3.22: A Critique of the Valence Shell Electron Pair Repulsion Model

During the last three decades the emphasis on teaching VSEPR theory in the general chemistry sequence has increased dramatically. In fact in the area of molecular structure it might be described as the theory of choice at the introductory level of the chemistry curriculum. However given long-term reservations in some quarters (see quotes below) regarding its validity, and given the tightness of the general chemistry curriculum the question of whether or not its use is justified should be a matter of discussion. This is an important issue because VSEPR is generally taught at the expense of more comprehensive and important bonding theories such as molecular orbital theory. I think it is important for the community of undergraduate chemistry teachers to discuss the question of whether or not VSEPR belongs in the chemistry curriculum.

Recently I analyzed the VSEPR model quantitatively using a simple quantum mechanical model for bonding created by Henry Bent (*1*) in the 1960s called the Tangent Spheres Model (TSM). The purpose of this paper is to share the results of my analysis with the general chemistry faculty in order to facilitate a discussion of the role VSEPR should play in the general chemistry curriculum. TSM is a rudimentary quantum mechanical model that yields quantitative predictions for molecular geometries with relative ease. Because of its simplicity as an electronic structure model, the conclusions drawn from an analysis of its results need to be validated by higher level quantum mechanical calculations. In other words the TSM can point us in the direction of further study.

Before proceeding to the TSM calculations, I would like to review a sample of the concerns that have been voiced about teaching and using VSEPR in the recent literature. As can be seen by the dates of these citations, there have been periodic expressions of caution about the use and interpretation of VSEPR since its first appearance in the chemistry curriculum.

*Recent articles in the literature have championed the use of the valence shell electron pair repulsion, VSEPR, approach to predicting molecular structure. Recently, the authors of general chemistry textbooks have grasped this idea and incorporated it into the curriculum. This approach leads to the impression that electron-electron repulsions determine the geometries of molecules, because the model is presented in the form of an explanation and structures are used to confirm the model. The factors that influence the geometry of molecules are much more complicated than the VSEPR model leads one to believe. **Drago, JCE 50, 244 (1973)**.*

*In teaching VSEPR theory, as in teaching any other simple model, the student should understand that such a simple approach neglects many other factors in bonding. Its emphasis on interelectronic repulsions rather than on bond formation contrasts sharply with other models in which replusions are considered only to refine structural details. VSEPR theory like most simple models, produces mostly correct predictions. However, such a simple theory can easily be misused or overused. It should be stressed that although VSEPR theory is an easy-to-use tool, such a simple tool - by the very nature of its simplicity - may not be as accurate as necessary. **McKenna and McKenna, JCE 61, 771 (1984)**.*

*On the whole, the VSEPR method predicts the geometries of main group compounds and complexes rather well. This is not the same thing as saying that it provides a correct explanation of molecular geometry. Indeed, in the opinion of some, its status and use is just that of prediction, that of an aid to getting the right answer. One is forced to remember a difficult lesson: a model that leads to a correct prediction is not necessarily a correct model. **Kettle, Physical Inorganic Chemistry, University Science Books, 1996, Appendix 2**.*

Among my concerns is the fact that much of the caution that is voiced in these quotations appears to be absent in our general chemistry textbooks. If it isn't stated explicitly, the impression one is left with after reading textbook presentations of VSEPR is that it is not just a predictive devise, but an explanation for the equilibrium geometries that molecules achieve. I will argue below that it does not have explanatory success because it is concerned only with electron-electron repulsions and they represent a relatively minor contribution to the total molecular energy.

The Tangent Spheres Model

The Tangent Spheres Model assumes electron pairs are spheres of radius R (an adjustable or variational parameter) and that the electron density within the spheres is uniform. As described, the TSM might be viewed as a primitive precursor of the current density functional theory (DFT). The Pauli Exclusion Principle is incorporated into the model by assuming that spheres are hard, that is that they occupy space to the exclusion of other spherical electron pairs. Quantum mechanics enters TSM through a $1/R^2$ dependence for electron kinetic energy. All potential energy contributions are calculated classically, as they are in any *ab initio* quantum mechanical calculation. In other words, quantum mechanics always manifests itself in the kinetic energy term. The consequence of de Broglie's hypothesis of wave-particle duality for matter is a non-classical expression for the kinetic energy of material objects such as the electron.

To take a specific example, VSEPR predicts tetrahedral geometry for methane because this geometry puts the electron pairs farthest apart and therefore minimizes valence electron repulsions. To challenge this approach the valence energy of methane was calculated assuming both square planar and tetrahedral geometry using the Tangent Spheres method. To build square planar or tetrahedral methane using TSM requires five spheres. A small sphere represents the nuclear kernel - the nucleus and non-valence electrons and carries a net +4 charge. Four larger spheres contain the four pairs of valence electrons each with a proton imbedded in the center. Each valence sphere, therefore, carries a net charge of -1. The arrangement of the spheres for the two geometries is shown schematically in the accompanying Mathcad worksheet showing the computational details.

As we shall see below, TSM also predicts tetrahedral geometry for methane, but clearly identifies electron-nuclear attractions as the driving force in determining the equilibrium geometry. The entire TSM calculation is appended as a Mathcad worksheet as mentioned above. For computational details **click here**.

In the TSM approach the total molecular energy for methane is partitioned into the following contributions:

- Electron kinetic energy: $9/(8R^2)$
- Intra-pair electron-electron repulsion: $6/(5R)$
- Inter-pair electron-electron repulsion: Coulomb's Law using point charges
- Nuclear-nuclear repulsion: Coulomb's Law using point charges

  - Hydrogen - hydrogen
  - Carbon - hydrogen

- Electron-nuclear attraction

  - For carbon: Coulomb's Law using point charges
  - For hydrogen: $-3/(2R)$

The results are summarized below in tabular form. The various energy contributions are reported in hartrees (1 hartree = 27.2 eV = 2.6255 MJ/mol). The results in the table show that the TSM calculations satisfy the virial theorem. That is total energy is half the potential energy and the kinetic energy is the negative of the total energy.

Methane	Square Planar	Tetrahedral	Difference
Electron kinetic energy	6.94	8.28	1.34
Electron-electron repulsion, total	13.73	16.11	2.38
Intra-pair electron repulsion	4.22	4.60	0.38
Inter-pair electron repulsion	9.51	11.51	2.00
Nuclear-nuclear repulsion, total	12.31	15.41	3.1
Nuclear-nuclear repulsion: H-H	2.38	2.88	0.50
Nuclear-nuclear repulsion: C-H	9.94	12.53	2.60
Electron-nuclear attraction, total	-39.92	-48.08	-8.16
Electron-carbon attraction	-19.87	-25.06	-5.19
Electron-hydrogen attraction: molecular	-9.51	-11.51	-2.00
Electron-hydrogen attraction: atomic	-10.54	-11.51	-0.97
Total energy	-6.94	-8.28	-1.34
Sphere radius	1.14	1.04	-0.10

In *ab initio* quantum mechanical geometry optimizations the total energy is minimized, thus, the VSEPR model seems suspect in concentrating on a single energy contribution to predict molecular geometry. The rudimentary quantum mechanical results provided in the table seem to support this suspicion. Nothing the VSEPR theory claims to be important is supported by the calculations based on TSM. For example, in going from square planar to tetrahedral geometry:

- inter-pair electronic repulsions increase rather than decrease
- the valence electrons get closer together rather than farther apart (see R in table)
- the inter-pair electron repulsion term is much smaller than the valence electron attraction for the carbon nucleus

In fact it can be stated that on the basis of the TSM analysis it appears that the major driving force for molecular geometry appears to be maximizing electron-nuclear attractions, not minimizing electron-electron repulsions. TSM suggest, therefore, that the acronym should be VSEPNA (valence shell electron pair nuclear attraction). According to TSM that geometry is best which allows electrons to get closest to the nucleus. This is, of course, a packing problem. In this example, the tetrahedral hole is clearly smaller than the square planar (octahedral) hole, allowing the negatively charged valence electrons to get closer to the positively charged nucleus. Or we could argue that the tetrahedral arrangement of valence electron pairs is close packing and the square planar arrangement isn't.

Reference:

1. Bent, H. A. *J. Chem. Educ.* **40**, 446-452 (1963).