The VSEPR Model Revisited

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1 Introduction

It is now over thirty years since the basic ideas of the VSEPR model were first proposed in a review entitled 'Inorganic Stereochemistry'.[1] The name Valence Shell Electron Pair Repulsion (VSEPR) model was proposed in 1963[2] and a comprehensive survey of the use of the model for the prediction and rationalization of molecular geometry was first published in 1972.[3] In the subsequent years the model has continued to be very useful as a basis for the discussion and understanding of molecular geometry while at the same time its basic ideas have been reformulated to some extent, and considerable progress has been made in understanding its physical basis.[4–6] A new detailed account of the model and its many applications has recently been published.[7] The purpose of this review is to give a brief up-to-date account of the model, with emphasis on an improved reformulation of some of the basic ideas, together with some examples of new applications.

2 The Points-on-a-Sphere Model

The VSEPR model is based on the Lewis diagram for a molecule in which electrons are considered to be arranged in pairs that are either bonding (shared) pairs or non-bonding (lone or unshared) or pairs. The basic postulate of the VSEPR model is that the arrangement of the electron pairs in a valence shell is that which places them as far apart as possible or, more precisely, that maximizes the least distance between any two pairs. A simple model is to consider each electron pair as a point on the surface of a sphere surrounding the core of the atom. The arrangement of the points that maximizes the least distance between any pair of points gives the expected arrangement of the same number of electron pairs. For two electron pairs the arrangement is linear, for three it is triangular, for four it is tetrahedral, and for six it is octahedral (Figure 1). For five pairs of electrons both a square pyramid and a trigonal bipyramid, and any arrangement between, maximizes the least distance between any pair. But if we also make the reasonable assumption that the number of least distances is minimized the trigonal bipyramid is the preferred arrangement. It is assumed that the core of the atom is spherical and therefore has no effect on the arrangement of the valence shell electron pairs. This assumption is usually, but not always, valid for main group elements but not for the transition metals as discussed later.

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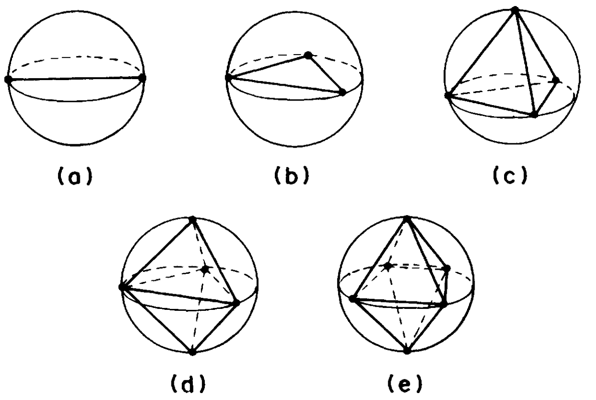


Figure 1 The-points-on-a-sphere model. Arrangements of points that maximize their distance apart: (a) linear arrangement of two points; (b) equilateral triangular arrangement of three points; (c) tetrahedral arrangement of four points; (d) trigonal bipyramidal arrangement of five points; (e) octahedral arrangement of six points.

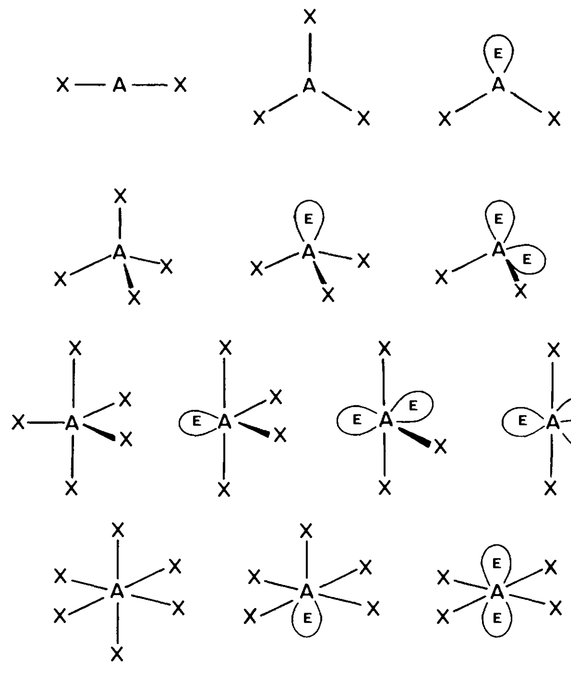


Figure 2 Predicted shapes for all molecules with a central atom A having up to six electron-pairs in its valence shell and a spherical core.

Each of the arrangements of three to six electron pairs can give rise to two or more molecular shapes, depending on how many of the electron pairs are non-bonding pairs. All the possible molecular geometries that can be derived in this way are summarized in Figure 2.

3 The Electron-pair Domain Model

Although the points-on-a-sphere model is useful for predicting the arrangements of a given number of electron pairs, it is more

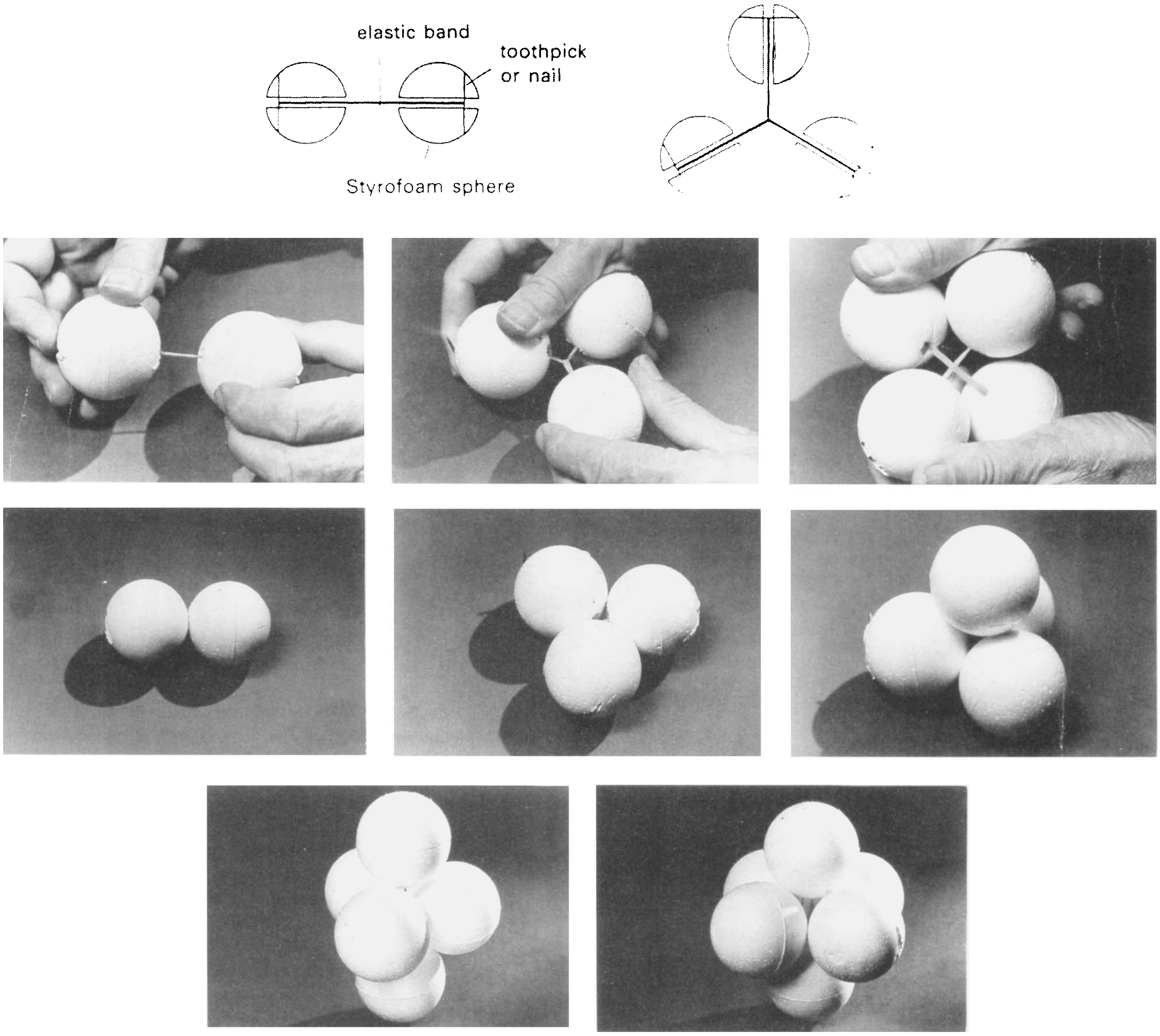


Figure 3 Styrofoam sphere models of electron-pair domain arrangements. Two or three styrofoam spheres are joined by elastic bands held in place by small nails or toothpicks. Each sphere represents an electron-pair domain. The elastic band models the electrostatic attraction of the positive core situated at the mid-point of the elastic band and the electron pairs. The spheres naturally adopt the arrangement shown. If they are forced into some other arrangement, such as the square planar arrangement of four spheres, they immediately adopt the preferred tetrahedral arrangement when the restraining force is removed.

realistic to consider an electron pair as a charge cloud that occupies a certain region of space and excludes other electrons from this space. That electrons behave in this way is a result of the operation of the Pauli exclusion principle, according to which electrons of the same spin have a high probability of being far apart and a low probability of being close together. As a consequence the electrons in the valence shell of an atom in a molecule tend to form pairs of opposite spin. To a first approximation, each pair may be considered to occupy its own region of space in the valence shell such that its average distance from other pairs is as large as possible.[3–7] We will call the space occupied by a pair of electrons in the valence shell of an atom an electron-pair domain. In its simplest form this model assumes that all electron-pair domains have a spherical shape, are the same size, and do not overlap with other domains. This model was first proposed by Kimball and by Bent[8,9] who called it the tangent-sphere model but we will call it the spherical domain model. These spherical domains (tangent-spheres) are attracted to the central positive core and adopt the arrangement that enables them to get as close as possible to the core, or, alternatively, that keeps them as far apart as possible if they are all at a given distance from the core. These arrangements can be demonstrated very simply. A styrofoam sphere is used to approximately represent the domain of an electron pair.[10] These spheres are then joined into pairs and triples by elastic bands (Figure 3). By twisting together the appropriate number of pairs and triples, arrangements of four, five, and six spheres can also be made. The elastic band represents the force of attraction between the nucleus imagined to be at the midpoint between the spheres. In each case, two to six spherical electron-pair domains adopt the same arrangements as predicted by the points-on-a-sphere model (Figure 3). If a model is distorted from its preferred arrangement a gentle shake will cause it to return to that arrangement.

Later we show that it is sometimes useful to use a better approximation for the shape of a domain such as an ellipsoid or a 'pear' or 'egg' shape.

The electron-pair domain version of the VSEPR model emphasizes the different sizes and shapes of the electron-pair domains rather than the relative magnitudes of lone-pair–lone-pair, lone-pair – bond-pair, and bond-pair – bond-pair repulsions.[1] The two versions of the model are equivalent and lead to the same predictions, but in general the domain version is simpler and easier to use. There would therefore be some advantage in replacing the acronym VSEPR with VSEPD standing for Valence Shell Electron Pair Domain.

4 Deviations from Regular Shapes

An important feature of the VSEPR model is that qualitative predictions about deviations from the bond angles and bond lengths corresponding to the regular geometries in Figure 2 can be made very easily. Deviations from the ideal bond angles and bond lengths may be attributed to differences in the sizes and shapes of electron-pair domains. For the valence shell of the central atom A in a molecule AX_mE_n, where X is a ligand and E is a lone pair, there are three important factors that influence the size and shape of an electron-pair domain:

(i) A bonding domain is subjected to the attraction of two positive cores and is shared between the valence shells of A and X whereas a non-bonding domain is entirely in the valence shell of A and spreads out around the core as much as it can. Thus a non-bonding domain is larger and occupies more space in the valence shell of A than a bonding-pair domain and is closer to the core than a bonding-pair domain.

(ii) Double- and triple-bond domains are composed of two and three electron-pairs, respectively, and are therefore larger than single-bond domains.

(iii) An increasing amount of electron density is drawn away from the valence shell of A and into the valence shell of the ligand X with increasing electronegativity of X. Thus the space occupied by a bonding domain in the valence shell of A decreases, and in the valence shell of X, increases with increasing electronegativity of X.

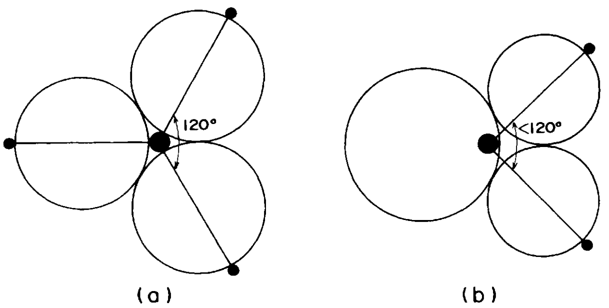


Figure 4 Lone pairs and bond angles: (a) equilateral triangular arrangement of three equivalent bonding domains with a bond angle of 120°; (b) triangular arrangement of two bonding domains and a lone-pair domain giving a bond angle of less than 120°.

Table 1 Bond angles (°) in AX_3E and AX_2E_2 molecules

AX_3E		AX_2E_2	
NH_3	107.2	H_2O	104.5
NF_3	102.3	F_2O	103.1
PF_3	97.7	SF_2	98.0
PCl_3	100.3	SCl_2	102.0
PBr_3	101.0	$S(CH_3)_2$	99.0
AsF_3	95.8	$Se(CH_3)_2$	96
$AsCl_3$	98.9	$TeBr_2$	104

5 Non-bonding or Lone Pairs

To a first approximation we may represent a lone-pair domain as a sphere that is larger than a bonding domain and which, because it is attracted only by one atomic core, tends to surround this core, and is therefore on average closer to the core than a bonding pair (Figure 4). As a consequence the bond angles in AX_3E molecules and AX_2E_2 molecules are smaller than the tetrahedral angle (Figure 4). Some examples are given in Table 1. Because it occupies more space and tends to surround the core a lone-pair domain tends to push adjacent bonding-pair domains away from the core thus increasing the bond lengths. This effect cannot be detected in AX_3E and AX_2E_2 molecules because all the bond lengths are affected equally. However, in AX_5E molecules the four bonds in the base of the square pyramid are closer to the lone pair than is the apical bond, consequently the four bonds in the base are longer than the apical bond (Figure 5). Some examples are given in Table 2.

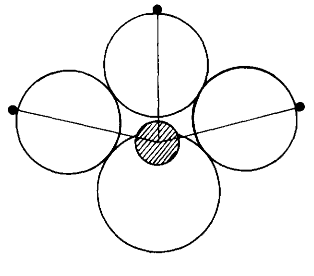


Figure 5 Lone pairs and bond lengths. A section passing through the lone pair and three ligands in an AX_5E molecule. The bonding domains adjacent to the lone-pair domain are pushed away from the central core more than the bonding domain *trans* to the lone pair. Thus the basal bonds are longer than the apical bond.

Table 2 Bond lengths (pm) and bond angles (°) in AX_5E square pyramidal molecules

	Bond lengths		Bond angle
	apical	basal	apical–basal
ClF_5	157	167	86
BrF_5	168.9	177.4	85.1
IF_5	184.4	186.9	83.0
$XeF_5^+(PtF_6^-)$	181.0	184.3	79
$(Rb^+)SF_5^-$	155.9	171.8	88
$(Na^+)TeF_5^-$	186.2	195.7	79
$(K^+)_2SbF_5^{2-}$	181.6	207.8	82
$(NH_4^+)_2SbCl_5^{2-}$	236	258 269	85

In a trigonal bipyramidal AX_5 molecule the equatorial positions have only two close neighbours at 90° whereas an axial position has three close neighbours at 90°. Thus an axial position is more crowded than an equatorial position. Consequently larger non-bonding domains are expected to occupy preferentially the equatorial positions. In all known AX_4E, AX_3E_2, and AX_2E_3 molecules the lone pairs do indeed occupy the equatorial positions. Some examples are given in Figure 6. The prediction of the shapes of AX_4E, AX_3E_2, and AX_2E_3 molecules in the first paper on the VSEPR model[1] involved counting the numbers of each kind of repulsion between electron pairs at 90°, ignoring the repulsions between electron pairs at 120°, and assuming that the relative magnitudes of electron-pair repulsions are:

lone-pair–lone-pair > lone-pair bond-pair > bond-pair bond-pair

This method also leads to the conclusion that the lone pairs occupy the equatorial positions. However, the electron-pair domain version of the VSEPR model in which a lone-pair domain is assumed to be larger than a bond-pair domain is simpler and leads directly to an unambiguous prediction of the structures of AX_4E, AX_3E_2, and AX_2E_3 molecules.

6 Multiple Bonds

A model of the ethene molecule that predicts its planar shape can be based on the tetrahedral arrangement of four electron-pair domains around each carbon atom with two bonding domains

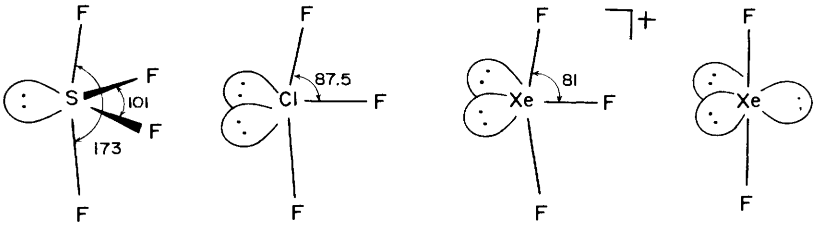


Figure 6 In molecules with five electron-pair domains in the valence shell of the central atom lone pairs always occupy the equatorial positions and never occupy the axial positions.

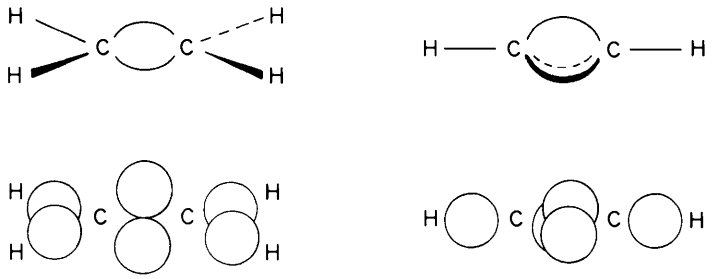


Figure 7 Geometry of ethene and ethyne: (a) bent-bond models; (b) electron-pair domain models.

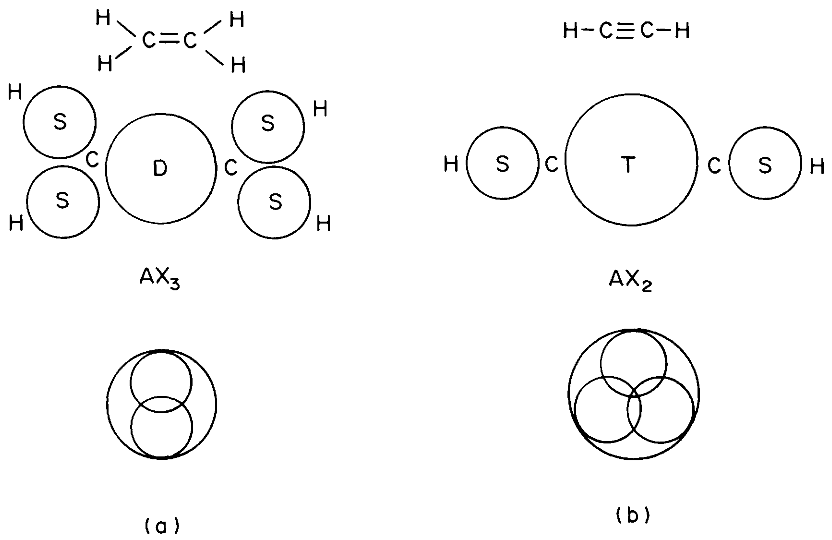


Figure 8 Multiple bond domains: (a) a double-bond domain and a model of ethene; (b) a triple-bond domain and a model of ethyne. S, single-bond domain; D, double-bond domain; T, triple-bond domain.

forming the double bond (Figure 7). This model corresponds to the classical bent-bond model for the double bond that is sometimes criticized because it appears to show that there is no electron density along the CC axis (Figure 7). But a bond diagram is only a very approximate representation of the electron distribution. The electron-pair domain model gives a better and less misleading, although still very approximate, representation of the electron distribution in ethene. The linear structure of ethyne is also predicted by the domain model in which both carbon atoms have a tetrahedral arrangement of four bonding domains in their valence shell (Figure 7).

The electron-pair domain model can be improved and also simplified by considering that the two electron-pair domains of a double bond are merged into one larger domain and that the three electron-pair domains of a triple bond are merged into one still larger domain (Figure 8). In ethene each of the two carbon atoms then has three domains in its valence shell, two single bond domains, and a double bond domain. These three domains adopt a triangular AX_3 arrangement giving a planar geometry around each carbon atom (Figure 8). In ethyne each carbon atom has only two domains in its valence shell, a single-bond domain and a triple-bond domain. These two domains adopt a linear AX_2 arrangement so that each carbon atom has a linear geometry (Figure 8). The shapes of some other related molecules containing double and triple bonds can be predicted in a similar manner as shown in Figure 9.

The otherwise very useful $\sigma - \pi$ model of the double bond cannot be used to predict the planar shape of the ethene molecule. The description of the bonds around each carbon atom in terms of sp^2 hybrid orbitals forming σ bonds plus a p orbital forming a π bond is based on the known geometry of the ethene molecule and so this description of the bonding cannot be used to predict the molecular geometry. The VSEPR model is the only simple model that predicts the planar geometry of the ethene molecule.

The above model of double- and triple-bond domains is particularly useful for discussing the structures of molecules in which there are more than four electron pairs in the valence shell of the central atom A. For example, according to this model SO_2

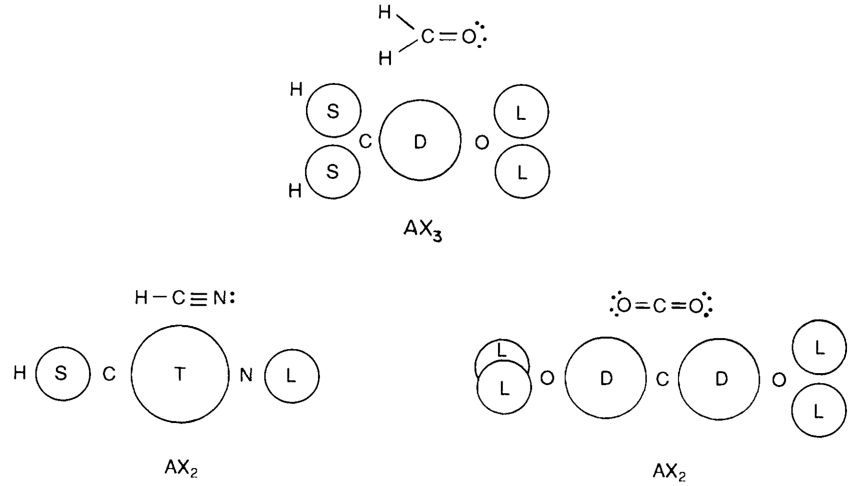


Figure 9 Electron-pair domain models of H_2CO, HCN, and CO_2. L, lone-pair domain.

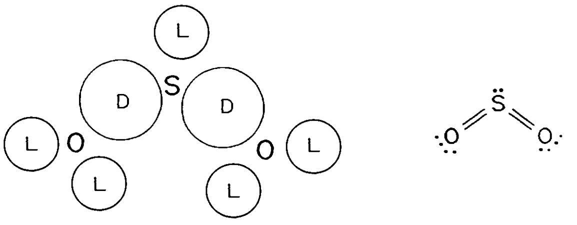


Figure 10 Electron-pair domain model of SO_2 in which the sulfur atom has an AX_2E geometry.

is an AX_2E molecule in which there is one lone-pair domain and two double-bond domains in the valence shell of sulfur (Figure 10). Other examples of molecules containing double and triple bonds are given in Table 3.

Because a double-bond domain is larger than a single-bond domain and a triple-bond domain is larger still, we expect that there will be deviations from the ideal bond angles in molecules containing double and triple bonds. In ethene we expect the angles between the double bond and the two CH bonds to be larger than 120° and the angle between the two CH bonds to be smaller than 120°. Experimental data for ethene, some substituted ethenes, and other molecules with an AX_3 geometry are given in Table 4. In each case the angle between the single bonds is less than 120° and the angle between a single bond and a double bond is greater than 120°. The experimentally determined bond angles for some AX_4 molecules containing multiple bonds are given in Table 5. In each case the db:db and db:sb angles are larger than the sb:sb angle.

In a trigonal bipyramidal molecule we expect a large double-bond domain preferentially to occupy one of the equatorial sites. All known trigonal bipyramidal molecules with a double-bonded ligand do indeed have the double-bonded ligand in an equatorial position. Some examples are given in Figure 11. The bond angles in these molecules are consistent with the larger size of the double-bond domain.

In the molecule $H_2C{=}SF_4$ the CH_2 group is perpendicular to the equatorial plane through the sulfur atom. This geometry is most easily accounted for in terms of the octahedral arrangement of six single electron-pair domains around the sulfur atom, two of which are used to form the S=C double bond (Figure 12). The tetrahedral arrangement of the four electron-pair domains in the valence shell of carbon then leads to the observed geometry.

The domain model of double and triple bonds can be improved by replacing the spherical shape with the more realistic prolate ellipsoidal 'egg' shape for a double bond and an oblate ellipsoidal 'doughnut' shape for a triple bond (Figure 13). In ethene the ellipsoidal double-bond domain minimizes its interactions with the other domains by having its long axis perpendicular to the plane of each CH_2 group so that the molecule has an overall planar shape (Figure 13). A cross-section through the calculated electron density of the ethene molecule perpendicular to the CC axis and through the mid-point of this axis has the expected ellipsoidal shape (Figure 13).[11]

An alternative model of the molecule $H_2C{=}SF_4$ can be based on a trigonal bipyramidal arrangement of five domains, one of which is an ellipsoidal double-bond domain. This double-bond domain will minimize its interactions with the other domains in the valence shell of sulfur by having its long axis in the equatorial plane, thus giving the observed molecular shape (Figure 14).

7 Ligand Electronegativity

A bonding domain can be conveniently represented by a non-spherical 'pear' or 'egg' shape when the electronegativity of X is not equal to that of A (Figure 15). In this figure also we represent the lone-pair domain as having an oblate ellipsoidal or 'doughnut' shape. The space occupied in the valence shell of A by the domain of a bonding pair decreases with increasing electronegativity of X. Thus in molecules with one or more lone pairs in the valence shell of A the bonding pairs are pushed closer together by the lone pair(s) as the electronegativity of X increases and so the angle between an AX bond and its neighbours decreases correspondingly. Some examples of the effect of the electronegativity of X on the bond angles in some AX_3E and AX_2E_2 molecules are give in Table 6.

In a trigonal bipyramidal molecule the larger domains of the bonds to less electronegative ligands will preferentially occupy the less crowded equatorial sites. Some examples are given in Figure 16.

8 Seven Electron-pair Domains

The prediction of the geometry of molecules in which there are more than six electron-pairs in the valence shell of the central atom A is less reliable than for molecules in which there are six or fewer electron-pairs in the valence shell. There may be several arrangements of points on a sphere that have similar least distances. In other words there may be alternative arrangements of the electron-pair domains that have similar energies. Differences in the sizes and shapes of the electron-pair domains may then cause an arrangement other than that predicted for equivalent domains to be favoured. Moreover, only small movements of the ligands through low energy barriers are required to convert one geometry into another when there are seven or more electron-pair domains in the valence shell, so that such molecules are often fluxional.

Despite the difficulty of making completely reliable predictions of geometry for molecules with more than six electron-pair

Table 3 Shapes of molecules containing multiple bonds

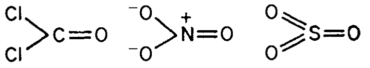
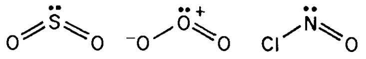
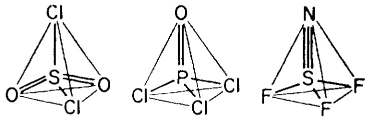
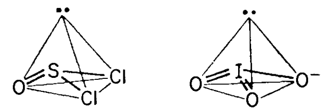
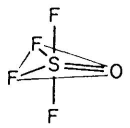
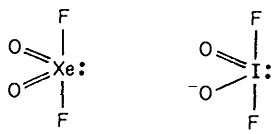
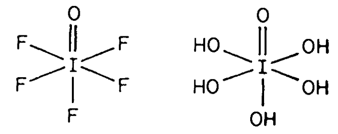
Domains	Arrangement	Bonding domains	Lone-pair domains	Molecular shape	
2	Linear	2	0	Linear	
3	Triangular	3	0	Triangular	
		2	1	V-Shape	
4	Tetrahedral	4	0	Tetrahedral	
		3	1	Trigonal pyramid	
		2	2	V-Shape	
5	Trigonal Bipyramid	5	0	Trigonal bipyramid	
		4	1	Disphenoid	
6	Octahedron	6	0	Octahedron	

Table 4 Bond angles in some molecules containing C=C and C=O double bonds

$X_2C{=}CY_2$	XCX	YCY	XCC	YCC
$H_2C{=}CH_2$	116.2	116.2	121.9	121.9
$F_2C{=}CH_2$	110.6	119.3	124.7	120.3
$F_2C{=}CF_2$	112.4	112.4	123.8	123.8
$Cl_2C{=}CCl_2$	115.6	115.6	122.2	122.2
$(CH_3)_2C{=}CH_2$	115.6	116.2	122.2	121.9

	XCX	XCO
H_2CO	116.5	121.7
Cl_2CO	111.8	124.1
F_2CO	107.7	124.1
HFCO	110	123

Table 5 Bond angles in AX_4 molecules containing multiple bonds

	sb–sb	sb–db (tb)		sb–sb	db–db
POF_3	101.3	117.7	F_2SO_2	96.1	124.0
$POCl_3$	103.3	115.7	Cl_2SO_2	100.3	123.5
$POBr_3$	104.1	115.0	$ClFSO_2$	99	123.7
PSF_3	99.6	122.7	$(NH_2)_2SO_2$	112.1	119.4
$PSCl_3$	101.8	117.2	$(CH_3)_2SO_2$	102.6	119.7
$PSBr_3$	101.9	117.1			
NSF_3	94.0	125.0			

domains in the valence shell of the central atom A, the VSEPR model can nevertheless make an important contribution to our understanding of the geometry of such molecules. Moreover, there is no other simple model that allows one to make comparable predictions. We discuss here some molecules with seven domains in the valence shell of A.

The arrangement of seven points on the surface of a sphere that maximizes the least distance between any pair of points is the monocapped octahedron (Figure 17a). But the monocapped trigonal prism and the pentagonal bipyramid have only slightly larger least distances and therefore have only slightly greater energies (Figure 17b, c). Among the compounds of the main group elements and transition metals with spherical cores AX_7 molecules are known with each of these geometries. For example $NbOF_6^{3-}$ has the 1:3:3 structure, NbF_7^{2-} and TaF_7^{2-} have the 1:4:2 structure, and IF_7 has the 1:5:1 structure. The pentagonal bipyramidal structure of iodine heptafluoride appears to be

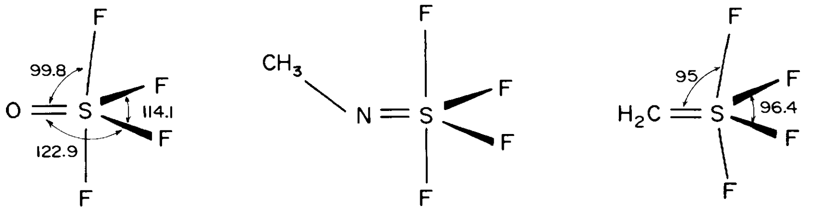


Figure 11 In trigonal bipyramidal AX_5 molecules a large double-bond domain always occupies an equatorial position.

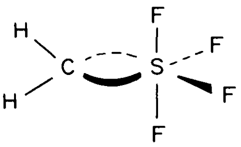


Figure 12 The bent-bond model of $H_2C{=}SF_4$ showing why the CH_2 group is perpendicular to the equatorial plane through sulfur.

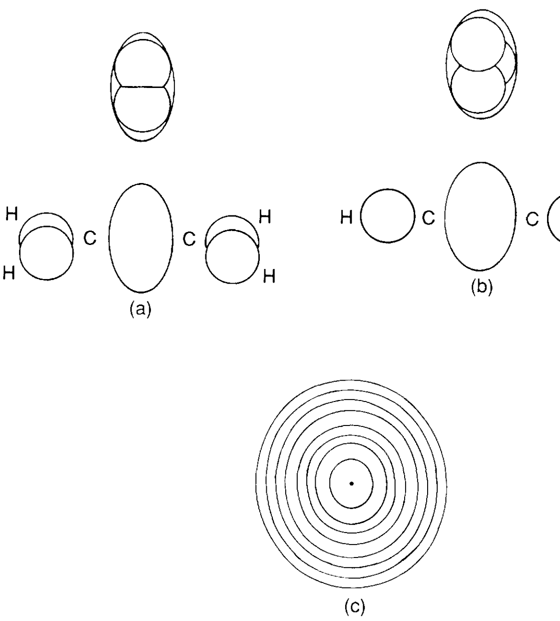


Figure 13 Multiple bond domains: (a) a prolate ellipsoidal double-bond domain and the corresponding model of ethene in which each carbon atom has a triangular AX_3 geometry; (b) an oblate ellipsoidal triple-bond domain and the corresponding model of ethyne in which each carbon atom has a linear AX_2 geometry; (c) a cross-section of the total electron density through the midpoint of the CC bond and perpendicular to this bond in the ethene molecule, showing contours of equal electron density.

slightly distorted by some buckling of the equatorial plane and the molecule is fluxional.[12]

If there are one or more lone-pair domains we expect these domains to occupy the least crowded positions. The monocapped octahedron or 1:3:3 arrangement has three non-equivalent sets of sites. The unique capping site has only three nearest neighbours and is therefore the least crowded site. So the lone pair in an AX_6E molecule is expected to occupy this site giving a distorted octahedral geometry for the molecule. Xenon hexafluoride is an AX_6E type molecule and it does indeed have a fluxional distorted octahedral geometry.[13]

We expect an AX_5E_2 molecule to have a structure in which both lone-pairs occupy sites that are less crowded than the remaining five. In the pentagonal bipyramid arrangement the two axial sites are less crowded than the five equatorial sites. The two axial sites have all their neighbours at 90° whereas each equatorial site has two close neighbours at 72°. So we expect the two lone-pairs to occupy the axial sites giving a planar pentagonal molecule. The XeF_5^- ion is an AX_5E_2 molecule and a recent structure determination[14] shows that it has a planar pentagonal geometry (Figure 18).

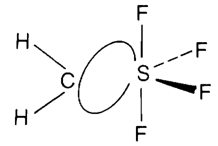


Figure 14 Model of the $CH_2{=}SF_4$ molecule with a prolate ellipsoidal double bond domain.

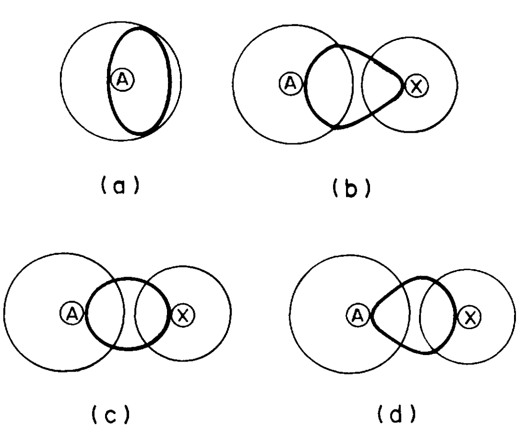


Figure 15 Electronegativity and bonding domain size. The space occupied by a bonding domain in the valence shell of the central atom A decreases with increasing electronegativity of the ligand X. (a) lone pair on A; (b) $\chi(X) < \chi(A)$; (c) $\chi(X) = \chi(A)$; (d) $\chi(X) > \chi(A)$.

Table 6 Effect of ligand electronegativity on bond angles

H_2O	104.5	F_2O	103.1				
SF_2	98.0	SCl_2	102.7				
NH_3	107.2	NF_3	102.3				
PI_3	102	PBr_3	101.0	PCl_3	100.3	PF_3	97.7
AsI_3	100.2	$AsBr_3$	99.8	$AsCl_3$	98.9	AsF_3	95.8

We similarly expect a double-bond domain to occupy an axial position in a pentagonal bipyramid. The ^{19}F NMR spectrum of a solution of IOF_6^- is consistent with five equatorial fluorines and an axial fluorine with a double-bonded oxygen presumably occupying the second axial position of a pentagonal bipyramid.[16,17]

A valence shell containing seven or more electron-pair domains is very crowded and appears only to be found for main group elements under two conditions: (a) The ligands are very electronegative, for example fluorine, so that the bonding domains in the valence shell of the central atom are small. (b) The central atom has a large valence shell and, in particular, is a fifth period element such as xenon.

Some molecules in which the central atom is from periods 3 and 4 and in which the ligands are less electronegative than fluorine do not, therefore, have sufficient space in their valence shell to accommodate six bonding domains and a large lone-pair

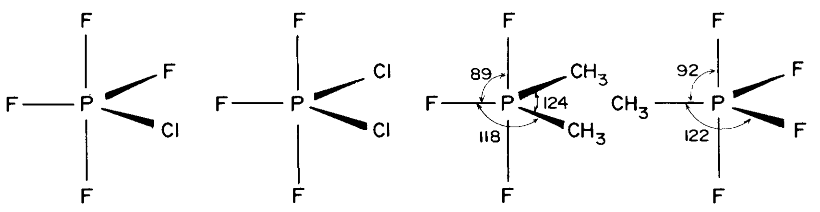


Figure 16 In molecules with five electron-pair domains in the valence shell of the central atom the smallest bonding domains and therefore the most electronegative ligands always occupy the axial positions.

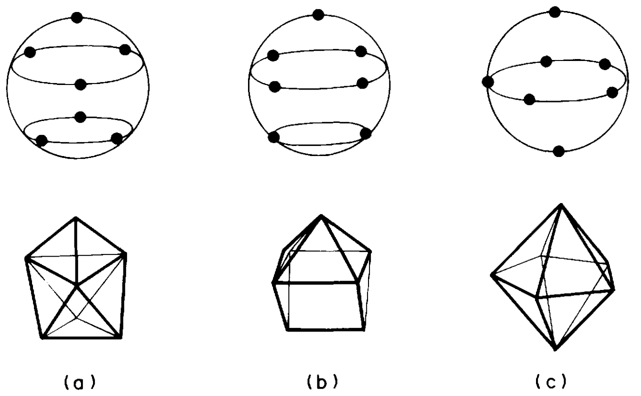


Figure 17 Arrangements of seven points on a sphere: (a) the monocapped octahedral or 1:3:3 arrangement; (b) the monocapped trigonal prism or 1:4:2 arrangement; (c) the pentagonal bipyramidal or 1:5:1 arrangement.

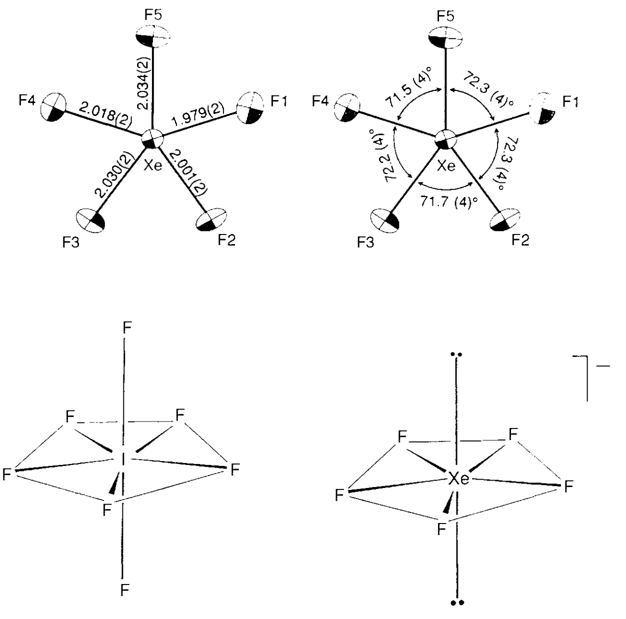


Figure 18 The pentagonal planar geometry of the XeF$_5^-$ ion and the (idealized) pentagonal bipyramidal geometry of the IF$_7$ molecule.

domain. In such molecules the lone pair is squeezed into a spherical domain surrounding the core and inside the bonding domains which therefore have an octahedral arrangement. Thus some AX$_6$E molecules such as SeCl$_6^{2-}$ and BrF$_6^-$ have a regular octahedral shape, but with longer than normal bonds. These and related molecules have been discussed in detail elsewhere.[2,3,7]

9 Non-spherical Cores

As it is usually presented in textbooks the VSEPR model is based, explicitly or implicity, on the assumption that the core beneath the valence shell of the central atom A is spherical and therefore has no influence on the geometry. There are, however, two cases in which this may not be the case: (a) When the core is very polarizable. (b) When the central atom A is a transition metal.

In this section we consider an example of the effect of a polarizable core on the shape of some main-group element molecules. Molecules of the transition metals are discussed in the following section.

There is good evidence that some dihalides of the group 2 metals are bent whereas they would be expected to have linear AX$_2$ structures. Experimental values for the bond angles in these molecules from gas-phase measurements at high temperature are given in Table 7. Although these molecules are rather flexible and the bond angles have not been determined with great accuracy it seems clear that the bent form is favoured for the heavier central atoms and lighter halogens.

Table 7 Bond angles (°) for the gaseous alkaline earth dihalides MX$_2$

M	X			
	F	Cl	Br	I
Be	180	180	180	180
Mg	180	180	180	180
Ca	133—155	180	173—180	180
Sr	108—135	120—143	133—180	161—180
Ba	100—115	100—127	95—135	103—105

If the outer shell of the core is completely filled, as it is for second and third period elements ($1s^2$ and $2s^22p^6$, respectively), we expect that the core will have a low polarizability and will be difficult to deform. However, for fourth and subsequent period elements, and in particular for Ca, Sr, and Ba, the spherical ns^2np^6 core has vacant d orbitals so it is much more polarizable than the core of a second or third period element such as Be or Mg and may be deformed by interaction with the bonding electron-pairs. It seems reasonable to suppose that in a dihalide of Ca, Sr, or Ba the repulsion between the two bonding electron-pairs and the eight electrons of the outer shell of the core causes these eight electrons to localize to some extent into four tetrahedrally arranged pairs. The two bonding pairs would tend to avoid these domains so that in the limit of a very strong interaction they would be located opposite two of the faces of the tetrahedron thus giving a bond angle of 109° (Figure 19). If the interaction with the core is weak then repulsion between the bond pairs will increase the bond angle which in the limiting case of a negligible interaction with the core will be 180°. The polarizability of the core increases from Be to Ba so there is an increasing tendency for the bond angle of the dihalides to decrease from Be to Ba. For the halide ligands the polarizability decreases and the charge density increases from the iodide to the fluoride, so we expect the interaction with the core electrons to increase from the iodide to the fluoride and the bond angle to decrease correspondingly.

10 Transition Metal Molecules

In most discussions of the VSEPR model it is assumed that it is not applicable to molecules of the transition metals unless they have d^0, d^5, or d^{10} configurations, because, for other configu-

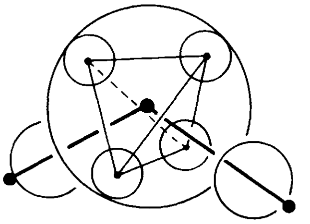


Figure 19 A bent AX_2 molecule such as CaF_2. The eight electrons of the outer shell of the ns^2np^6 core are to some extent localized into four tetrahedrally arranged pair domains. Interaction between the two bonding domains and the four core domains causes the molecule to be bent rather than linear.

rations, the assumption that the core is spherical is not valid. However, the VSEPR model can be used to predict the geometry of a transition metal molecule if it is assumed that for these *d* configurations the core has an ellipsoidal shape rather than a spherical shape.

An important feature of molecules of the transition metals that distinguishes them from molecules of the main-group elements is that there are no lone pairs in their valence shells. Any non-bonding electrons are *d* electrons from the penultimate shell. These *d* electrons may be considered to constitute a subshell that forms the outer layer of the core. Therefore the basic shapes of transition metal molecules are simply the AX_2, AX_3, AX_4, AX_5, and AX_6 shapes. These basic shapes are not distorted by spherical d^0, d^5 (five unpaired electrons) and d^{10} subshells as shown by the examples in Table 8.

Table 8 Shapes of transition metal molecules with d^0, d^5, and d^{10} spherical subshells

	Shape	Number of *d* electrons	Example
AX_2	Linear	10	$Ag(NH_3)_2$
AX_3	Equilateral	5	$FeCl_3(g)$
	Triangle	10	$Cu(CN)_3^{2-}$
AX_4	Tetrahedron	0	$TiCl_4$
		5	$FeCl_4^-$
		10	$ZnCl_4^{2-}$
AX_5	Trigonal	0	$NbCl_5$
	Bipyramid	5	$FeCl_5^{2-}$
		10	$CdCl_5^{3-}$
AX_6	Octahedron	0	WF_6
		5	CoF_6^{3-}
		10	$Zn(NH_3)_6^{2+}$

If the core is non-spherical the simplest assumption that we can make about its shape is that it is ellipsoidal, either prolate or oblate. The core may have a more complex shape in some cases but an ellipsoidal shape appears to be a reasonable approximation in most cases and it allows us correctly to predict the shapes of many molecules. An ellipsoidal shape is expected, for example, for a d^9 configuration. Removing an electron from a $d_{x^2-y^2}$ orbital or a d_{z^2} orbital in a spherical d^{10} subshell gives a prolate or an oblate ellipsoidal core respectively (Figure 20). It cannot be predicted whether a non-spherical *d* subshell will have an oblate or a prolate ellipsoidal shape but this same problem arises in a more conventional treatment in which the direction of a Jahn–Teller distortion cannot be predicted.

10.1 AX_4 Molecules

Figure 21 shows how an ellipsoidal core distorts the tetrahedral AX_4 geometry. An oblate ellipsoid will cause an elongation of the tetrahedral geometry but this type of distortion has not been observed. A prolate ellipsoid distorts the tetrahedral geometry to a disphenoid and in the limit to a square planar geometry. The disphenoidal geometry is rare but an example is provided by the $CuCl_4^{2-}$ ion in Cs_2CuCl_4 that has bond angles of 104° and 120° compared with 109.5° for the tetrahedral geometry and 90° and 180° for the square planar geometry. There are many examples of square planar molecules in which the transition metal has a d^8 subshell, such as $Ni(CN)_4^{2-}$, $PdCl_4^{2-}$, $Pd(NH_3)_4^{2-}$, $Pt(CN)_4^{2-}$, $PtCl_4^{2-}$, and $AuCl_4^-$.

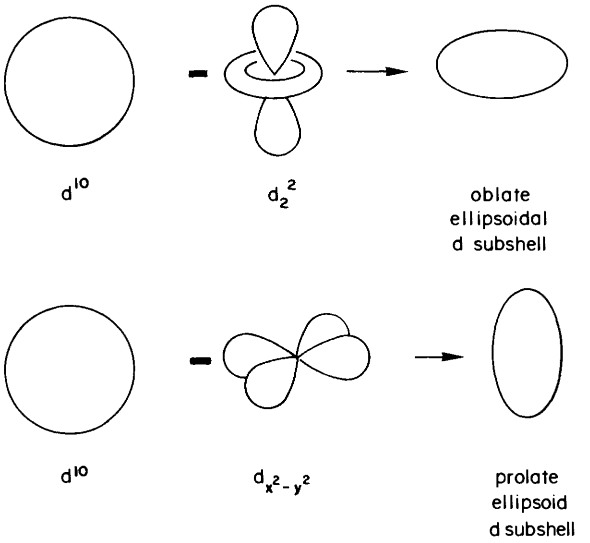


Figure 20 (a) Removing a d_{z^2} electron from a spherical d^{10} subshell gives an oblate ellipsoidal *d* subshell; (b) removing a $d_{x^2-y^2}$ electron from a spherical d^{10} subshell gives a prolate ellipsoidal *d* subshell.

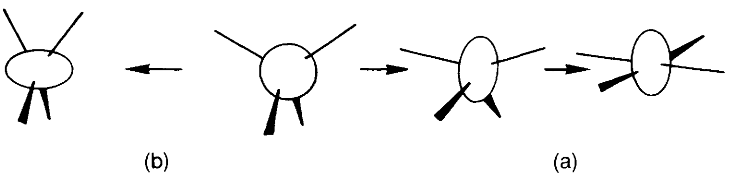


Figure 21 Distortion of the tetrahedral AX_4 geometry by an ellipsoidal *d* subshell. (a) A prolate ellipsoid produces a disphenoid that may be described as a 'flattened' tetrahedron and in the limit a square plane; (b) an oblate ellipsoid produces a disphenoid that may be described as an 'elongated' tetrahedron.

10.2 AX_6 Molecules

Figure 22 shows how an ellipsoidal core distorts the octahedral AX_6 geometry. An oblate ellipsoid causes a flattening of the octahedron while a prolate ellipsoid causes the more commonly observed elongation of the octahedron, which in the limit gives a square planar AX_4 geometry with the loss of two ligands. Some examples of tetragonally distorted octahedral geometry in some d^9 copper compounds are given in Table 9. Many other examples are known.[2,7]

10.3 AX_5 Molecules

Transition metal molecules of this type exhibit a number of interesting and instructive features as do AX_5 molecules of the main group elements. Figure 23 shows how the trigonal bipyramidal AX_5 geometry is distorted by an ellipsoidal core. In all trigonal bipyramidal molecules with a spherical core the axial bonds are longer than the equatorial bonds because of the greater crowding in the axial sites compared to the equatorial sites. An oblate ellipsoidal core repels the axial bond domains less than the equatorial domains thus reducing the normal difference in the axial and equatorial bond lengths. This difference may be reduced to zero, or even reversed to give longer equatorial than axial bonds (Table 10).

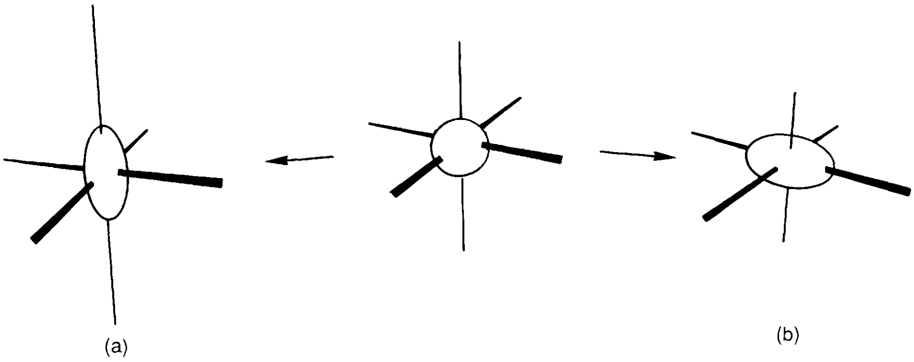


Figure 22 Distortion of the octahedral AX_6 geometry by an ellipsoidal *d* subshell. (a) A prolate ellipsoid produces a square bipyramid that may be described as an elongated octahedron; (b) An oblate ellipsoid produces a square bipyramid that may be described as a 'flattened' octahedron.

Table 9 Bond lengths (pm) in some tetragonal d^9 copper compounds

Elongated octahedron (prolate ellipsoidal *d*-shell)			Flattened octahedron (oblate ellipsoidal *d*-shell)		
CuF_2	193	227	$KCuF_3$	196	207
Na_2CuF_4	191	237	K_2CuF_4	195	208
$(NH_4)_2Cl_4$	231	279			
$CuCl_2$	230	295			
$KCuCl_3$	229	303			

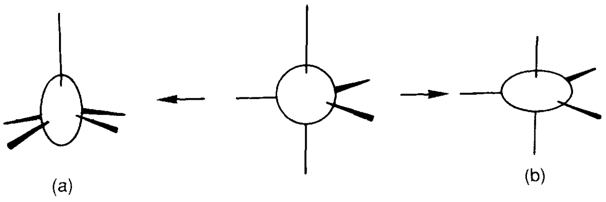


Figure 23 Distortion of the AX_5 trigonal bipyramidal geometry by an ellipsoidal *d* subshell. (a) A prolate ellipsoid stabilizes the square pyramidal geometry with respect to the trigonal bipyramid; (b) an oblate ellipsoid decreases the axial bond lengths and increases the equatorial bond lengths of the trigonal bipyramid.

A prolate ellipsoidal core will destabilize the trigonal bipyramid with respect to the square pyramid which even for spherical cores has only a slightly higher energy. Therefore we expect some AX_5 molecules of the transition metals to have a square pyramidal geometry as is observed (Table 10). The geometry of these molecules differs in an important way from AX_5E square pyramidal molecules of the main-group elements. In the latter the four bonds in the base of the square pyramid are longer than the apical bond (Figure 5) but in the AX_5 square pyramidal molecules of the transition metals interaction with a prolate ellipsoidal core causes the apical bond to be longer than the equatorial bonds (Table 10).

Thus although we cannot predict which AX_5 molecules of the transition metals will have a trigonal bipyramidal shape and which will have a square pyramidal shape we can make some useful predictions about the deviations from these ideal shapes that show interesting differences from main group molecules with the same basic shape.

In general the basic shapes of the molecules of the transition metals follow directly from the VSEPR model and distortions of these shapes by a non-spherical core can be readily predicted on the basis of the assumption that the core (or *d* subshell) is not spherical but has either a prolate or an oblate ellipsoidal shape.

Table 10 Bond lengths (pm) in AX_5 molecules of the transition metals

	Trigonal Bipyramid Molecules	
	Axial	Equatorial
$Fe(CO)_5$	181	183
$Co(CNCH_3)_5^+$	184	188
$Pt(SnCl_3)_5^{3-}$	254	254
$Ni(CN)_5^{3-}$	184	190
$CuCl_5^{3-}$	230	239
	Square Pyramid Molecules	
	Apical	Basal
$MnCl_5^{3-}$	258	230
$Ni(CN)_5^{3-}$	217	186
$RuCl_2(PPh_3)$, Ru–P	239	223
$PdBr_2(PPh_3)_3$, Pd–Br	293	252
$TriarsNiBr_2$, Ni–Br	269	237

11 Postscript

The VSEPR model remains the simplest and most reliable qualitative method for predicting molecular geometry. It is not based on any orbital model, and in general for the qualitative discussion of molecular geometry it is superior to such models. The VSEPR model may be expressed in orbital terms by representing each electron-pair domain by an appropriate localized (hybrid) orbital, such as an sp^3 orbital. However, it is not necessary to express the VSEPR model in orbital terms and indeed there is little advantage in doing so. The VSEPR domain model gives a very approximate description of the electron distribution in a molecule that is based on the role of the Pauli exclusion principle in determining the electron density distribution. This very approximate description of the electron density of a molecule is, moreover, consistent with accurate electron density distributions calculated by *ab initio* methods and, in particular, with the analysis of such distributions in terms of the Laplacian of the electron density.[4–7] Although theoretical calculations[17] show that, in general, electrons are not as localized into discrete pairs as the VSEPR model assumes, the Laplacian shows that there are local concentrations of electron density that have all the properties of relative size and location that are ascribed to the electron-pair domains of the VSEPR model.[4–7]

12 References

1 R. J. Gillespie and R. S. Nyholm, *Quart. Rev. Chem. Soc.*, 1957, **11**, 339.
2 R. J. Gillespie, *J. Chem. Educ.*, 1963, **40**, 295.
3 R. J. Gillespie, 'Molecular Geometry', Van Nostrand Reinhold, London, 1972.
4 R. F. W. Bader, P. J. MacDougall, and C. D. H. Lau, *J. Am. Chem. Soc.*, 1984, **106**, 1594.

5 R. F. W. Bader, R. J. Gillespie, and P. J., MacDougall, *J. Am. Chem. Soc.*, 1988, **110**, 7320.

6 R. F. W. Bader, R. J. Gillespie, and P. J. MacDougall, in 'From Atoms to Polymers: Isoelectronic Analogies' in Vol. 11 of 'Molecular Structure and Energetics', ed. J. F. Liebman, and A. Greenberg, VCH, 1989.

7 R. J. Gillespie, and I. Hargittai, 'The VSEPR Model of Molecular Geometry', Allyn and Bacon, Boston, 1991; Prentice Hall International, London, 1991.

8 G. E. Kimball, References to unpublished work by Kimball and his students are given by H. A. Bent (reference 9).

9 H. A. Bent, *J. Chem. Educ.*, 1963 **40**, 446, 523; 1965, **42**, 302, 348; 1967, **44**, 512, 1968, **45**, 768.

10 R. J. Gillespie, D. A. Humphreys, N. C. Baird, and E. A. Robinson, 'Chemistry', 2nd Edn., Allyn and Bacon, Boston, 1989; Prentice Hall International, London, 1989.

11 R. F. W. Bader, T. S. Slee, D. Cremer, and E. Kraka, *J. Am. Chem. Soc.*, 1983, **105**, 5061.

12 J. W. Adams, H. B. Thompson and L. S. Bartell, *J. Chem. Phys.*, 1970, **53**, 4040.

13 L. S. Bartell, R. M. Gavin, and H. B. Thompson, *J. Chem. Phys.*, 1965, **42**, 2547; L. S. Bartell and K. M. Gavin, *J. Chem. Phys.*, 1968, **46**, 2466.

14 K. O. Christe, E. C. Curtis, D. A. Dixon, H. P. Mercier, J. C. P. Sanders, and G. J. Schrobilgen, *J. Am. Chem. Soc.*, 1991, **113**, 3351.

15 K. O. Christe, J. C. P. Sanders, G. J. Schrobilgen, and W. W. Wilson, *J. Chem. Soc., Chem. Commun.*, 1991, 837.

16 A. R. Mahjoub, A. Hoser, J. Fuchs, and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1526.

17 R. F. W. Bader, and M. E. Stephens, *J. Am. Chem. Soc.*, 1975, **97**, 7391. R. F. W. Bader, 'Atoms in Molecules: A Quantum Theory', Oxford University Press, Oxford, 1990.