

Testing and Extending VSEPR with WebMO and MOPAC or GAMESS

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As noted recently in this *Journal* (1), it is more than 50 years since the first appearance of the VSEPR model (2, 3). In that time it has become a standard topic in first-year chemistry. As with any model, it has strengths and weaknesses. Its strengths include an almost infallible ability to predict the correct point group of compounds containing main-group elements, ease of application, and frequently correct predictions of the effects that lone pairs on the central atom have on angles, bond lengths, and point group. Among its weaknesses are the occasional qualitatively wrong predictions for the effect of lone pairs and an inability to predict the correct point group for a few compounds containing metals (both main-group and transition).

VSEPR can be used to make quantitative predictions of bond angles in molecules with no lone pairs on the central atom. It also makes qualitative predictions of (i) *changes* in bond angles for molecules with lone pairs on the central atom, (ii) *changes* in bond lengths as a consequence of differing electronegativities of substituents, and (iii) bond-length differences between axial and equatorial ligands.

Various computer exercises that use freely available semiempirical (MOPAC, 4) and ab initio (GAMESS, 5) computer programs are described. The input to MOPAC and GAMESS is sufficiently complicated to make them unattractive for use in introductory chemistry; however, the availability of a convenient interface in WebMO (6) to prepare the input to these programs has removed that impediment to their use. This exercise uses these programs to test quantitatively the qualitative VSEPR predictions. These qualitative predictions follow from the basic VSEPR premises that (i) electron-pair domains adopt a geometry that keeps them as far apart as possible (7), (ii) volume of nonbonding domains > volume of multiple-bond domains > volume of single-bond domains, and (iii) bonding domains at the central atom decrease in size with increase in electronegativity of the substituent or decrease in electronegativity of the central atom (8). Detailed discussions of the basis of VSEPR have been published by Gillespie (7, 8) for those readers who require an in-depth understanding of the model. This exercise also looks at some situations where the VSEPR predictions are equivocal or wrong.

The exercises are designed to help students appreciate the predictive power of the VSEPR model, while going beyond its qualitative predictions using readily available Web and public-domain software¹ whose attractive output and ease of use appeals to our computer-savvy students. The exercises showing some of the limitations of VSEPR predictions act as a salutary warning that the theory can make incorrect predictions, although the reasons for these failures are now well understood (9). The molecules used to illustrate the various predictions were chosen based on the availability of experimental data, ease of computation, and availability of basis sets.

Qualitative Predictions of the VSEPR Model

The qualitative predictions of the VSEPR theory can be organized into nine areas for the purpose of the quantitative evaluation:

1. For molecules with lone pairs and single bonds on a central atom, the angles subtended by the single bonds are smaller than the ideal angle because lone-pair regions are larger than single-bond regions (8, p 95).
2. Bond angles decrease as the electronegativity of the substituent increases because the electrons are farther away from the central atom and require less volume at the central atom. Similarly, bond angles increase as the electronegativity of the central atom increases because the electrons are closer to the central atom and require a greater volume (8, p 99).
3. Bond angles involving multiple bonds are larger than those involving only single bonds because multiple-bond regions are larger than single-bond regions (8, p 105).
4. The axial bonds are longer than the equatorial bonds for $AX_{5-n}E_n$ molecules ($n = 0-2$) because the axial positions have more close neighbors (three at 90°) than the equatorial positions (two at 90°), pushing the axial substituents farther from the central atom (8, p 107).
5. The equatorial bonds are longer than the axial bonds for AX_5Y molecules (where Y is a lone pair or multiply bonded atom) because Y pushes the equatorial bonding domains away from itself (8, p 98).
6. Introducing a more electronegative substituent at the less electronegative of two bonded atoms decreases the bond length to the more electronegative atom (10).
7. Lone pairs are always equatorial in $AX_{5-n}E_n$ molecules ($n = 1-3$) because there is more space available in the equatorial positions (8, p 108).
8. Double bonds are equatorial in AX_4Y because there is more space available in the equatorial positions (8, p 109).
9. The less-electronegative substituents occupy the equatorial positions in $AX_{5-n}Y_n$ molecules ($n = 0-2$) and $AX_{5-(m+n)}Y_mE_n$ molecules ($m = 2-4$, $n = 1, 2$; $m + n < 5$) because the less-electronegative substituents produce expansion of their bonding region close to the central atom, forcing them into the less crowded equatorial positions (8, p 108).

Computational Strategies

MOPAC is a program that uses semiempirical techniques to determine molecular properties. It contains five different models based on the NDDO method, AM1, MNDO, MNDO-d, PM3, and PM6 (see ref 11 for a description of the first four models and

Table 1. Bond Lengths and Bond Angles for Common Homoleptic Systems

Entry	System	Example	Bond length	Calculated/Å (Experimental/Å)	Bond Angle	Calculated/deg (Experimental/deg)
1	AX ₂	CO ₂	C–O	1.170 (1.162)	O–C–O	180 (180)
2	AX ₃	BF ₃	B–F	1.310 (1.307)	F–B–F	120 (120)
3	AX ₂ E	SnCl ₂	Sn–Cl	2.340 (2.35)	Cl–Sn–Cl	98.2 (97.7)
4	AX ₄	SiH ₄	Si–H	1.488 (1.481)	H–Si–H	109.5 (109.5)
5	AX ₃ E	PCl ₃	P–Cl	2.027 (2.043)	Cl–P–Cl	100.7 (100.1)
6	AX ₂ E ₂	SCl ₂	S–Cl	2.023 (2.014)	Cl–S–Cl	104.0 (102.7)
7	AX ₅	PCl ₅	P–Cl ax	2.119 (2.124)	Cl eq–P–Cl eq	120 (120)
			P–Cl eq	2.011 (2.020)	Cl ax–P–Cl ax	180 (180)
8	AX ₄ E	TeCl ₄	Te–Cl ax	2.455 (2.435)	Cl eq–Te–Cl eq	104.8 (103.7)
			Te–Cl eq	2.402 (2.294)	Cl ax–Te–Cl ax	152.7 (176.4)
9	AX ₃ E ₂	ClF ₃	Cl–F ax	1.699 (1.697)	F ax–Cl–F ax	169.7 (174.9)
			Cl–F eq	1.629 (1.597)		
10	AX ₂ E ₃	XeF ₂	Xe–F	2.039 (1.977)	F–Xe–F	180 (180)
11	AX ₆	SF ₆	S–F	1.553 (1.556)	F ax–S–F eq	90 (90)
12 ^a	AX ₅ E	BrF ₅	Br–F eq	1.805 (1.768)	F ax–Br–F eq	83.6 (85.0)
			Br–F ax	1.784 (1.699)	F eq–Br–F eq	89.3 (89.5)
13 ^b	AX ₄ E ₂	XeF ₄	Xe–F	1.765 (1.953)	F–Xe–F	90 (90.0)

^aMNDO-d used. ^bPM3 used.

ref 4 for a description of PM6). GAMESS contains both ab initio and semiempirical options. The great advantage of semiempirical methods is that they are much faster than ab initio methods. The advantage of ab initio methods is that for a sufficiently good basis set, they yield better energies and geometries than the semiempirical methods. In this exercise, MOPAC is used to determine geometries (computational time 1 s) to test predictions 1–6, whereas ab initio methods in GAMESS are used to calculate the lowest-energy geometries (computational time 2 min) to test predictions 7–9.

For ease of presentation, the PM6 method was used in geometry calculations with MOPAC, except for when that method failed to give sensible results (wrong point group or failure to reproduce qualitative trends). In that small number of cases, a note has been included to show the method used. The supporting information includes tables showing the optimal method for each molecule. The ab initio method used is MP2 because it accounts for most of the electron correlation energy that the simplest method (Hartree–Fock, HF) ignores (12), while giving results with sufficient speed and accuracy (13) for these student exercises. The input to the two programs was created using WebMO. The supporting information contains details of how to create the initial geometry with WebMO that the two programs use to generate the final geometry (MOPAC, Tables 1–3, 6–10) and energy (GAMESS, Tables 4 and 5).

Experimental and Calculated Results That Are Consistent with the VSEPR Model

Bond Lengths and Bond Angles for Common Homoleptic Systems

Examples of molecular systems dealt with in a standard introductory chemistry course in the study of VSEPR are shown in Table 1. Prediction 1 is supported by comparing entries 2 and 3 (decrease from ideal 120°); 4, 5, and 6 (decrease from ideal 109.5°); 7, 8, and 9 (decrease from ideal 120° and 180°); 11 and 12

Table 2. Effect of Electronegativity on Bond Angles and Bond Lengths

Entry	System	Example	Parameter	Calculated (Experimental)
1	AX ₃ E ^a	SbF ₃	F–Sb–F	92.6° (94.9°)
		AsF ₃	F–As–F	95.6° (95.9°)
		PF ₃	F–P–F	98.0° (97.7°)
		NF ₃	F–N–F	102.6° (102.4°)
2	AX ₃ E ^a	AsI ₃	I–As–I	111.3° (101.0°)
		AsBr ₃	Br–As–Br	103.3° (99.7°)
		AsCl ₃	Cl–As–Cl	100.3° (98.9°)
		AsF ₃	F–As–F	99.9° (96.0°)
3	AX _{4–n} Y _n	CH ₃ F	C–F	1.370 Å (1.383 Å)
		CH ₂ F ₂	C–F	1.357 Å (1.351 Å)
		CHF ₃	C–F	1.341 Å (1.328 Å)
		CF ₄	C–F	1.320 Å (1.318 Å)

^aAM1 used for all AX₃E.

(decrease of ax–eq angle from ideal 90°). Prediction 4 is supported by entries 7, 8, and 9. Prediction 5 is supported by entry 12. Although VSEPR correctly makes qualitative predictions of the direction of change of bond angles in all of these cases, the calculations show how well computational methods can give quantitative values to the bond lengths and bond angles.

Effect of Electronegativity on Bond Angles and Bond Lengths

Table 2 illustrates predictions 2 and 6. Entry 1 in Table 2 shows the increase in bond angle as the electronegativity of the central atom increases, whereas entry 2 shows the decrease in bond angle as the electronegativity of the substituent increases, as required by prediction 2. Entry 3 illustrates prediction 6; the C–F bond length gets shorter as more fluorine atoms replace hydrogen atoms. As well as confirming the qualitative predictions of the VSEPR model, the calculations again give good

Table 3. Effect of Multiple Bonds on Bond Angles

Entry	System	Example	Parameter	Ideal/deg	Calculated/deg (Experimental/deg)
1	AX ₂ Y	CCl ₂ O	Cl-C=O	120	125.0 (124.4)
			Cl-C-Cl	120	109.9 (111.3)
2	AX ₃ Y	PF ₃ O	F-P=O	109.5	118.5 (116.9)
			F-P-F	109.5	99.1 (101.1)
3		SF ₃ N	F-S≡N	109.5	125.3 (122.4)
			F-S-F	109.5	89.9 (94.0)
4	AX ₂ Y ₂	SO ₂ F ₂	O=S=O	109.5	126.8 (124)
			O=S-F	109.5	107.7 (108)
			F-S-F	109.5	94.3 (96)
5	AX ₄ Y	SF ₄ O	O=S-F eq	120	120.6 (124.9)
			O=S-F ax	90	100.5 (90.7)
			F eq-S-F eq	120	118.9 (110.2)
6	AX ₅ Y	IF ₅ O	O-I-F eq	90	96.8 (98.0)
			F eq-I-F eq	90	89.2 (88.9)

Table 4. Lone Pairs and Multiple Bonds Occupy Equatorial Positions

Entry	System	Example	Energy/hartrees	Equatorial Lone Pair or Multiple Bond	Point Group
1	AX ₄ E	SF ₄	-791.542	1	C _{2v}
			-791.520	0	C _{3v}
2	AX ₃ E ₂	ClF ₃	-754.105	2	C _{2v}
			-753.946	1 ^a	C _s
			-754.104	0	D _{3h}
3	AX ₂ E ₃	XeF ₂	-7398.582	3	D _{∞h}
			-7398.469	2 ^b	C _{2v} (90°)
			-7398.487	1 ^b	C _{2v} (120°)
4	AX ₄ Y	SF ₄ O	-866.019	1	C _{2v}
			-866.004	0	C _{3v}

^aIt was not possible automatically to optimize the geometry in this point group. The energy given here was obtained using the default geometry obtained from the molecule editor. ^bAssuming the default Xe-F bond lengths of 2.03 Å.

agreement with the actual values of bond angles and bond lengths.

Effect of Multiple Bonds on Bond Angles

Table 3 illustrates prediction 3; in each case the bond angles that involve a multiple bond are calculated to be larger than the ideal value, in agreement with experiment. The qualitative predictions of the VSEPR model are confirmed, with the calculations again giving good agreement with experiment.

Lone Pairs and Multiple Bonds Occupy Equatorial Positions

Table 4 illustrates predictions 7 and 8; namely, that lone pairs and multiple bonds occupy the equatorial positions. The 3-21G basis set was used with the MP2 method. Entries 1, 2, and 3 show that the geometry with the maximum number of lone pairs in the equatorial plane has the lowest energy and is therefore the preferred geometry. Entry 4 shows that the geometry with the double bond equatorial is the preferred geometry. These predictions made by computational methods agree with both the experimental observations and those of the VSEPR model, while improving on the model by providing bond lengths and angles (not shown).

Effect of the Less-Electronegative Substituent's Location on Molecular Energies of PF_{5-n}Cl_n Isomers

Prediction 9 says that the less-electronegative substituents occupy the equatorial positions. Table 5 shows the energies for various isomers of PF_{5-n}Cl_n. The restricted Hartree-Fock (RHF) method using the 6-31G(d) basis set was used for all calculations in this table because the MP2 method was too time-consuming and the default 3-21G basis set was not extensive enough for the small energy differences shown in some cases. This exercise is the most computationally demanding of those described, each geometry optimization needing about 2 min of CPU time on a standard desktop computer. The length of time it takes for a calculation to converge to the equilibrium geometry depends on how close the initial geometry is to the equilibrium geometry (14). Almost invariably, the semiempirical geometry is closer to the ab initio geometry than is the default molecule editor geometry; therefore, the ab initio calculations can be sped up by using the semiempirical geometry as input rather than the editor geometry. In each case, the lowest-energy structure has the maximum number of less-electronegative atoms in the equatorial plane, in agreement with prediction 9 and experiment. In addition to correctly predicting the

point group, these results go beyond the VSEPR model by providing bond lengths and bond angles (not shown).

Effect on Bond Angles of Having Lone Pairs and Multiple Bonds

Table 6 shows bond angles for examples where the central atom has lone pairs and double bonds, a situation where VSEPR makes no prediction. The lone-pair domain is larger than the multiple-bond domain in entries 1–3. Entry 4 has the angle involving the double bonds compressed by the lone-pair domain; however, the angles involving the single bond are bent *toward* the lone pair. Entries 5 and 6 show the double-bond domain being larger than the lone-pair domain. The experimental and calculated results show that no general statement is possible about the relative effects when a central atom contains both lone-pair domains and multiple-bond domains. Although VSEPR is unable to offer any help in the geometry of these molecules beyond correctly predicting the point group, computational methods improve on that by also giving trends that are in agreement with experiment.

Inconsistencies between VSEPR Predictions and Experimental and Calculated Results

Bond Angles in Trisubstituted Amines

Table 7 contains some examples of amines with bond angles that are larger than the ideal angle. VSEPR is not the only

technique that has problems with bond angles in amines; it is well documented that the PM3 method produces amine structures that are too strongly pyramidal (11, p 151). The observation of angles greater than the ideal angle has been ascribed to the less electronegative atoms in the ligands failing to localize the valence electrons on N, reducing their influence on the geometry so that ligand–ligand repulsions dominate with this small central atom and increase the angle above the ideal tetrahedral angle (9).

Effect of Electronegativity on Bond Angles for AX_2E_2 and AX_3E Systems

Table 8 shows examples where the more electronegative substituent has a larger bond angle than the less electronegative substituent, contrary to prediction 2. Failures of prediction 2 have been explained as resulting from the steric effect, which is well explained by the ligand close-packing model (15). The calculations correctly predict these trends in bond angles, in contrast to the predictions of the VSEPR model.

Axial versus Equatorial Bond Lengths in an AX_5Y System

Table 9 shows a comparison of axial and equatorial bond lengths where prediction 5 fails, the axial bond length is experimentally determined to be longer than the equatorial bond length in this case, as correctly predicted by the theoretical calculation.

Table 5. Energies of $PF_{5-n}Cl_n$ Isomers as a Function of Geometry

Molecule	Number of Equatorial Cl Atoms	Point Group	Energy/hartrees ^a
PF ₄ Cl	1	C _{2v}	-1198.0670
	0	C _{3v}	-1198.0603
PF ₃ Cl ₂	2	C _{2v}	-1558.0840
	1	C _s	-1558.0765
PF ₂ Cl ₃	0	D _{3h}	-1558.0690
	3	D _{3h}	-1918.1022
PFCl ₄	2	C _s	-1918.0937
	1	C _{2v}	-1918.0854
PFCl ₄	3	C _{3v}	-2278.1124
	2	C _{2v}	-2278.1029

^aThe small energy differences suggest that some of the molecules may be fluxional.

Table 7. X–N–X Bond Angles in Amines

Compound	Calculated/deg (Experimental/deg)
N(CH ₃) ₃	110.3 (110.9)
N(CF ₃) ₃	120.0 (117.9)
N(SiH ₃) ₃	120.0 (120.0)

Table 8. Effect of Electronegativity on Bond Angle

Entry	System	Compound	Calculated/deg (Experimental/deg)
1	AX ₂ E ₂	Cl ₂ O	111.3 (110.9)
		H ₂ O	107.6 (104.5)
2	AX ₃ E	PCl ₃	100.7 (100.1)
		PH ₃	100.4 (93.6)

Table 6. Angles for Molecules Containing Lone Pairs and Multiple Bonds

Entry	System	Example	Parameter	Ideal/deg	Calculated/deg (Experimental/deg)
1	AXYE	ClNO	O=N–Cl	120	118.6 (113.3)
2 ^a	AXYE	NSF	N≡S–F	120	115.8 (116.9)
3	AX ₂ YE	SOF ₂	O=S–F	109.5	107.8 (106.8)
			F–S–F	109.5	89.3 (92.8)
4 ^b	AX ₂ Y ₂ E	XeO ₂ F ₂	O=Xe=O	120	107.0 (105.7)
			lp–Xe–F	90	83.5 (87.4)
5 ^c	AX ₄ YE	XeOF ₄	O=Xe–F	90	94.1 (91.8)
6	AX ₂ E ₂	XeO ₂	O=Xe=O	109.5	123.9 (111.8) ^d

^aMNDO-d used. ^bMNDO used. ^cPM3 used. ^dThis molecule has not been experimentally observed. The value given here is the result of a very high level ab initio calculation (CCSD(T)) performed using an extended basis set to obtain a better predicted geometry than could be expected from the lower level ab initio methods used elsewhere in this exercise.

Table 9. Axial and Equatorial Bond Lengths

System	Compound	Parameter	Calculated/Å (Experimental/Å)
AX ₅ Y	IF ₅ O	I–F ax	1.784 (1.863)
		I–F eq	1.769 (1.817)

Table 10. Geometry Prediction

Entry	Compound	Geometry	Energy/eV
1	[AuCl ₄] [−]	square planar	−1569.54
		tetrahedral	−1568.88
2	[PtCl ₄] ^{2−}	square planar	−1462.50
		tetrahedral	−1460.85
3	cis-PtCl ₂ (NH ₃) ₂	square planar	−1392.02
		tetrahedral	−1387.34

Geometry of Some d⁸ Transition-Metal Complexes

VSEPR was introduced specifically to predict the geometry of discrete molecules in which the central atom is a main-group element. Transition-metal ions do not have any lone pairs in their valence shell; therefore, their geometry may be predicted using the rules for AX_n systems. This is frequently successful for transition-metal species; however, VSEPR does not predict the square-planar geometries exhibited by some d⁸ 16-electron low-spin transition-metal AX₄ compounds, nor the trigonal-prismatic geometries of some d⁰ transition-metal AX₆ compounds (16). Table 10 gives three examples of planar species that VSEPR predicts would be tetrahedral rather than square planar. The energies, calculated using MOPAC with the PM6 method, show that the square-planar geometry is the lowest-energy geometry, in agreement with experiment.

Summary

This article has described a wide-ranging set of exercises suitable for introductory and more advanced classes in inorganic chemistry in which freely available and visually attractive software is used to test and extend the applicability of the VSEPR model. The students who performed the exercise have been delighted to create such attractive pictures of molecules so easily and found the ability to test quantitatively the qualitative VSEPR predictions helpful to their understanding of the applicability of the model. Students working individually were able to obtain bond angles and bond lengths for all of the molecules in Table 1 in a single 3 h session, as well as rotating the molecules to decide if they had a nonzero dipole moment and sketching the molecules in their worksheets.

Note

1. Commercially available software such as Chem 3D Ultra, Gaussian, Molpro, and Spartan can also be used.

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Supporting Information Available

Instructions for using the WebMO interface to run calculations; the computational method that gave best agreement with experiment when it was not the PM6 method; hardware and software requirements; a detailed example; a bibliography referencing the source of all experimental data used in the paper. This material is available via the Internet at <http://pubs.acs.org>.