

R. J. Gillespie
McMaster University
Hamilton, Ontario
Canada, L8S 4M1

A Defense of the Valence Shell Electron Pair Repulsion (VSEPR) Model

Drago¹ has claimed that the factors that influence the geometry of molecules are more complicated than the VSEPR model would lead one to believe, and he has proposed a set of empirical rules which he claims are intellectually more satisfying than the VSEPR model. It is obvious that the prediction of the structure of a polyatomic molecule from first principles is a very complicated problem which at present necessitates the expenditure of very large amounts of computer time. Qualitative theories which enable one to "understand" and to predict the geometry of molecules are therefore still useful and the VSEPR model is such a qualitative theory.² It does not pretend to give a complete explanation for the geometry of a molecule, but it does attempt to provide a simple model for the prediction of molecular geometry which is soundly based on quantum mechanics and which is in fact, in the author's opinion, more intellectually satisfying than a set of entirely empirical rules.

The Pauli Exclusion Principle and the Arrangement of Electron Pairs in Valence Shells

The VSEPR model is based on the idea that the distribution of electrons in the valence shells of atoms in molecules is determined largely by the operation of the Pauli Exclusion Principle.³ The important physical consequence of the exclusion principle is that electrons with parallel spins have a maximum probability of being found as far apart as possible and this in turn leads to the conclusion that for a central atom forming two or more covalent bonds the electrons in the valence shell are localized in pairs which maximize their distance apart. These most probable arrangements for electron pairs in a valence shell are summarized in Table 1; they are identical with those proposed by Drago¹ in his Table 1 and empirical rule 3. However, according to the VSEPR theory these electron pair arrangements are not empirical but are based on a fundamental property of electrons, namely the exclusion principle.

The Prediction of the General Shapes of Molecules

If one takes account of the fact that in general there are both bonding and non-bonding or unshared pairs of electrons in a valence shell, one arrives at an explanation of the general shapes of *all* molecules of the non-transition elements which have up to six pairs of electrons in their valence shells, as summarized in Table 2. Molecules containing multiple bonds are also included very readily, by assuming that any single bond in the molecular shapes summarized in Table 2 may be replaced by a multiple bond (Table 3). Tables 1-3 form the fundamental basis of the VSEPR theory and with their aid a student can predict and understand the general shape of any molecule AX_n with up to six electron pairs in the valence shell of the central atom A. No attempt is made at this stage to discuss small differences in bond angles, e.g., the deviation of the angles in the molecules NH_3 and H_2O from the ideal tetrahedral angle of 109.5° , and for elementary students at least these small differences can well be ignored. A useful and simple approximation is to assume that the electron pairs in a valence shell may be represented by spheres—this is the tangent sphere model long advocated

Table 1. The Most Probable Arrangements of Electron Pairs in a Valence Shell

Number of electron pairs	Arrangement
2	Linear
3	Equilateral triangle
4	Tetrahedron
5	Trigonal bipyramid
6	Octahedron

Table 2. General Shapes of Molecules of Non-Transition Elements

Number of electron pairs	Arrangement	Number of lone-pairs	Type of molecule	Shape of molecule	Examples
2	Linear	0	AX_2	Linear	$BeCl_2$
3	Equilateral triangle	0	AX_3	Equilateral triangle	BF_3
4	Tetrahedron	1	AX_3E	V-shape	$SnCl_2$
		0	AX_4	Tetrahedron	CCl_4
		1	AX_3E	Trigonal pyramid	NF_3
5	Trigonal bipyramid	2	AX_2E_2	V-shape	H_2O
		0	AX_5	Trigonal bipyramid	PCl_5
		1	AX_4E	SF_4 -shape	SF_4
		2	AX_3E_2	T-shape	ClF_3
		3	AX_2E_3	Linear	XeF_2
6	Octahedron	0	AX_6	Octahedron	SF_6
		1	AX_5E	Square pyramid	IF_5
		2	AX_4E_2	Square	XeF_4

by Bent.⁴ This approximation gives rise to a useful, practical model in which electron pairs are represented by Styrofoam balls, joined together by elastic bands representing the force of attraction of the nucleus for the electron pairs (Fig. 1). As shown in Figure 2, this model provides a student with a simple and instructive method for visualizing and understanding the origin of the electron pair arrangements given in Table 1.

It should be noted that the VSEPR theory makes no use of atomic orbitals or of hybrid orbitals formed from these atomic orbitals, and it thus avoids the possibility of misleading a student into thinking that hybrid orbitals give an explanation for molecular geometry when, in fact, they provide nothing more than an approximate description of the bonding when one already knows the geometry. This is recognized by Drago¹ who points out that after deciding the structure of a molecule by his rules "one can then guess at which hybrid orbitals would be used to point towards the atoms surrounding the central atom." It should be emphasized that the description of electrons in molecules in terms of atomic orbitals and hybrid orbitals

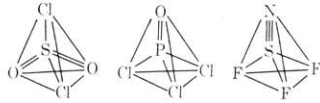
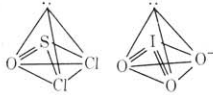

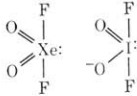
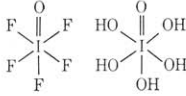
¹Drago, R. S., J. CHEM. EDUC., 50, 244 (1973).

²Gillespie, R. J., "Molecular Geometry," Van Nostrand Reinhold Co., London, 1972.

³Linnet, J. W., "The Electronic Structure of Molecules," Methuen, 1964; Daudel, R., "The Fundamentals of Theoretical Chemistry," Pergamon Press, Inc., N.Y., 1968; Leonard-Jones, J. E., *Advan. Sci.*, 51, 136 (1954).

⁴Best, H. A., J. CHEM. EDUC., 40, 446, 523 (1963); 42, 302, 748 (1965); 44, 512 (1967); 45, 108 (1968).

Table 3. Shapes of Molecules Containing Multiple Bonds

Total Number of Bonds and Lone-Pairs	Arrangement	Number of Bonds	Number of Lone Pairs	Shape of Molecule	Examples
2	Linear	2	0	Linear	$O=C=O$ $H-C\equiv N$
3	Triangular	3	0	Triangular	$Cl-C(=O)Cl$ $^-O-N^+=O$ $O=S=O$
		2	1	V-shape	$O=S=O$ $^-O-\overset{+}{O}=O$ $Cl-\ddot{N}=O$
4	Tetrahedral	4	0	Tetrahedral	
		3	1	Trigonal pyramid	
		2	2	V-shape	$O=Cl-O^-$ $O=Xe=O$
5	Trigonal bipyramid	5	0	Trigonal bipyramid	
		4	1	Irregular tetrahedron	
6	Octahedron	6	0	Octahedron	

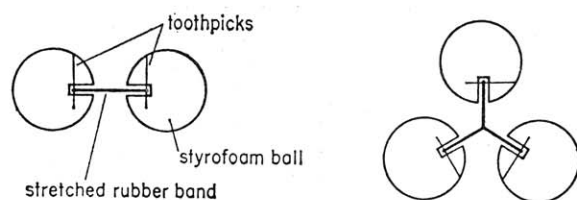


Figure 1. Illustration of the construction of models for illustrating electron-pair arrangements according to the hard-sphere model.

formed from them is an approximation, which is not necessarily any more "correct" or any more useful than the approximation of representing each pair of electrons by a sphere.

Consequences of the Non-Equivalence of Electron Pairs

From this point the theory can be extended by taking into account the fact that not all pairs of electrons are equivalent. In general, in any given valence shell there may be non-bonding and bonding electron pairs and the bonding pairs may bind different ligands or form part of a double or triple bond. Bonding pairs being under the influence of two nuclei rather than one are smaller than non-bonding electron pairs, and their size decreases with increasing electronegativity of the ligand. The two electron pairs of a double bond are together obviously larger than a single electron pair, although they occupy together somewhat less volume than two single electron pairs because they are somewhat squashed together in the same internuclear space. Electron pairs in a valence shell behave as if they repel each other and these "repulsions" are a consequence of the overlap of the electron pairs in

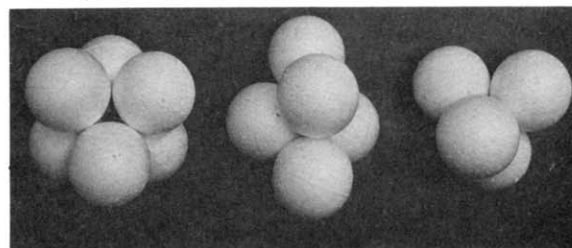


Figure 2. The hard-sphere models for the tetrahedral, trigonal bipyramidal, and octahedral arrangements of four, five and six electron pairs, respectively.

space. It is evident that larger unshared electron pairs will have a greater tendency to overlap adjacent electron pairs than will smaller shared electron pairs, which leads to the conclusion that lone pairs "repel" more than bonding pairs. In order to avoid the possibility of giving the misleading impression that the VSEPR theory is a classical "electrostatic" theory,⁵ it is probably preferable to emphasize the different sizes of electron pairs rather than the magnitude of the repulsions between different electron pairs as in early versions of the theory, recognizing that these are simply two alternative descriptions of the same

⁵This mistaken idea is prevalent in a number of introductory textbooks; e.g., Busch, Daryle H., Shull, Harrison, and Conley, Robert T., "Chemistry," Allyn and Bacon, Inc., Boston, 1973. The potential energy of any given system of nuclei and electrons arises from their mutual electrostatic repulsions and attractions, but the distribution of the electrons around the central nucleus is determined by the exclusion principle.

electron-pair interactions. The larger size of lone-pair electrons (or the greater repulsion that they exert) leads to the conclusion that angles between bonds in valence shells containing lone pairs are always smaller than the ideal angles based on the assumption that all the electron pairs are equivalent. A large number of examples have been discussed,² and there appear to be no exceptions for valence shells containing up to six electron pairs. In the same way one predicts that, in molecules containing multiple bonds, the angles involving these multiple bonds will be larger than the angles between the single bonds. A number of examples have been given previously² and again exceptions are rare. Finally, one predicts that the angles between bonds to electronegative ligands will be smaller than the angles between bonds to less electronegative ligands. Some examples are given in Table 4 and again exceptions to this prediction are rare.

Molecules with Five Electron Pairs in the Valence Shell of the Central Atom

These molecules provide a very convenient illustration of all the important aspects of the VSEPR theory and at the same time enable a useful comparison to be made both with Drago's empirical rules and with hybrid orbital theory.

The arrangement of five electron pairs which maximizes their distance apart and therefore minimizes their interactions is the trigonal bipyramid and not, for example, the square pyramid. On this basis, the VSEPR theory correctly predicts the general shape of all molecules of the types AX_5 , AX_4E , AX_3E_2 and AX_2E_3 with only two exceptions: $Sb(C_6H_5)_5$ and $InCl_5^{2-}$.²

The equatorial and axial positions of a trigonal bipyramid are not equivalent: the axial positions have three close neighbors, whereas the equatorial positions have only two. Consequently, if all the electron pairs were to be situated at the same distance from the nucleus, there would be a greater repulsion on the axial pairs than on the equatorial pairs and one would not have an equilibrium situation. Thus, the axial pairs are, in fact, at a greater distance from the nucleus than the equatorial pairs; i.e., the axial bonds are predicted to be longer than the equatorial bonds, e.g., PCl_5 $r_{ax} = 2.19$ Å, $r_{eq} = 2.04$ Å, and there appear to be no exceptions to this prediction. There is no *a priori* reason to believe that the equatorial groups are bonded by sp^2 hybrids and the axial ligands by 4-electron 3-center bonds or by pd hybrids in order to "explain" the difference in bond lengths. The equatorial ligands could equally well be bonded by p^2d hybrids and the axial ligands by sp hybrids, leading to the conclusion that the axial bonds would be shorter than the equatorial bonds.

An alternative and equivalent description of the non-equivalence of the equatorial and axial positions of a trigonal bipyramid is that there is more space available for an electron pair in an equatorial position than in a more crowded axial position. Accordingly, large electron pairs, that is lone pairs, bonding pairs bonding less electronegative ligands, and of course double bonds, are always found in equatorial positions. Thus, only one stable isomer is known for CH_3PF_4 , SF_4 , and SOF_4 where the methyl group, the lone pair, and the double bond are in the equatorial position in each case. Other examples are given in Table 2 and again there appears to be no exceptions. Drago quotes the empirical rule of Muetterties and Schunn⁶ that the most electronegative ligands are found in the axial positions; the above discussion shows that this rule is in fact a logical extension of the fundamental ideas of the VSEPR theory.

Exceptions: Real and Imaginary

The simple ideas of the VSEPR theory are much more successful than one might expect, and it is not surprising that there are a few exceptions, some of which Drago has

drawn attention to. The basic idea that electron pairs in a valence shell maximize their distance apart gives rise to the prediction of correct molecular shapes, with only two known exceptions, for valence shells of up to six electron pairs, and leads one to suspect that this is indeed the dominant factor in determining molecular shape in the vast majority of cases. It is, of course, not the only factor, and this becomes clear as one attempts to refine the theory to account for small differences in bond lengths and bond angles. Here one encounters further exceptions which, even so, are surprisingly rare. Most of the exceptions or apparent exceptions can be grouped into two classes.

Molecules of the Elements Carbon, Nitrogen, and Oxygen

In virtually all the compounds of these elements, the central atom has a filled valence shell of four electron pairs. There is considerable crowding of these four pairs of electrons in these small valence shells, and an important consequence is that bond angles in compounds of these elements never differ by more than a few degrees from the tetrahedral angle. Within this narrow range there are indeed exceptions to the general rules discussed above, such as those quoted by Drago. It is evident that other factors must be taken into account including no doubt interactions between the non-bonding electron pairs of the ligands which are relatively close together when attached to these very small central atoms. Although it must therefore be admitted that the VSEPR theory is inadequate to predict detailed variations of bond angles for these molecules, it should also be pointed out that no other theory can make any more successful predictions, nor can a simple set of empirical rules be drawn up which will account for all of the observed angles.

Hydrides

Drago draws attention to the fact that the angle in PH_3 is smaller than in NH_3 , and he claims that this is not predicted by VSEPR theory because one does not know on passing from NH_3 to PH_3 whether lone-pair bond-pair or bond-pair bond-pair interactions will decrease the most. In fact, however, it follows logically from our previous discussion, as we will now see, that bond-pair bond-pair interactions will decrease the most and therefore that the bond angle in PH_3 will be smaller than in NH_3 . PH_3 belongs to an important class of molecules in which the valence shell is not filled to capacity. In the case of virtually all the stable molecules of carbon, nitrogen, and oxygen there are four electron pairs in the valence shell (the L shell) which can only accommodate four pairs of electrons. For the elements silicon, phosphorus, and sulfur, however, the valence shell is in the M shell, which can contain more than four pairs of electrons. In principle, at least from the point of view of the atomic orbitals that are available in the free atom, the M shell can contain up to nine pairs of electrons, although actually in compounds of these elements the maximum number of electron pairs that is found is six. A possible explanation for this has been discussed elsewhere.² In any case, four electron pairs in a valence shell that can contain at least six pairs are relatively far apart and their mutual interactions are weak. When one of the pairs is a lone pair which tends to spread out and surround the central nucleus as much as possible, it pushes the bonding pairs together until they begin to touch each other and interact strongly; for a valence shell that can contain six electron pairs this occurs when they approach an angle of 90° (the ideal angle for an octahedral arrangement of six electron pairs). Consequently, one finds that the bond angles in all PX_3 and

⁶Muetterties, E. L., and Schunn, R. A., *Quart. Rev. Chem. Soc.*, 10, 245 (1966).

Table 4. Effect of Ligand Electronegativity on Bond Angles

PF ₃ 97.8°	PCl ₃ 100.3°	PBr ₃ 101.5°	PI ₃ 102°
AsF ₃ 96°	AsCl ₃ 98.7°	AsBr ₃ 99.7°	AsI ₃ 100.2°

Table 5. Comparison of Bond Angles in NX₃ and PX₃ Molecules and in OX₂ and SX₂ Molecules

NH ₃ 107.3°	NF ₃ 102°	NHF ₂ 102.9°	OH ₂ 101.5°	OCl ₂ 111°	O(CH ₃) ₂ 111°
PH ₃ 93.3°	PF ₃ 97.8°	PHF ₂ 99°	SH ₂ 92.2°	SCH ₂ 98°	S(CH ₃) ₂ 105°

SX₂ compounds are smaller than the angles in the corresponding NX₃ and OX₂ compounds. Some examples are given in Table 5. It must be admitted, however, that the angles in the hydrides PH₃ and H₂S are surprisingly small and indeed anomalous, when compared with other PX₃ and SX₂ compounds—thus, as Drago points out, the angle in PF₃ is larger than in PH₃, whereas, because fluorine is more electronegative than hydrogen, it is predicted to be smaller. It appears to be the hydrides which are anomalous, because for other ligands X and for molecules other than those of carbon, nitrogen, and oxygen there appear to be no exceptions to the rule that bond angles decrease with increasing ligand electronegativity. While bearing in mind the dangers of pressing the theory too far, the anomalous behavior of hydrides can nevertheless be rationalized. Hydrogen is a unique ligand in that it has no bonding or non-bonding electron pairs in its valence shell except the single pair bonding it to the central atom. This means that the electron pair of an X—H bond not only occupies the bonding region between X and H, but must also surround the hydrogen nucleus, i.e., occupy a region of space which for other elements is occupied by other pairs of electrons. Consequently, the electron density in the bonding region is less than would be predicted on the basis of its electronegativity alone, and therefore it forms anomalously small bond angles. One expects this anomaly to become increasingly evident with decreasing electronegativity of the central atom, which allows more electron density to move away from the bonding region into the non-bonding region around the hydrogen nucleus, and, consequently, the anomalous bond angles involving hydro-

gen are more apparent for the hydrides of the heavier elements than for nitrogen and oxygen.

Conclusions

Bearing in mind that no approximate theory can be perfect and that exceptions are always to be expected, it nevertheless seems reasonable to claim that the VSEPR theory is a useful, simple theory for the prediction of molecular geometry and that, in particular, it is more successful, more soundly based, and more intellectually satisfying than either Drago's empirical set of rules or the hybrid orbital theory. Drago's claim that the VSEPR theory involves a set of arbitrary rules which have to be memorized by the student is not justified, as these so-called rules are in fact a logical set of deductions based on the assumption that the fundamental property of electrons described by the Pauli exclusion principle is the most important factor in the determination of molecular geometry. The overall success of the theory seems to justify the conclusion that, in the vast majority of cases, the dominant factor in the determination of molecular shape is indeed the interactions between the largely localized electron pairs in the valence shell of a central atom. The justification for any theory is its reliability and usefulness for the prediction of new facts, and the VSEPR theory is more reliable for predicting molecular shape than any other theory we have at present. In this sense it is the best theory we have, and it should surely therefore be taught to students, if only as one of several alternatives. Moreover, a logical and consistent theory is undoubtedly more satisfying and more stimulating for the student than any empirical set of rules, such as those proposed by Drago. It is surely not a valid criticism of a theory to say that it is incomplete—many successful theories are admittedly approximate and incomplete. The test of a theory is that it should be useful and should lead to correct predictions, or at least to more correct predictions than rival theories. Most theories are eventually shown to be inadequate and are replaced by others, and undoubtedly the VSEPR theory, along with the valence bond and molecular orbital theories will sooner or later suffer this fate; however, this is no reason why we should not use the theory today. Were the teachers of 50 years ago wrong to teach Bohr's theory of the hydrogen atom?