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TEACHING THE VSEPR MODEL AND ELECTRON DENSITIES

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ABSTRACT: This paper gives a simple pictorial introduction to the VSEPR model of molecular geometry and its physical basis: the Pauli exclusion principle. The treatment of the VSEPR model range from a simple empirical set of rules to help freshmen students predicting the geometry of molecules to more advanced treatments based on a careful analysis of the electron density (for advanced undergraduate or graduate students). The density can be readily calculated using *ab initio* or density functional theory (DFT) methods and it can also be obtained experimentally by X-ray crystallography. Unlike an orbital model of a molecule, the electron density is a physical observable. There are therefore advantages in interpreting the electron density to obtain information about bonding, advantages which are not as widely appreciated as they deserve to be. We also give a simple introduction to the quantum theory of Atoms in Molecules (AIM) and of its analysis of the electron density. We show how it provides a clear, rigorous and unambiguous definition of an atom in molecule that can be used as the basis for calculating the charge of the atom and indeed any of its other properties. [*Chem. Educ. Res. Pract. Eur.*: 2001, 2, 73-90]

KEY WORDS: *VSEPR; Pauli principle; electron density; atoms-in-molecules (AIM); bonding theory; atomic properties; quantum chemistry; theoretical chemistry.*

INTRODUCTION

Students usually begin their study of bonding and molecular geometry with Lewis structures and the VSEPR model. Both are very approximate models of the distribution of the electrons, that is of the electron density in a molecule. Now that electron densities can be easily calculated by *ab initio* and density functional theory (DFT) methods using readily available programs it is important to bring them into the discussion of bonding and molecular geometry at the undergraduate level. Because the electron density is an experimentally accessible real physical property of a molecule it has the advantage of being more readily understood by a student than are orbitals which are abstract mathematical functions that have no direct physical meaning.

Although the VSEPR model is so well known it has not always been correctly presented and as a consequence of its development over the years it has a number of features that are not widely appreciated. The purpose of this article is to draw attention to these features and to discuss the relationship of the VSEPR model to the electron density. The VSEPR model can be taught at various levels and with increasing sophistication from high school and beginning university general chemistry courses to higher level inorganic chemistry and quantum chemistry courses.

THE PAULI PRINCIPLE

The fundamental basis for the VSEPR model is provided by the Pauli principle and not by electrostatics. The fundamental assumption of the model is that the electron pairs in the valence shell of an atom keep as far apart as possible, in other words they appear to repel each other. Electrons exhibit this behavior as a consequence of the Pauli exclusion principle of same spin electrons and not primarily as a consequence of their electrostatic repulsion. The role of the Pauli principle was clearly stated in the first papers on the VSEPR model (Gillespie & Nyholm, 1957; Gillespie & Nyholm, 1958) but this role has sometimes been ignored and the model has been incorrectly presented in terms of electrostatics.

Because the Pauli principle may not be easily understood by beginning students the model is best taught at the beginning level simply as an empirical model. Starting with Lewis structures we add the rule that the electron pairs in a valence shell, both bonding and non-bonding, behave as if they repel each other and therefore keep as far apart as possible; three pairs forming a planar triangle, four pairs a tetrahedron, five pairs a trigonal bipyramid and six pairs an octahedron. This basic rule provides a rationale for many different basic molecular shapes. To explain the deviations of the bond angles in molecules with lone pairs from the angles in the regular polyhedra we need to add the additional rule that electron pair repulsions increase in magnitude in the order bond pair - bond pair < bond pair - lone pair < lone pair - lone pair. On the basis of these two simple rules we get a rationale for the overall geometry and the bond angles in a large number of AX_nE_m molecules where A is the central atom, X a ligand, and E a lone pair.

To go further than this we need to go a little more deeply into the physical basis of the model. First we need to understand the role played by the Pauli principle. In its most general form this can be stated as follows:

- (1) *The wave function for an electronic system must be antisymmetric to electron interchange.*

In this form the Pauli principle cannot be understood by students who have not studied quantum mechanics and its consequences for the distribution of electrons in a molecule is not apparent. Even before they take a course in quantum mechanics beginning university students are, however, introduced to the idea that the electrons in a molecule are in constant motion and that according to quantum mechanics we cannot determine the path of any one electron but only the probability of finding an electron in an infinitesimal volume surrounding any particular point in space. It can be shown that a consequence of the Pauli principle is that

- (2) *Electrons with the same spin have a zero probability of being found simultaneously at the same point in space, a low probability of being found close together, and are most probably to be found as far apart as possible.*

The more generally familiar forms that are usually presented to beginning students in their study of the orbital model for atoms:

- (3) *No more than two electrons, which must be of opposite spin, can occupy an orbital.*
- (4) *No two electrons can be described by the same four quantum numbers.*

also follow from the more fundamental statement (1). The concept of electron spin and the Pauli principle were first found necessary to account for atomic spectra and generally for the

behavior of electrons. These do not follow directly from the Schrodinger formulation of quantum mechanics but they were simply incorporated into this formulation. Later Dirac found that spin and the Pauli principle arise naturally in his relativistic treatment of quantum mechanics. Statement (2) is the most convenient for discussing the physical basis of the VSEPR model and understanding electron densities. In Appendix I we show how statement (2) follows from the statement (1) of the Pauli principle.

Let us consider the common case of a valence shell containing eight electrons, four of one spin (α) and four of opposite spin (β). Because same spin electrons keep as far apart as possible the *most probable relative location* of the four α electrons is at the vertices of a tetrahedron which, in a free atom, may have any orientation in space. Similarly the most probable location of the four β electrons is at the vertices of another tetrahedron which may take any orientation with respect to the tetrahedron of α electrons so that there is an equal probability of finding an electron anywhere in the valence shell of the atom (Figure 1). Thus any free atom or monoatomic ion with an octet of electrons in its valence shell, such as Ne, F^- and O^{2-} has a spherical total electron density (as does any other free atom or monoatomic ion or radical of course). However, in a molecule in which a central atom is forming bonds to two or more ligands, the attraction of the nuclei of the combining atoms causes the α and β tetrahedra to come into approximate coincidence thereby increasing the probability that a pair of electrons will be found in the two bonding regions and also in the other two tetrahedral directions, that is the lone pair directions (Figure 1). Consequently the electron density is no longer spherical.

There are four regions of enhanced electron density corresponding to the four electron pairs and regions of diminished electron density between these regions. It should be noted that pairs of electrons of opposite spin are not formed because of any special attraction between opposite spin electrons. Indeed all electrons repel each other electrostatically. As we have seen there are no electron pairs in a free atom or ion with an octet of electrons. Pairs of opposite spin electrons are only formed by the attraction of the cores of ligand atoms. This attraction overcomes the electrostatic repulsion between the electrons and pulls two electrons of opposite spin into a bonding region. The Pauli principle prevents the formation of pairs of same spin electrons (Gillespie, 2000; Gillespie & Hargittai, 1991; Gillespie & Popelier, 2001; Gillespie & Robinson, 1996).

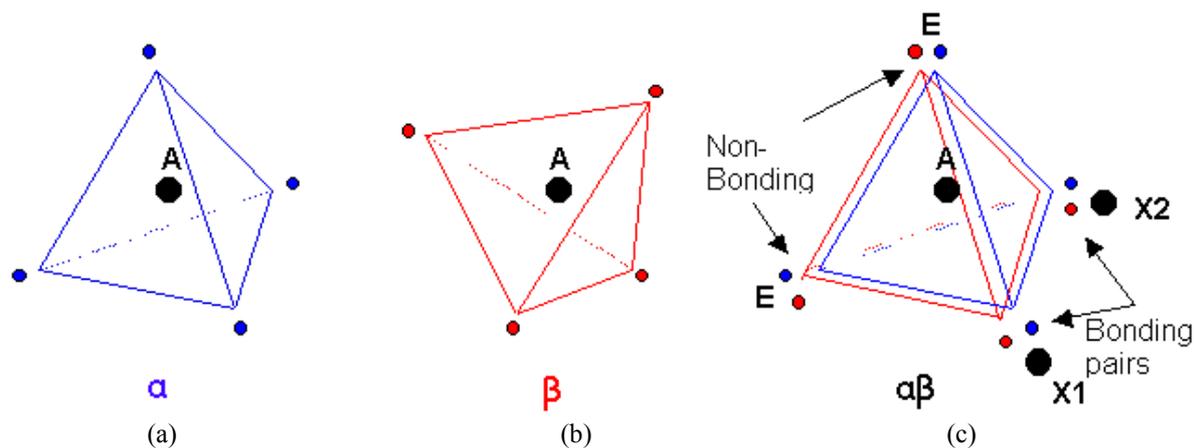


FIGURE 1. Pauli principle for octet. (a) The most probable relative arrangement of four α -spin electrons. (b) The most probable relative arrangement of four β -spin electrons. Both arrangements may adopt any relative orientation in space. (c) In the presence of the nuclei of two combining ligands ($X1$, and $X2$), as in H_2O or SCl_2 , the two tetrahedra are brought into approximate coincidence at the two bonding apexes (sufficient to bring all of the four apexes into coincidence) forming two bonding pairs and two non-bonding pairs (E).

ELECTRON PAIR DOMAINS

The simplest form of the VSEPR model postulates that eight electrons in a valence shell form four pairs with a tetrahedral arrangement. But we have just seen that there are not four fully localized lone pairs, rather there are four regions where there is an enhanced probability of finding an electron pair. It is convenient to call a region where there is a high probability of finding an electron pair an electron pair domain (Gillespie, 2000; Gillespie & Hargittai, 1991; Gillespie & Popelier, 2001; Gillespie & Robinson, 1996). An electron pair domain extends around the most probable position of the electron pair as determined by the Pauli principle, the probability of finding an electron pair decreasing with increasing distance from the most probable position. We can think of each domain as having a boundary at some arbitrary value of the probability of finding an electron pair. Although, clearly, this not a rigorous definition of a domain we can usefully assign these domains relative sizes and approximate shapes. A lone pair domain can be thought of as generally larger than a bonding domain and also more spread out round the nucleus because the electrons are subject to the attraction of only one nucleus rather than two, as illustrated for the ammonia molecule in Figure 2.

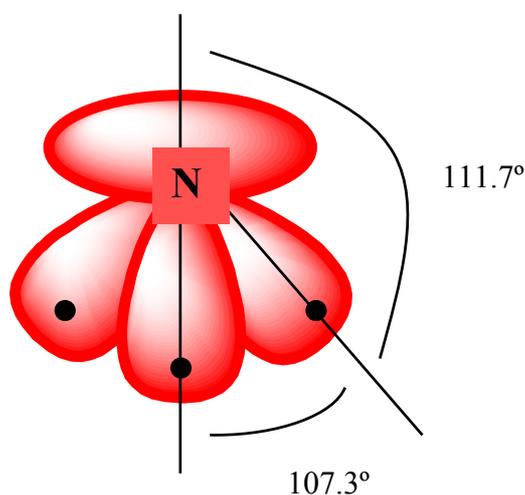


FIGURE 2. Representation of the bonding and nonbonding electron pair domains in an AX_3E molecule (ammonia).

A bonding domain takes up less space in the valence shell of the central atom because it is stretched out toward the ligand. These differences in the relative sizes and shapes of lone pair and bonding pair domains provide a rationale for the relative sizes of the bond angles around a central atom in molecules with lone pairs that is an alternative to the purely empirical rule that electron pair repulsion increase in magnitude in the order bond pair - bond pair < bond pair - lone pair < lone pair - lone pair. The angles between ligands are always smaller than the angles involving lone pairs so that the bond angles in AX_3E and AX_2E_2 are predicted to be < 109.5° as we see in Tables 1 and 2. Moreover, the greater the electronegativity of the ligand atom and the smaller the electronegativity of the central atom the less space the bonding domain occupies in the valence shell of the central atom (Figure 3). Thus, bond angles decrease with increasing electronegativity of the ligands and decreasing electronegativity of the atom A as we can see from the examples in Table 1 and 2.

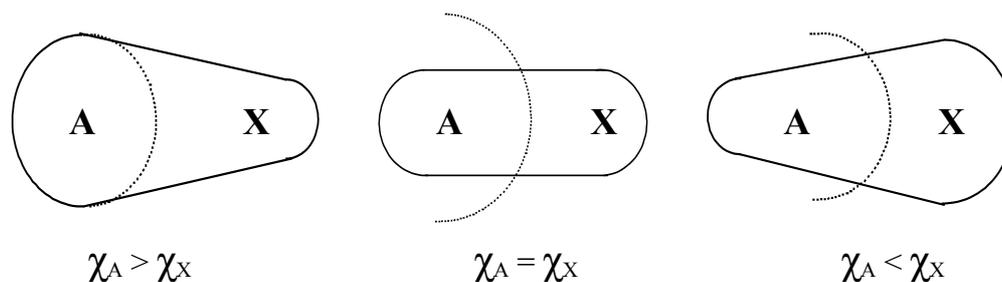


FIGURE 3. The size of a bonding pair domain in the valence shell of A decreases with increasing electronegativity (χ) of X.

TABLE 1. Bond angles in selected trigonal pyramidal AX_3E molecules.

Molecule	Bond Angle ($^\circ$)	Molecule	Bond Angle ($^\circ$)
NH ₃	107.3	PBr ₃	101.1
PH ₃	93.8	AsBr ₃	99.8
AsH ₃	91.8	SbBr ₃	98.2
SbH ₃	91.7	PI ₃	102
NF ₃	102.2	AsI ₃	100.2
PF ₃	97.8	SbI ₃	99.3
AsF ₃	96.1	NMe ₃	110.9
SbF ₃	87.3	PMe ₃	98.6
NCl ₃	107.1	AsMe ₃	96.0
PCl ₃	100.3	SbMe ₃	94.2
AsCl ₃	98.6	SF ₃ ⁺	97.5
SbCl ₃	97.2	SeF ₃ ⁺	94.5

TABLE 2. Bond angles in selected trigonal pyramidal AX_2E_2 molecules.

Molecule	Bond Angle ($^\circ$)	Molecule	Bond Angle ($^\circ$)
H ₂ O	104.5	ClF ₂ ⁺	96
H ₂ S	92.3	BrF ₂ ⁺	92
H ₂ Se	90.6	ICl ₂ ⁺	93
H ₂ Te	90.3	HOCl	97.3
OF ₂	103.1	HOCl	102.5
SF ₂	98.2	CF ₃ OF	104.8
SeF ₂	94	CH ₃ OH	108.6
OCl ₂	111.2	CH ₃ SH	96.5
SCl ₂	102.8	CH ₃ SeH	95.5
SeCl ₂	99.6	CH ₃ SCl	98.9
TeCl ₂	97.0	CF ₃ SF	97.1
OMe ₂	111.7	CF ₂ SCl	98.9
SMe ₂	99.1	NH ₂ ⁻	99.4
SeMe ₂	96.3	NF ₂ ⁻	96.7

It is important to understand that electrons are not always paired. We have seen that in a free atom the tetrahedron of α electrons may have any orientation with respect to the tetrahedron of β electrons so that there is no formation of pairs and the total electron density is spherical. Although it is sometimes convenient to depict free atoms or ions such as Ne, F^- , and O^{2-} as having four pairs of electrons, this is strictly speaking not correct. Similarly, in the valence shells of any singly bonded ligand not all the electrons are formed into pairs as was first pointed out by Linnett (Linnett, 1964). For example, in the HF molecule, the tetrahedra of α and β electrons are brought into coincidence at only one vertex to form the single bond but the remaining three vertices are free to take up any relative position. Thus the most probable positions of these electrons form a circle of unpaired electrons as we see in Figure 4.

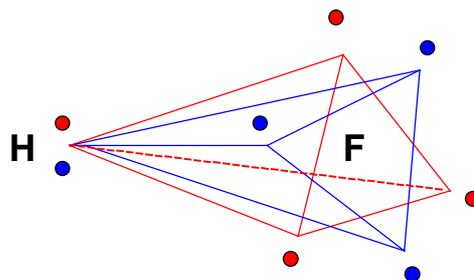


FIGURE 4. Pauli principle for a diatomic molecule e.g.HF. In any diatomic molecule, the two Tetrahedra (Fig. 1a, 1b) of opposite spin electrons in the valence shell of an atom are brought into coincidence only at one apex, leaving the most probable locations of the remaining six electrons equally distributed in a ring.

There are not therefore three lone pair nonbonding domains but a nonbonding domain containing six electrons having the form of a torus around the fluorine atom. This is the situation for all atoms, except hydrogen atoms, in any diatomic molecule, as we have seen for the fluorine atom in HF, and for any singly bonded ligand.

In a molecule in which the ligands around a central atom are only weakly electronegative the electrons of the central atom are only weakly localized into pairs so that the central atom becomes more like a spherical negative ion. Such poorly localized lone pairs have only a weak effect on the geometry of a molecule which is more determined by ligand-ligand interaction than by the lone pairs. An example is disiloxane $H_3SiOSiH_3$ in which the SiOSi bond angle of 154° is not in agreement with the VSEPR model which predicts a bond angle of $<109.5^\circ$. The large bond angle is a result of the weak pairing of the electrons on the central oxygen by the weakly electronegative SiH_3 groups and also to the electrostatic repulsion between the SiH_3 groups. Another similar example is $N(SiH_3)_3$ which has a planar geometry rather than the pyramidal geometry predicted by the VSEPR model. We note also that the only molecules in Tables 1 and 2 that have bond angles slightly greater than 109.5° are those in which the central atom is either oxygen or nitrogen both of which are very electronegative attached to less electronegative ligands. Further examples are given in (Gillespie, 2000; Gillespie & Popelier, 2001; Gillespie & Robinson, 1996). In general the VSEPR rules only apply when the ligand has an electronegativity comparable to, or greater than, that of the central atom.

LIGAND-LIGAND REPULSIONS

The importance of ligand-ligand repulsions in determining molecular geometry has been somewhat overshadowed by the success of the VSEPR model. We have just discussed two molecules in which ligand-ligand repulsions dominate the geometry. In general, ligand-ligand repulsions are particularly important in molecules with small central atoms such as the

period 2 atoms, when the ligands are only weakly electronegative or large compared to the central atom, or when there are 5 or more ligands around a central atom (Gillespie, Bytheway, & Robinson, 1998; Gillespie & Robinson, 1998; Robinson, Johnson, Tang, & Gillespie, 1997). With small central atoms such as B, C and N the effect of ligand-ligand repulsions is quite evident in the comparison of the bond lengths of AX_3 and AX_4 molecules. Three ligands can pack more closely around a central atom so the bonds are always shorter in an AX_3 molecule such as BF_3 than in the corresponding AX_4 molecule BF_4^- as shown by the examples in Table 3.

TABLE 3. Bond lengths in AX_3 and AX_4 molecules. *

AX_3 molecules	Length AX (pm)	AX_4 molecules	Length AX (pm)
BF_3	130.7	BF_4^-	138.2
BCl_3	174.2	BCl_4^-	183.3
$B(OH)_3$	136.1	$B(OH)_4^-$	148.1
$B(OCH_3)_3$	136.8	$B(OCH_3)_4^-$	145.8
CF_3^+	124.4	CF_4	131.9
CCl_3^+	166.3	CCl_4	177.1
$(HO)_2CO$	131.5	$C(OH)_4^-$	138.4

* For more data and references to the source of the data in this table see references 4 and 8

In such molecules we can think of the ligands as being hard approximately spherical objects and as having a constant interligand radius that is transferable from one molecule to another. Table 4 gives values of the interligand radius for some common ligand atoms obtained by taking the mean of half the interligand distance between identical ligands in a number of different molecules. As we can see in Table 4, the radius of a given ligand atom depends on the nature of the central atom to which it is bonded. The interligand radius increases with decreasing electronegativity of the central atom and the corresponding increase in the negative charge on the ligand. The additivity of these radii is illustrated by the agreement between the experimental interligand distances and those calculated from the interligand radii as shown by the selected examples in Table 5. In molecules with lone pairs, the lone pairs push the ligands together until they reach the interligand distance given by the sum of the ligand radii as illustrated by the examples in Figure 5. According to this model geometry is determined by the packing of ligands around a central atom so it has been called the *ligand close packing (LCP) model* (Gillespie, Bytheway, & Robinson, 1998; Gillespie & Popelier, 2001; Gillespie & Robinson, 1998; Robinson, Johnson, Tang, & Gillespie, 1997)

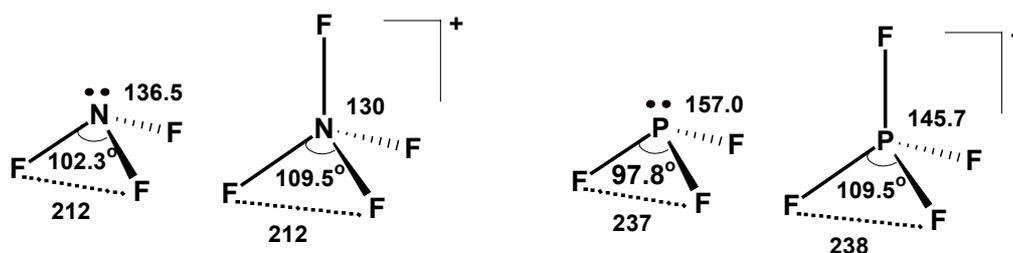


FIGURE 5. Bond angles (degrees), bond distances, and intramolecular contact distances (pm) in some AX_3E and AX_4 systems.

TABLE 4. *Interligand radii (pm).*

Ligand	Central Atom			
	Be	B	C	N
H	-	110	90	82
C	-	137	125	120
N	144	124	119	-
O	133	119	114	-
F	128	113	108	106
Cl	168	151	144	142

TABLE 5. *Interligand distances in some oxofluorocarbon molecules.*

Molecule	Bond length (pm)		Bond angle (E)	O—F (pm)
	C-F	C-O	FCO	
CF ₃ OCF ₃	132.7	136.9	110.2	221
CF ₃ O ⁻	139.2	122.7	116.2	223
CF ₃ OF	131.9	139.5	109.6	223
COF ₂	131.7	117.0	126.2	223
CH ₃ COF	134.2	118.1	121.4	223
FCO.OF	132.4	117.0	126.5	223
FOCCOF	132.9	118.0	124.2	233
		sum of interligand radii		222

If we treat a lone pair domain as fulfilling the role of a ligand in the LCP model, this model and the VSEPR model lead to the same predictions. In other words it is difficult to distinguish between the bond - bond and bond - lone pair repulsions of the VSEPR model and the ligand - ligand and ligand - lone pair repulsions of the LCP model. An advantage of the LCP model is that it is more quantitative, particularly for period 2 molecules; if we know the bond lengths we can calculate the bond angle from the predicted interligand distance. One difference between the two models is that the effect of the electronegativity of the ligand in the VSEPR model is replaced by the ligand size in the LCP model. In most cases these two models lead to the same qualitative bond angle predictions because the most electronegative ligands such F and O are also the smallest. We can see in Tables 1 and 2 that in the halides of P and S the bond angle increases with increasing size of the halogen as expected from the LCP model but also with decreasing electronegativity of the halogen as predicted by the VSEPR model.

ELECTRON DENSITIES AND THE THEORY OF ATOMS-IN-MOLECULES (AIM)

The VSEPR model and Lewis structures are very approximate models of the distribution of the electrons in a molecule. We cannot determine the position of a particular electron in a molecule but we can determine the probability of finding an electron in an infinitesimal volume surrounding any particular point in space, that is the probability density. When the probability distribution of an electron is multiplied by the total number of electrons in the molecule we obtain what is known as the electron density distribution or simply the electron density. We can think of the electrons in a molecule as forming a cloud of electronic charge that is more dense in some places than in others. We can obtain the electron density of a molecule in the solid state by careful accurate X-ray crystallography. However, given the power and speed of modern computers and the availability of programs for carrying out

ab initio and density functional calculations (DFT) it is usually simpler and more rapid to calculate the electron density of an isolated molecule. Many electron density maps have been published in the literature and a large number have been included in a recent textbook (Gillespie & Popelier, 2001). Electron density maps can provide useful information about bonding and geometry and they can greatly enhance a student's understanding of these topics.

The electron density (ρ) varies in three dimensions so a full description of how ρ varies throughout a molecule requires a fourth dimension. A common solution to this problem is to show how ρ varies in one or more particular planes of the molecule. Figure 6a shows a relief map of the electron density, ρ , of the SCl_2 molecule in the plane through all three atoms, the $\sigma_h(xy)$ plane. The most striking feature of this figure is that the electron density is very large in an almost spherical region around each nucleus but very small between these regions. Indeed, the very large maxima have been truncated at 2.00au in order to make it possible to show the features of the electron density between the nuclei (au stands for "atomic units", discussed briefly in Appendix II). In particular there is a ridge of increased electron density between the sulfur atom and each of the chlorine atoms. The electron density has values of $3.123 \times 10^3 \text{au}$ and $2.589 \times 10^3 \text{au}$ at the S and Cl nuclei respectively but a value of only $1.662 \times 10^{-1} \text{au}$ at the minimum of the ridge between the peak around the sulfur nucleus and each of the chlorine nuclei. This ridge of increased electron density between the S atom and each of the Cl atoms, small as it is, is the density in the binding region that is responsible for an attractive force between the nuclei. Along a line along the top of this ridge the electron density is locally greater than in any direction away from the line. This line coincides with the bond between the S and Cl atoms as it is normally drawn and is called a **bond path**, and the point of minimum electron density along the bond path is called the **bond critical point** (Bader, 1990). Figure 6b shows a relief map of the electron density of the water molecule. It shows similar features to the density map for SCl_2 although the electron density around the hydrogen atoms is much smaller than around the oxygen atom as we would expect. The electron density at the maximum at the oxygen nucleus has a value of $2.947 \times 10^2 \text{au}$, whereas that at the hydrogen nucleus is only $4.341 \times 10^{-1} \text{au}$, which is only slightly greater than the value of the density of $3.963 \times 10^{-1} \text{au}$ at the minimum at the bond critical point. The very small electron density surrounding the hydrogen nucleus is due to even less than one electron because the more electronegative oxygen atom attracts electron density away from the hydrogen atom so that it has a positive charge.

Another common method of representing the electron density distribution is as a contour map, just as we can use a topographic contour map to represent the relief of a part of the earth's surface. Figure 7a shows a contour map of the electron density of the SCl_2 molecule in the $\sigma_h(xy)$ plane. The lines in which the interatomic surfaces, that are discussed later, cut this plane are also shown. Figure 7b shows a corresponding map for the H_2O molecule.

Here we see clearly the large concentration of density around the oxygen nucleus, and the very small concentration around each hydrogen nucleus. The outer contour is an arbitrary choice because the density of a hypothetical isolated molecule extends to infinity. However, it has been found that the 0.001au contour corresponds rather well to the size of the molecule in the gas phase, as measured by its van der Waal's radius, and the corresponding isodensity surface in three dimensions usually encloses more than 98% of the total electron population of the molecule (Bader, 1990). Thus this outer contour shows the shape of the molecule in the chosen plane. In a condensed phase the effective size of a molecule is a little smaller. Contour maps of some period 2 and 3 chlorides are shown in Figure 8. We see that the electron densities of the atoms in the LiCl molecule are only very little distorted from the spherical shape of free ions consistent with the large ionic character of this molecule. In

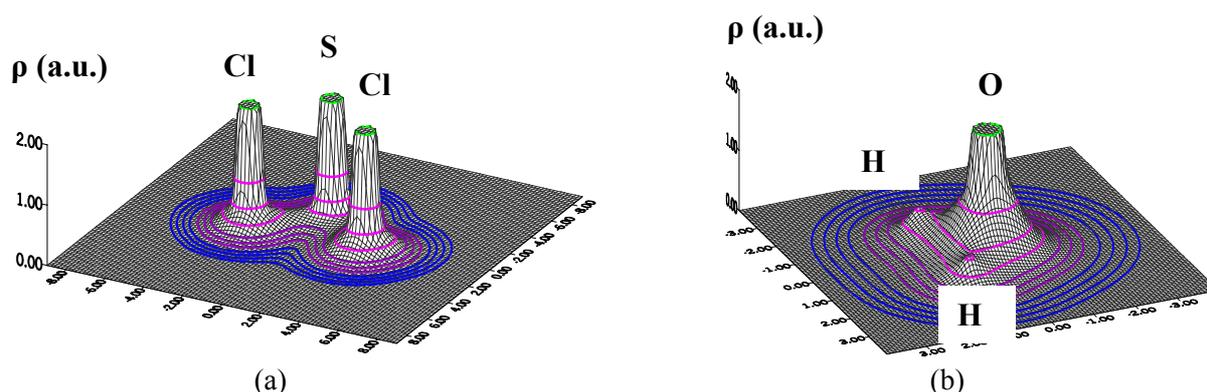


FIGURE 6. Isodensity contour maps of the electron density of SCl_2 (a) and H_2O (b) in the plane of the nuclei (density and distances from the origin of the coordinate system in au). Isodensity contour lines are shown in color in the order 0.001, 0.002, 0.004, 0.008 (blue); 0.02, 0.04, 0.08 (violet); 0.2, 0.4, 0.8 (magenta). The density is truncate at 2.00 au (green contour).

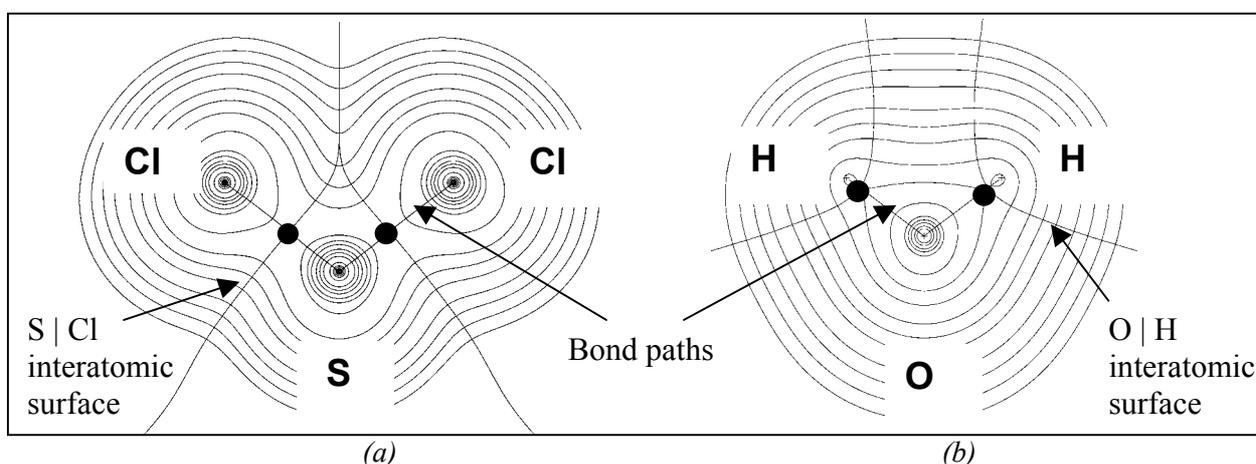


FIGURE 7. Contour maps of the electron density of SCl_2 (a) and H_2O (b). The density increases from the outermost 0.001au isodensity contour in steps of 2×10^n , 4×10^n , and 8×10^n au with n starting at -3 and increasing in steps of unity. The same values for the contours apply to subsequent contour plots in this paper. The lines connecting the nuclei are the bond paths, and the lines delimiting each atom are the intersection of the respective interatomic surface with the plane of the drawing. The bond critical points (intersections of each bond path with its associated interatomic surface) are depicted by heavy black dots.

the more covalent molecules the electron density of each atom is more distorted in the bonding direction. We also see the distortion of the electron density in the lone pair direction in NCl_3 and in the two lone pair directions in the σ_v plane of the SCl_2 molecule.

If we wish to give a three dimensional picture of the electron density distribution we can easily show one particular surface, namely that for a given value of the electron density. If we choose the 0.001au surface we get a picture of the overall shape of the molecule as shown by the examples in Figure 9. By making the outer 0.001au surface transparent as we have done in Figure 9 we can fairly easily show one inner surface, but showing further surfaces becomes increasingly difficult. The particular inner surface in Figure 9 is for the density at the bond critical point at which the single surface encompassing all the nuclei at lower values of ρ just breaks into separate surfaces, one surrounding each atom and just touching at the bond critical point. This surface only is shown for either the fluoride or the chloride of the period 2 elements Li to O in Figure 10.

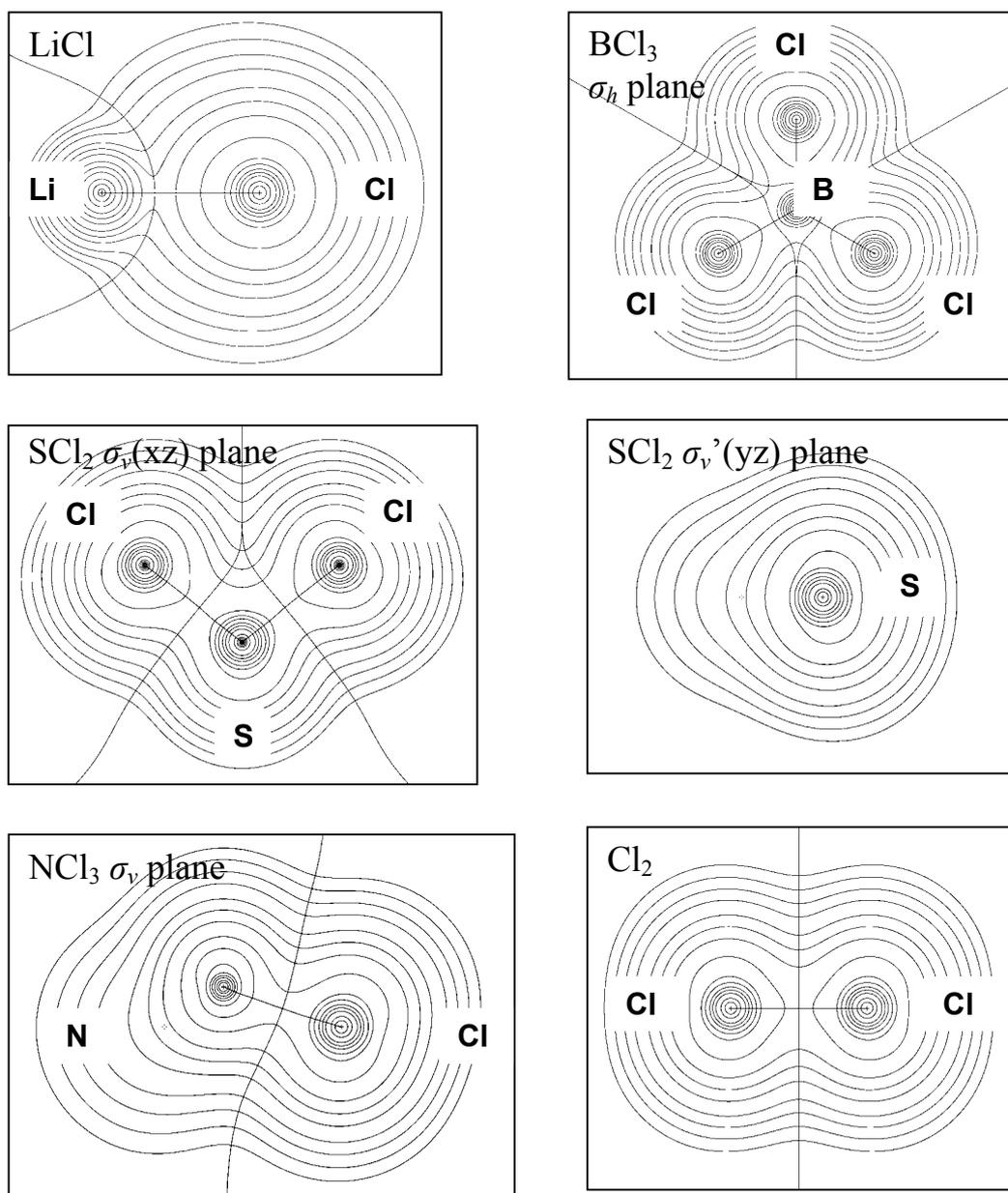


FIGURE 8. Contour maps of the electron density of LiCl, BCl₃, SCl₂ in the $\sigma_v(xz)$ plane (the plane containing the three nuclei) and in the $\sigma_v'(yz)$ plane [the plane bisecting the Cl-S-Cl angle perpendicularly to the $\sigma_v(xz)$ plane], NCl₃ in the σ_v plane (plane containing one N-Cl bond and bisecting the Cl-N-Cl angle formed by the remaining two bonds), and Cl₂.

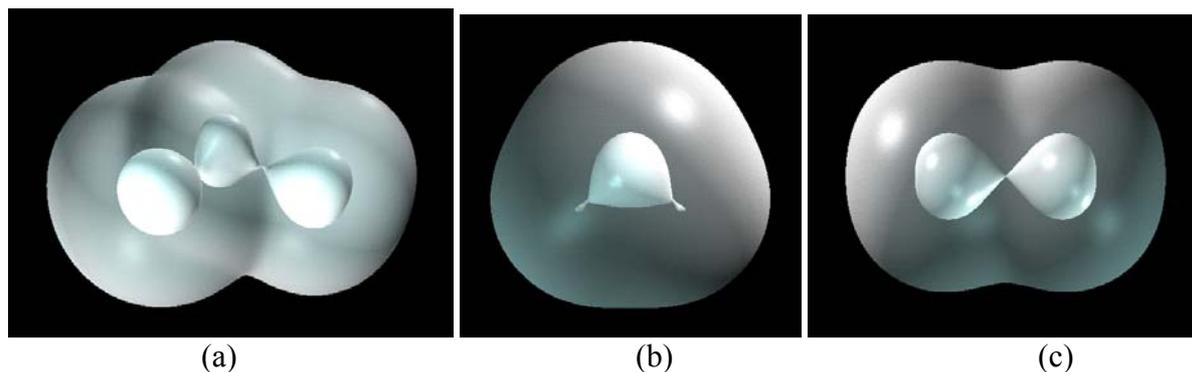


FIGURE 9. Three-dimensional isodensity envelopes of (a) SCl_2 , (b) H_2O , and (c) Cl_2 . The outer envelope has the value of 0.001 au , the van der Waals envelope, and the inner one is the bond critical point density envelope (ρ_b -envelope).

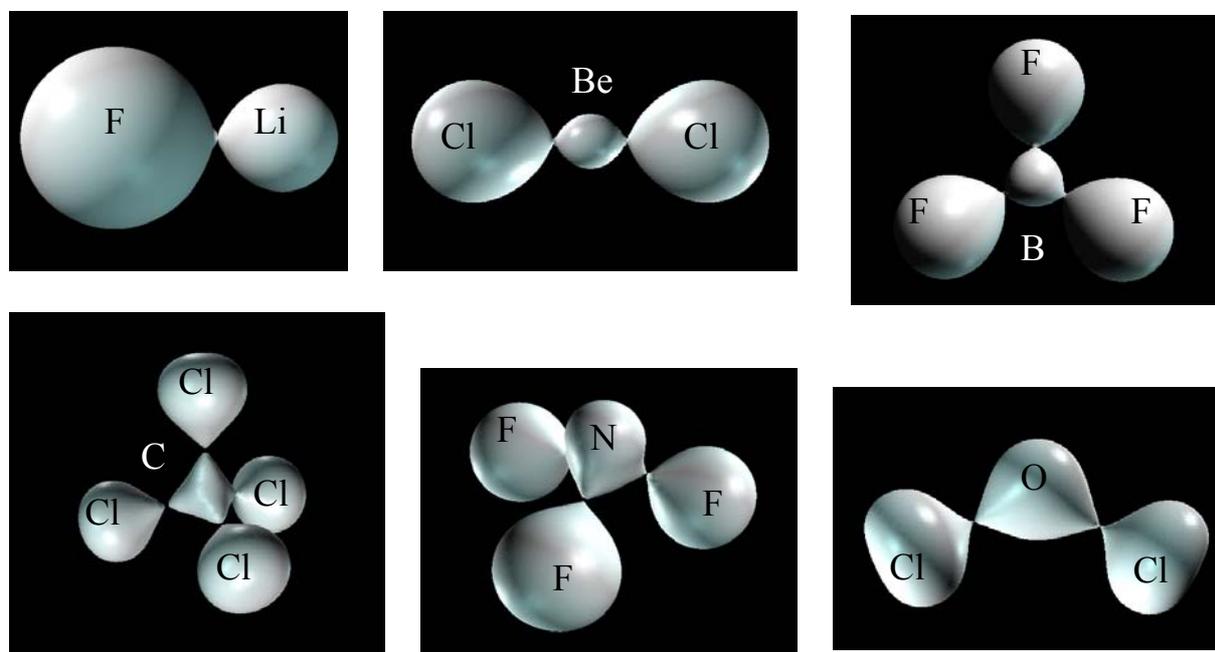


FIGURE 10. Three-dimensional isodensity envelopes of the bond critical point density (ρ_b -envelope) of LiF , BeCl_2 , BF_3 , CCl_4 , NF_3 , and OCl_2 .

These surfaces show even more clearly than the contour maps the distortion of the electron density from a spherical shape. The electron density of each atom is extended out towards its neighbor due to the concentration of the electron density along the bond direction as expected from the increased probability of finding a pair of electrons in this region. The tetrahedral shape of this electron density isosurface in CCl_4 is particularly striking. In addition to the distortion of the electron density toward each neighboring atom we can see other changes. The electron density of the ligand has an increasingly squashed shape with increasing electronegativity of the central atom being increasingly flattened on the opposite side of the ligand atom from the bond direction, giving an overall “onion” shape. These changes can be understood in the light of the Pauli principle as illustrated in Figure 4. In this figure we see that the nonbonding electrons have a most probable location in a circle around the ligand so that the electron density is concentrated in this region and correspondingly

depleted at the back of the ligand atom opposite the bond giving the “onion” shape to this isodensity surface.

The value of the electron density at the bond critical point, ρ_b also gives us valuable information. It can be taken as a measure of the electron density in the bonding region and therefore of the covalent character of the bond. In Table 7 we see that ρ_b increases from LiF to CF₄ as expected. In general in a very polar molecule the value of ρ_b is typically small usually less than 0.1au while for a covalent single bond it has a higher value. For example, 0.25au for the C-C bond in ethane. For double and triple bonds we expect still higher values for ρ_b . For example, the value for the C=C double bond in ethene is 0.36au and for the C/C triple bond in ethyne is 0.43au.

TABLE 7. Period 2 fluorides and chlorides.*

Molecule	Bond length (pm)		ρ_b (au)	$q(X)$	$q(A)$
	Calc.	Exp.			
LiF	157.3	156.4	0.075	-0.92	+0.92
BeF ₂	137.8	140	0.145	-0.88	+1.75
BF ₃	131.4	130.7	0.217	-0.81	+2.43
CF ₄	132.6	131.9	0.309	-0.61	+2.45
NF ₃	138.2	138.5	0.314	-0.28	+0.83
OF ₂	140.4	140.5	0.295	-0.13	+0.27
F ₂	139.9	141.8	0.288	0	0
LiCl	202.2	220.1	0.047	-0.91	+0.91
BeCl ₂	179.8	--	0.097	-0.84	+1.68
BCl ₃	175.0	174.2	0.157	-0.64	+1.93
CCl ₄	179.7	177.1	0.182	-0.09	+0.35
NCl ₃	179.1	175.9	0.176	+0.08	-0.24
OCl ₂	172.8	170	0.184	+0.23	-0.46
FCI	166.5	162.8	0.187	+0.38	-0.38

* Data, obtained at the DFT level using the B3LYP functional and a 6-311+G(2d,p) basis set, is taken from Ref. (4). $q(X)$ refers to the charge of the ligand X (here the halogen atom) and $q(A)$ refers to the charge of the period 2 atom.

The point of minimum electron density along the bond path between two atoms, the bond critical point, is on the boundary between the two atoms, that is the interatomic surface. In the contour map of the density of SCl₂ (Figure 7) we see that there are two valleys in the electron density, one on each side of the bond path leading up to the saddle point at which the bond critical point is situated. A line along the bottom of each of these valleys is the line on which the two atoms meet in this particular plane - the interatomic line. In three dimensions we have a corresponding **interatomic surface**. The exact definition of this surface and the procedure by which such surfaces are found are described within the context of the theory of atoms in molecules (AIM) which is fully discussed in (Bader, 1990; Popelier, 2000). More elementary and less mathematical descriptions of this theory have been given in several recent publications (Gillespie & Popelier, 2001; Matta & Gillespie, 2001). We can see such surfaces in the familiar space-filling molecular models. In these models the interatomic surfaces are assumed to be planar which is the case only in homonuclear diatomic molecules; in general real interatomic surfaces are curved (Figure 8). These interatomic surfaces define

the atoms as they exist in the molecule. All the properties of an atom in a molecule are determined by their electron density. A simple example is provided by the charge which can be obtained by finding the total number of electrons in the atom by integrating the density over the volume of the atom and then subtracting the nuclear charge. The atomic charges in the fluorides and chlorides of the elements of periods 2 and 3 are given in Table 7. We see that the ligand charges decrease as expected as the electronegativity of the central atom increases, while the positive charge of the central atom at first increases with increasing number of electronegative ligands but then decreases again as the electronegativity of the central atom increases. In Figure 11 we see that the charge of the ligand is a smooth function of the electronegativity.

Several methods have been used for analyzing the electron density in more detail than we have done in this paper. These methods are based on different functions of the electron density and also the kinetic energy of the electrons but they are beyond the scope of this article. They include the Laplacian of the electron density ($L = -\nabla^2\rho$) (Bader, 1990; Popelier, 2000), the electron localization function ELF (Becke & Edgecombe, 1990), and the localized orbital locator LOL (Schinder & Becke, 2000). These methods could usefully be presented in advanced undergraduate quantum chemistry courses and at the graduate level. They provide further understanding of the physical basis of the VSEPR model, and give a more quantitative picture of electron pair domains.

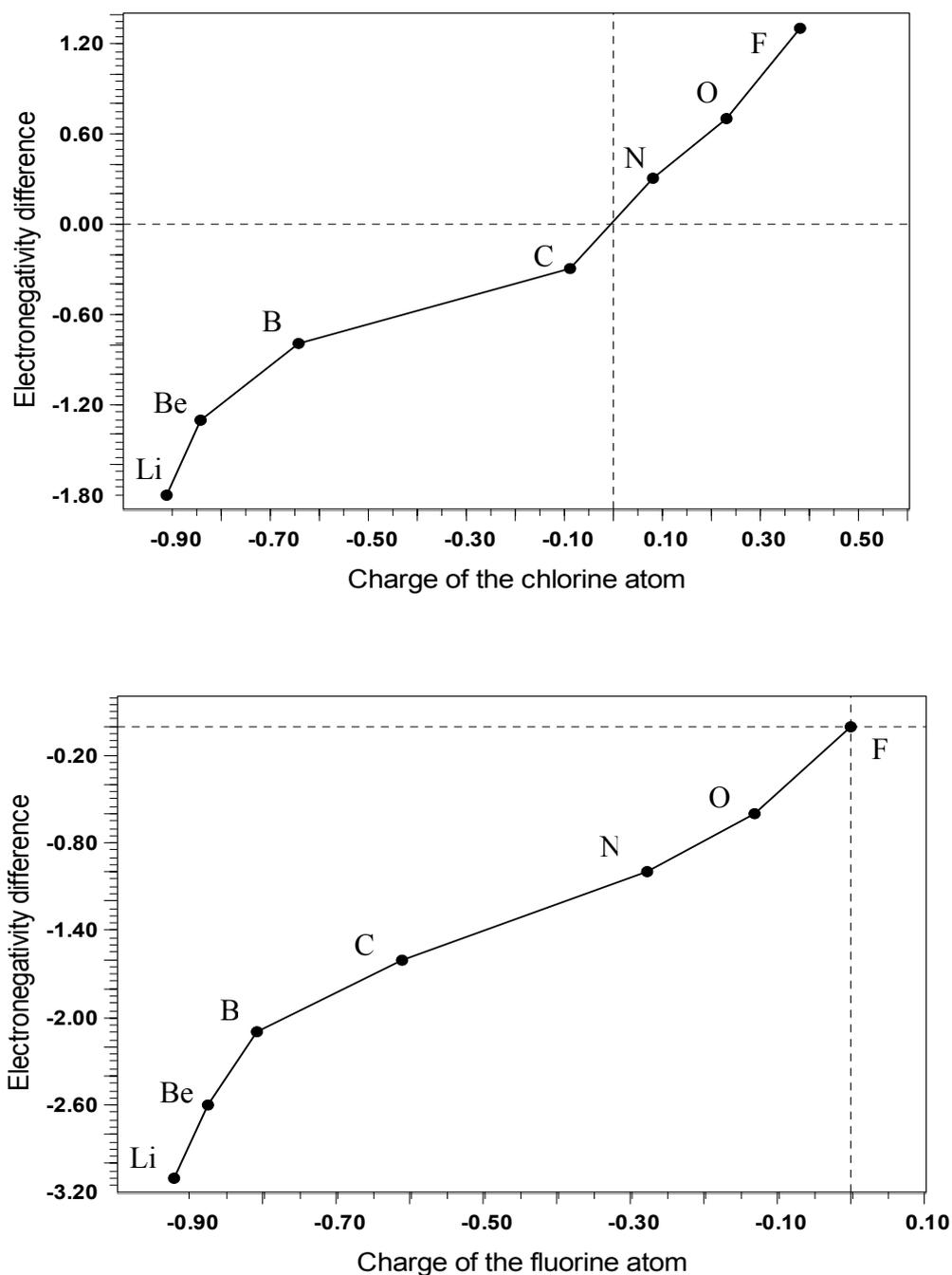


FIGURE 11. Electronegativity difference between the halogen atom (X) and the atom to which it is bonded (A) in the halides of period 2 (A_nX) as a function of the atomic charge of the halogen atom $q(X)$. (**Top**) $X = \text{Cl}$, (**Bottom**) $X = \text{F}$. Shown in the figures is atom A of the halide. Charges were obtained at the DFT level using the B3LYP functional and a 6-311+G(2d,p) basis set.

SUMMARY

The VSEPR model is a useful tool for understanding chemical bonding and molecular geometry at all levels from high school through university. It can first be introduced as an empirical model just after Lewis structures have been presented. Then after some basic quantum mechanical ideas, in particular the concept of charge clouds and the Pauli principle, have been introduced the VSEPR model can be presented in a more sophisticated and less empirical manner in terms of electron pair domains. At this level the electron density and its presentation in the form of two- and three- dimensional contour and surface maps can be introduced and discussed and shown to provide further support for, and understanding of, the VSEPR model. The fundamental physical basis of the model can then be better understood, bond lengths and bond angles that deviate from the ideal values can be accounted for, and exceptions to the basic rules such as the large bond angle in disiloxane, can then be understood. At this point the importance of ligand-ligand repulsions and their relationship to the VSEPR model can be discussed and the ligand close packing (LCP) model introduced. Finally the AIM theory and the functions such as the Laplacian, ELF and LOL can be introduced at the advanced undergraduate or graduate levels.

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APPENDIX I: THE PAULI PRINCIPLE

The Pauli antisymmetry principle is a requirement a many-electron wavefunction must obey. *A many-electron wavefunction must be antisymmetric (i.e. changes sign) to the interchange of the spatial and spin coordinates of any pair of electrons i and j* , that is:

$$\Psi(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_i, \dots, \mathbf{q}_j, \dots, \mathbf{q}_n) = -\Psi(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_j, \dots, \mathbf{q}_i, \dots, \mathbf{q}_n) \quad (I.1)$$

where \mathbf{q}_k is the spatial and spin coordinates of the k^{th} electron. If two electrons have the same space and spin coordinates, i.e. $\mathbf{q}_j = \mathbf{q}_i = \mathbf{q}_k$, then:

$$\Psi(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_k, \dots, \mathbf{q}_k, \dots, \mathbf{q}_n) = -\Psi(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_k, \dots, \mathbf{q}_k, \dots, \mathbf{q}_n) \quad (I.2)$$

which means that the wavefunction is equal to its own negative. The only function which is equal to its negative is zero, i.e. $\mathbf{q}_j = \mathbf{q}_i = \mathbf{q}_k$ is an impossibility since the wavefunction would collapse. In other words, two electrons of the same spin have zero probability of occupying the same position in space, i.e. two same-spin electrons *exclude* each other in space. Since Ψ is continuous, every electron is surrounded by a region where there is very little chance of finding another electron of the same spin, this exclusion fading gradually as we move away from the electron in question. Thus the physical consequence of the Pauli principle is that the movement of electrons of similar spin is not independent but rather correlated, since it requires them to avoid each other as much as possible. This correlation is known as *Fermi correlation* which is a direct consequence of the Pauli principle. Fermi correlation is not to be confused with the *Coulomb correlation* where the mere electrostatic repulsion of electrons, regardless of their respective spins, causes their movement to be correlated. The Coulomb correlation is referred to simply as “correlation” by theoretical chemists.

APPENDIX II: THE ATOMIC UNITS SYSTEM

The atomic units system (au system) is a system of units meant to simplify the equations of molecular and atomic quantum mechanics. The units of the au system are combinations of the fundamental units of mass (mass of the electron), charge (charge of the electron), and of Planck’s constant. By setting these three quantities to unity one gets simpler equations. Si in the usual SI system, Schrödinger equation takes the form:

$$\left[-\frac{\hbar}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right] \Psi = E \Psi \quad (II.1)$$

This equation can be cast into a dimensionless form in which all the quantities are expressed in atomic units:

$$\left[-\frac{1}{2} \nabla'^2 - \frac{1}{r'} \right] \Psi' = E' \Psi' \quad (II.2)$$

The au system has a simple relation to the SI and to the Gaussian (cgs) systems of units. For example: 1 au of length = a_0 (Bohr radius) = 5.29×10^{-9} cm = 0.529 \AA , 1 au of charge = $e = 1.602 \times 10^{-19}$ C = 4.803×10^{-10} esu, 1 au of charge density = $e/a_0^3 = 6.748 \text{ e\AA}^{-3} =$

$1.081 \times 10^{12} \text{ Cm}^{-3}$. For a formal discussion of how the au system of units naturally arises in quantum chemistry the reader is referred to (Szabo & Ostlund, 1989).

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