

Acknowledgments. We wish to thank Professors Michael J. S. Dewar and Jeremy I. Musher for valuable comments. Professor Dewar pointed out that most of Walsh's orbital diagram discussions may be summarized by saying that "placing electrons in antibonding orbitals is energetically unfavorable and leads to distortions." This encouraged us to seek a simple way of selecting the correct valence bond structures from a

---

(34) A. D. Walsh, *Trans. Faraday Soc.*, **43**, 158 (1947).

(35) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **45**, 3682 (1966).

(36) J. H. Current and J. K. Burdett, *J. Phys. Chem.*, 73, 3605 (1969); L. Pauling, *J. Chem. Phys.*, **51**, 2768 (1969).

(37) For example, C. A. Coulson and A. H. Nielsen, *Discuss. Faraday Soc.*, **35**, 71 (1963); D. Peters, *Trans. Faraday Soc.*, **62**, 1353 (1966); C. A. Coulson and B. M. Deb, *Int. J. Quantum Chem.*, **5**, 411 (1971); and many references to *ab initio* MO analyses by L. C. Allen and coworkers given in: O. Sinanoglu and K. B. Wiberg, "Sigma Molecular Orbital Theory," Yale University Press, New Haven, Conn., 1970, Chapter IV. Also see L. C. Allen, *Theoret. Chim. Acta*, **24**, 117 (1972).

(38) W. A. Bingel, "Molecular Orbitals in Chemistry, Physics and Biology," P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 191; C. E. Wulfman, *J. Chem. Phys.*, **31**, 381 (1959); *ibid.*, **33**, 1567 (1960); K. H. Hansen and E. Frenkel, *Theor. Chim. Acta*, 20, 2 (1971); H. A. Bent, *Fortschr. Chem. Forsch.*, **14**, 1 (1970).

postulate about the localized description. Professor Musher called our attention to the connection between our closed shell discussion and the crystal field theory. Professors Charles A. Coulson, Benjamin M. Gimarc, and H. Bradford Thompson also have furnished helpful suggestions.

A New Model of Liquid Water

Oleh Weres[1] **and Stuart A. Rice***

Contribution from the Department of Chemistry and The James Franck Institute, University of Chicago, Chicago, Illinois 60637. *Received April 5, 1972*

Abstract: A new model for liquid water is developed upon the basis of the intermolecular potential function proposed by Ben-Naim and Stillinger and some simple and clearly defined structural assumptions. It is primarily a model of the cell theory of fluids tradition, but it also includes a fairly well-developed treatment of the structural entropy contributions. It is demonstrated that the original Ben-Naim–Stillinger potential contains a rather serious error in its curvature in the rotational degrees of freedom and that the quantum effects in water are much too large to safely ignore. In the model proposed properties are expressed as functions of the concentrations of the various varieties of cells dealt with, and their equilibrium concentrations are obtained by minimizing the free energy. When proper account is taken of the potential function insufficiency, and of quantum effects, the calculated values of the thermodynamic properties and density are in fairly good agreement with experiment. Most of the discrepancy between calculation and experiment is easily explained, at least qualitatively, by the known defects of the cell model.

I. Introduction

The theoretical study of all but the simplest liquids has been and remains extremely difficult. The complexity of the intermolecular interactions has as yet in most cases precluded the development of realistic and tractable model intermolecular potential functions. Also, the existence of five or more degrees of freedom per molecule has made extensive numerical calculations nearly impossible. Water, because it is the simplest of the "nonsimple" liquids, and because of its importance, may be considered to be a test case for such studies.

Until recently theoretical structural and statistical mechanical studies of water have been limited to descriptions in terms of rather simply conceived structural entities whose interrelations and properties could be easily dealt with. All of the treatments of this school suffer from severe structural underdefinition, or excessive reliance on adjustable parameters, or both. Some of them have the additional quality of grossly disagreeing with available experimental data.

One group of simple models postulates the existence of microphases within the liquid. Usually the various microphases are supposed to have markedly different densities. Those models which require the existence of such regions of different densities are invalidated by the results of X-ray scattering studies by Narten, *et al.*,[2a] discussed by Narten and Levy,[2b] which deny the existence of density variations larger than those arising from thermal fluctuations. The most advanced models of this type are those proposed by Nemethy and Scheraga,[3] Vand and Senior,[4] and Jhon, *et al.*[5,6]

Another popular model of the structure of water is that of an ice-like hydrogen-bonded structure with non-hydrogen-bonded "interstitial" molecules in the lattice cavities. A typical example is the model proposed by Marchi and Eyring[7] and subsequently retracted by Eyring,[6] who cited Stevenson's[8] interpretation of the ultraviolet spectrum of water as strong evidence for the nonexistence of significant concentrations of non-hydrogen-bonded molecules at any temperature in the normal liquid range. The models proposed by Nemethy and Scheraga[3] and Vand and Senior[4] also fail on this score.

A "simple" model which we feel deserves more thorough discussion has been proposed by Angell.[9] He interprets the properties of water in terms of the concentrations of broken and unbroken hydrogen bonds without reference to other molecular properties. This scheme can be used to generate the classical two state thermodynamics often used to describe the properties of water. Since it is not at all necessary to associate the existence of microphases or non-hydrogen-bonded molecules with broken hydrogen bonds, this model does not conflict with the available spectroscopic data. Although it suffers from structural underdefinition, we find it rather elegant and note that it generates some impressive results. We consider Angell's model to be the best and least restrictive of the "simple" category. It may turn out to be a useful simplification for the classification of the molecular states derived from a more complete statistical mechanical model, but that is not now known. We do have one objection to Angell's model, however, in that it assumes that

---

(1) Fannie and John Hertz Foundation Fellow.

(2) (a) A. H. Narten, M. D. Danford, and H. A. Levy, *Discuss. Faraday Soc.*, **43**, 97 (1967); (b) A. H. Narten and H. A. Levy, *Science*, **165**, 447 (1969).

(3) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962); **41**, 680 (1964).

(4) V. Vand and W. A. Senior, *ibid.*, **43**, 1878 (1965).

(5) M. S. Jhon, J. Grosh, T. Ree, and H. Eyring, *ibid.*, **44**, 1456 (1966).

(6) M. S. Jhon, E. R. Van Artsdalen, J. Grosh, and H. Eyring, *ibid.*, **47**, 2231 (1967).

(7 R. P. Marchi and H. Eyring, *J. Phys. Chem.*, **68**, 221 (1964).

(8) D. P. Stevenson, *ibid.*, **69**, 2145 (1965).

(9) C. A. Angell, *ibid.*, **75**, 3698 (1971).