A CRITIQUE ON SOME RECENT THEORIES OF CHEMICAL BONDING

Part II. Non-Quantum Mechanical Models

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Abstract: In part II are discussed the charge cloud model, the tangent sphere model, and the VSEPR model. These models, although essentially qualitative in nature, have been extremely helpful as interpretive tools. Basic assumptions in the charge cloud, the tangent shere and the VSEPR models have been given. In comparing these models, attempt has been made to bring out clearly their similarities and differences. A short summary and conclusions (for Part I and II) are given at the end of of this paper.

In the previous paper, quantum mechanical models of molecular structure have been discussed in some detail. These include, besides some prerequisite discussions on the Pauli principle and linear transformations, an elementary treatment on the SCF method, Walsh diagrams, the Linnett 'double spin set' model and the FSGO model. All these models have been successfully used for the interpretation of molecular energies and geometries although some models yield better energy values than others.

More recently, however, semiempirical models such as the tangent sphere model and the valence shell electron pair repulsion model, find extensive use in organic and inorganic chemistry in the interpretation and development of structural arguments. These models have been used in elementary general chemistry text books to qualitatively explain properties of certain well known molecules such as H_2, N_2, O_2, H_2O, NH_3, HF and the like. These methods are simple, straightforward and essentially non-mathematical. Because of these qualities, they have become increasingly popular from the academic as well as scientific viewpoint. The following pages attempt to bring out the salient features of the tangent sphere and the VSEPR models.

Non-Quantum Mechanical Models

The Charge Cloud and the Tangent Sphere Models. The basic assumption in the charge cloud as well as the tangent sphere model is the same, namely that the electron is a uniformly charged sphere. The Pauli exclusion principle applied to this model may be stated to read that the electron clouds of electrons with parallel spin do not overlap. The idea that electrons behave like nonoverlapping uniformly charged spheres was first conceived by Kimball,[1] and Neumark did calculations on simple systems like H, He+, He, and H_2 using the model. Later, Bent[2] developed the tangent sphere model on similar grounds and applied the model to explain some regularities in molecular geometries. King[3] has also developed a qualitative picture of the architecture of molecules from similar assumptions. The energetics of some elementary reactions, based on the charge cloud model, has been discussed by Strong.[4] The most logical way to develop the charge cloud model is by the application of the Pauli principle.

The Kimball model uses floating spherical orbitals containing pairs of electrons. The same, of course, is true of the tangent sphere model except that the orbitals are not allowed to float—the nuclei are always situated at the centres of electron clouds, nevertheless both the models yield similar sort of results and whatever follows is essentially due to Bent and King. The electronic arrangement around a spherical K-shell core, according to the tangent sphere model, is strictly due to the Pauli exclusion principle. For example two electrons of the same spin due to the spin correlation tend to orient themselves linearly. Similarly for three and four electrons the most probable configuration is trigonal planar and tetrahedral respectively. Here, it is not at all necessary that the electron should possess coulombic interactions. In fact, the charge on nuclei may be switched on after they had reached the most favourable geometry entirely on the basis of spin correlation. The electrons may now be paired to leave the basic geometry unaltered. The configuration for 2, 3, and 4 electron spheres is given in Fig. 1.

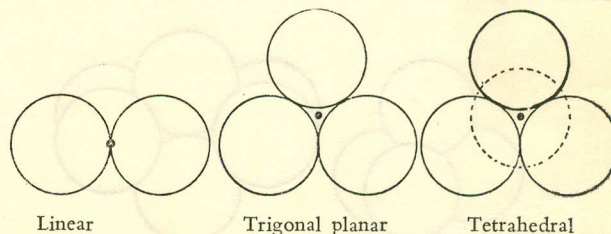| Linear | Trigonal planar | Tetrahedral |

Fig. 1. Tangent sphere model for two, three and four 'electron pairs'. Each sphere stands for an 'electron pair'.

The actual construction of models from styrofoam or plastic balls is not treated here. There are excellent articles available which describe the construction for such a model,[2,3] The model is effective in a number of ways. It depicts the space filling property of matter and in a straightforward manner shows a three-dimensional arrangement of nuclei and electrons to give a simple picture of bond length and bond angles. A single structure may stand for a number of molecules. For example the following geometrical arrangements represent the molecules listed in Fig. 2. The nuclei

with inner shells occupy the holes created by packing together the spheres.

Here each sphere stands for a pair of electrons which may or may not contain hydrogen nuclei. It means that bond-pairs and lone-pairs are treated to be equivalent. This apparently is a defect in the model which leads to erroneous bond angles for NH_3 and H_2O molecules. It predicts $109.28°$ angles for CH_4, NH_3, and H_2O as compared to the experimental values of CH_4 ($109.28°$), NH_3 ($107.3°$), and H_2O ($104.5°$). However, its resemblance with the electron pair model is striking. For example, in tetrahedral CH_4 molecule, the four sphere of the tetrahedron stand for four electron pairs of the C—H bonds in CH_4. Furthermore, the angles for NH_3 and H_2O are nearer to the tetrahedral angles than the $90°$ angle predicted by non-hybridized molecular orbital model.

The model is particularly effective when applied to hydrocarbons. It gives the right geometries for single, double and triple bond compounds, shows free rotation along the single bond in ethane and pictures nicely the eclipsed and staggered structure of C_2H_6 (Fig. 3).

The parts of the carbon–carbon bonds in ethylene[2] and acetylene[3] are equivalent (Fig. 3). This is different from the σ or π-classification of bonds in the MO theory but then, as has been shown previously, a set of equivalent localized bonds may be converted into a set of delocalized orbitals by linear transformation.

In the charge cloud model, the deviation of bond angles from a tetrahedral CH_4 ($109.28°$) to NH_3 ($107.3°$) and H_2O ($104.5°$), is explained primarily on the basis of nuclear–nuclear repulsion. As a matter of fact, nuclear–nuclear repulsion plays a fundamental role in practically all explanations in geometrical as well as energetical considerations.[2] The decrease in the NH_3 angle from a tetrahedral one is accounted for by saying that the protons push out the nitrogen nucleus toward the lone-pair. This explanation does seem to agree with the observation that the N—H bond lengths increase from NH_4^+ to NH^{2-} (Table 1) as the angle decreases from a tetrahedral one to $86.4°$

for NH_2^-. For water, however, the explanation is hardly adequate. Although the angle decrease from a tetrahedral for $[H_4O]^{+2}$ to H_2O ($88.4°$) is in the right direction, the bond lengths decrease, which does not seem to agree with the idea of central atom being pushed out of its equilibrium position. If this explanation is taken seriously the bond lengths from $[H_4O]^{+2}$ to H_2O must increase.

The presence of double and triple bonds has a profound effect on the molecular geometry. It is seen, for example, that the bond angles and bond distances in multiple bond molecules like ethylene and acetylene deviate from the parent saturated hydrocarbons. The carbon–carbon bond distance decreases from ethane (1.53), ethylene (1.34) to acetylene (1.20). The presence of multiple bonds also affects the C—H bond distances in ethane, ethylene and acetylene. The distance decreases from 1.093 to 1.086 to 1.059 respectively. The decrease in carbon–carbon bond distance is predicted by the charge cloud model. It, however, gives a too small value for carbon–carbon bond distance in acetylene. The decrease in carbon–hydrogen bond distance and variation in HCH angle in ethylene can also be rationalized[5] on the basis of the model but hard to justify entirely on the grounds of nuclear nuclear repulsion argument.

The Electron Pair Repulsion Model. The valence shell electron pair repulsion model (VSEPR) in its present form was first proposed by Gillespie and Nyholm.[6] The model rests on a similar sort of

TABLE 1. BOND ANGLES AND BOND DISTANCES FOR NH_3 AND H_2O SERIES.

Molecule	Bond distance* (Å)	Bond angle*	Molecule	Bond distance* (Å)	Bond angle*
NH_4^+	1.876	Tetrahedral	$[H_4O]^{+2}$	1.760	Tetrahedral
NH_3	1.910	87.6	$[H_3O]^+$	1.700	90.2
NH_2^-	1.964	86.4	H_2O	1.666	88.2

*A.A. Frost, J. Phys. Chem., 72, 1289 (1968).

CH$_4$, NH$_3$, H$_2$O, HF   C$_2$H$_4$,O$_2$, CH$_2$O

C$_2$H$_2$, HCN, N$_2$,CO   C$_2$H$_6$, CH$_3$OH, H$_2$O$_2$, F$_2$
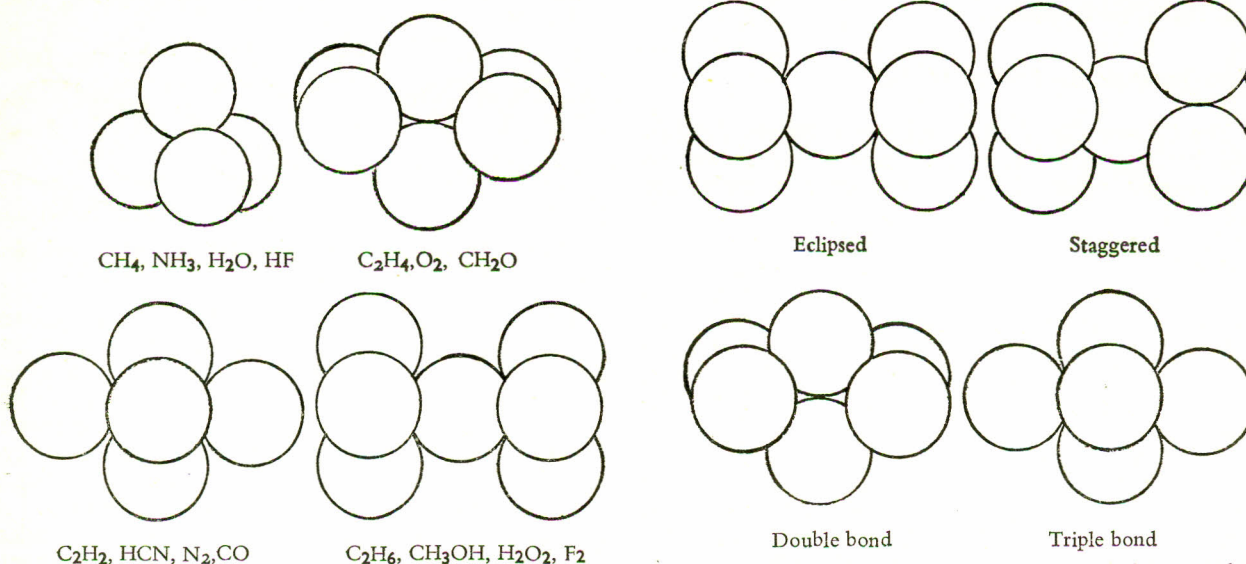
Fig. 2. Tangent sphere models for various well-known molecules.

Eclipsed   Staggered

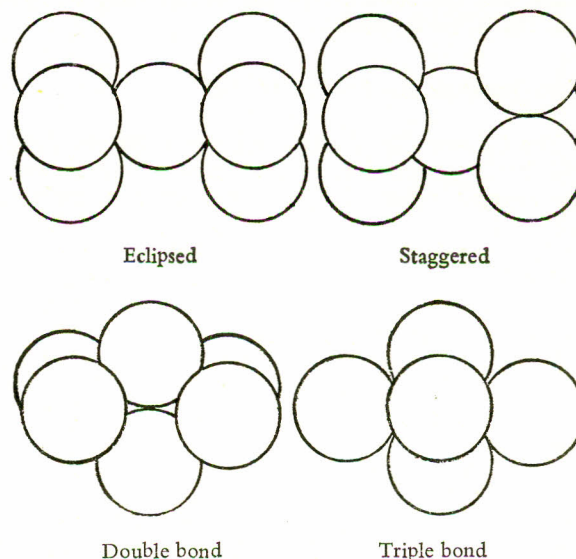Double bond   Triple bond

Fig. 3. Tangent sphere models showing single (eclipsed and staggered conformation), double and triple bond structures.

argument as the charge cloud model using the Pauli principle. The electron correlation works to minimize the repulsion between pairs of electrons and the preferred arrangement of electron pairs around a central atom turns out to be the one in which they are at a maximum distance apart. Consequently, each pair of electron occupies a well-defined region of space from which other electrons are excluded. It is further assumed that repulsion between lone-pairs is greater than between bonding-pairs. Therefore, the sequence that repulsions, 1p–1p > 1p–bp > bp–bp immediately follows. In some more recent articles, Gillespie[7,8] looks at electron pairs as geometrical objects in space rather than as repelling particles, which is only another way to look at the same problem.

With this in mind, the assumptions in the VSEPR model may be summed up as follows:

(a) A lone-pair occupies more space than a bonding-pair. The size of a lone-pair in a molecule is, therefore, larger than a bonding-pair.

(b) A bonding-pair takes up less and less room in a molecule as the electronegativity of the ligand atom increases.

(c) A bonding-pair in a single bond occupies less room than two or three bonding-pairs in double and triple bonds respectively.

If the condition of maximum distance between electron pairs is satisfied, the most stable electronic configuration around a nucleus for a given number of pairs turns out to be linear for two, trigonal planar for three, tetrahedral for four, trigonal bipyramid for five, and octahedral for six pairs. Furthermore, these geometries may be somewhat distorted, as is often found, in cases where electron pairs are of different type—have lone-pairs and bonding-pairs. The deviation from the exact geometry will be explained with the help of assumptions (a), (b) and (c). The following examples shall make it clear.

For four electron pairs, the tetrahedral angle in CH_4 decreases to NH_3 (107.3°) and H_2O (104.5°). The decrease in bond angle here is successfully explained with the assumption that the lone-pairs due to their large size occupy all the space around the central atom. This squeezes the bonding-pairs and the bond angle decreases. The effect increases as one passes from CH_4 (4bp) to NH_3 (3bp, 1lp) to H_2O (2bp, 2lp) in agreement with VSEPR model.

Replacement of hydrogen atoms in NH_3 and H_2O by more electronegative fluorine atoms decreases the bond angle to NF_3 (102°) and F_2O (102°). Although the decrease for NF_3 is larger than for F_2O, the assumption that the bonding-pair occupies less and less room as the electronegativity of the ligand atom

increases, reasonably explains the shortening of the bond angles. However, the assumption hardly seems tenable for the following series considered in entirety (Table 2). It is seen here that the bond angle for higher molecules does not vary according to the VSEPR prediction.

The best arrangement for five electron pairs is trigonal bipyramid and the distortion from the regular bipyramidal structure when electron pairs are made unequal takes place according to the rules discussed above. In the ideal trigonal bipyramidal PF_5, the five electron pairs are not equivalent. Two axial pairs are at 90° angle to the three equivalent equatorial pairs which lie in one plane at a 120° angle.

Furthermore, the axial pairs because of their three neighbours lie further away from the central nucleus than the equatorial pairs which have only two neighbours. Consequently, the axial bonds are longer than the equatorial bonds (Fig. 4).[9,10]

Another important point that contributes significantly to the structural arguments here, as previously, is that of the size of the electron pairs. The fact that there is more room available at the equatorial positions as compared to the axial ones makes one to expect that larger electron pairs would occupy equatorial positions and the smaller pairs the axial positions. The replacement of fluorine atom by CH_3 groups follows that trend. The less electronegative CH_3 groups as compared to fluorine, preferably occupy equatorial positions.

The VSEPR model makes an attempt to explain angle deviations from the regular trigonal planar, tetrahedral and octahedral geometries by bringing into play the concept of bp–bp, 1p–1p, and bp–1p repulsions and their space filling properties. These ad hoc assumptions in the VSEPR model are now compared with some of the results obtained for the H_2O molecule by the FSGO model.[11] These results include two electron (closed shell) interactions (VEE) by various electron pairs as a function of the H—O—H
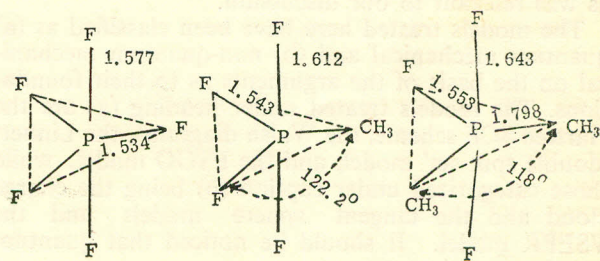

Fig. 4. Structures of phosphorus pentafluoride and its methyl substituents.

TABLE 2. BOND ANGLE DATA FOR THE HYDRIDES AND THE HALIDES OF SOME ELEMENTS IN THE PERIODIC TABLE.

H_2O	104.5°	F_2O	102°	Cl_2O	110°				
H_2S	92.2°	—		Cl_2S	102°				
H_2Se	91.0°	—		—					
H_2Te	88.5°	—		—					
NH_3	107.3°	NF_3	102°						
PH_3	93.0°	PF_3	104°	PCl_3	100°	PBr_3	101.5°	PI_3	98°
AsH_3	91.5°	ASF_3	102°	$AsCl_3$	98°	$AsBr_3$	101.0°	AsI_3	98.5°
SbH_3	91.3°	SbF_3	88°	$SbCl_3$	99.5°	$SbBr_3$	97.0°	SbI_3	99°

bond angle with all other parameters fixed. The values for nuclear attraction (VEN), nuclear repulsion (VNN), and kinetic energy (TE) terms that contribute in the energetics of the angle variation were also obtained.

The data on various electron pair interactions reveal that a qualitative picture as is commonly conceived by the tangent sphere and the VSEPR model can hardly be justified on the basis of *ab initio* molecular computations such as the FSGO. The complications are primarily due to the kinetic energy and nuclear attraction terms which are almost entirely neglected by the tangent sphere and the VSEPR models. The FSGO calculations show that the most significant changes occur in these terms. Furthermore, the electron repulsion terms for the bonding-pairs which are of fundamental importance in non-quantum mechanical models hardly seem to be as effective as predicted by them. For example, the FSGO calculations show that lp–lp repulsion changes by a very small amount as compared to the bp–bp repulsion as the angle in H_2O varies from 80° to 120°. This is quite contrary to the expectations of non-quantum mechanical models which predict larger contributions for lp–lp interactions as compared to the bp–bp interactions in determining the molecular geometry.

Summary and Conclusions

We have attempted here to give a brief (and by no means an exhaustive) account of various theories of the chemical structure with particular emphasis on models developed after the advent of quantum mechanics. Two basic principles namely, the Pauli exclusion principle and the concept of linear transformations have been treated in some detail because of their importance in showing correlation between different models discussed in this article. Some of the well known quantum mechanical theories have either been completely left out or treated in as little detail as was relevant to our discussion.

The models treated here have been classified as (a) quantum mechanical and (b) non-quantum mechanical on the basis of the arguments as to their foundations. The models treated under heading (a) are the Hartree SCF scheme, the Walsh diagrams, the Linnett 'double spin set' model, and the FSGO model, while those categorized under caption (b) being the charge cloud and the tangent sphere models and the VSEPR model. It should be noticed that quantum mechanical models yield data for important molecular parameters while the non-quantum mechanical models give only qualitative results. Nevertheless, the charge cloud and the VSEPR models have been extremely helpful as interpretive tools. Furthermore, many authors have attempted to put these semiempirical models on a theoretical footing. Beside others, this includes later work of Bent and Gillespie. More recently, Allen[12] has shown that the VSEPR model can be described by way of a rigorous quantum mechanical definition. In fact, Allen has shown through a physical–mathematical proof that the VSEPR model and the Walsh diagrams are equivalent.

In the last part of this article using the FSGO model,[11] we have shown that the analysis of energy terms taking each term as an independent contributor furnishes additional information which is a step towards better understanding of the nature of forces involved in determining the molecular geometries.

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