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Review

Fifty years of the VSEPR model

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Contents

Abstract

The history and development of the VSEPR model since its inception in 1957 are reviewed. Exceptions to the model are discussed and are shown to have led to improvements in the model and to the development of another model – the LCP model – which supplements the VSEPR model. It is shown how recent developments in the analysis of electron densities have provided both strong evidence for the physical basis of the model, and a further understanding of the model and its exceptions. Attempts to extend the VSEPR model to the transition metals are discussed.

Keywords: VSEPR model; LCP model: Lone pairs; Molecular geometry

1. Introduction

It is 50 years since the ideas of the VSEPR model were first introduced in an article by Ron Nyholm and myself entitled Inorganic Stereochemistry [1]. So it is an appropriate time to survey the history and development of the model and to comment on how it has subsequently been modified, on its relationship to other developments in our understanding of molecular geometry, on how its physical basis is now more clearly understood, and on its continued relevance and usefulness today.

In 1956, I was teaching chemical bonding in the Chemistry Department of University College London. I became dissatisfied with the conventional treatment of molecular geometry in terms of the simple valence bond model using hybrid orbitals which seemed in most cases to be a circular argument: methane is known to be tetrahedral therefore we must use tetrahedral sp^3 orbitals to describe the bonding and then when geometry is discussed the methane molecule is tetrahedral because the bonding orbitals are formed from sp^3 orbitals. Moreover, valence bond theory could not be used to explain the non-tetrahedral bond angles in molecules such as H_2O and NH_3. Using p orbitals to form localized bonding orbitals leads to 90° bond angles, while sp^3 hybrids predict 109.5° bond angles, and there is no *a priori* way to determine the actual degree of hybridization in H_2O and NH_3. Sometimes the large deviation of the observed angles from the predicted 90° angles has been attributed to ligand–ligand repulsion. But this is not consistent with the assumed orbital picture. An increased angle due to ligand–ligand repulsion implies either bent bonds or a change in the degree of hybridization

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but the extent of the hybridization can only be derived from the experimental bond angle.

It had become clear to me at that time that an alternative and more satisfactory approach to molecular geometry could be developed, particularly for the main group elements, and I used this approach as a basis for the main group section of the paper and for the development of what came to be known as the VSEPR model. At the same time Ron Nyholm was teaching transition metal chemistry and he wanted to introduce students to a simple method for understanding the geometry of transition metal molecules, namely the crystal field theory. So we got together to write an article covering the geometry of both main group and transition metal molecules [1].

2. The VSEPR model

The ideas of the VSEPR model were first presented in that part of the paper dealing with the geometry of main group molecules, although this now commonly used name was not proposed until 1963 [2]. In 1956, I had read a paper by Sidgwick and Powell [3] published in 1940 in which they showed that in many cases the general shape of a molecule of the type AX_nE_m, where X denotes a ligand and E a lone pair, appears to depend simply on the total number of electron pairs, both bonding and non-bonding, in the valence shell of the central atom A, as envisaged by the Lewis structure for the molecule. Indeed, much earlier Lewis [4] had already postulated that four electron pairs in a valence shell have a tetrahedral arrangement leading to the prediction of the tetrahedral geometry of methane, the pyramidal geometry of the ammonia molecule, and the angular geometry of the H_2O molecule. Sidgwick and Powell extended this idea to include three pairs with a planar triangular arrangement, five pairs with a trigonal bipyramidal or square pyramidal arrangement and six pairs with an octahedral arrangement thus explaining, the geometries of a large number of molecules, such as the square shape of ICl_4^-, the square pyramidal shape of BrF_5, and the octahedral shape of SF_6. They noted the importance of the lone pairs in determining molecular shape which had been first recognized by Lewis in 1916 [4] for four valence-shell electron pairs. They noted there were very few exceptions to these predictions for the main group nonmetals but substantially more among molecules of the transition metals.

I found that the predictions of Sidgwick and Powell were equally valid for a large number of molecules whose structures had been determined since that time and I showed that their predictions could be understood on the basis that the electron pairs in the valence shell of the central atom are arranged so as to be as far apart as possible—they behave *as if* they repel each other [1]. For two, three, four and six electron pairs, these arrangements are intuitively obvious and can be predicted, for example, by the points-on-a-sphere model [5] in which a given number of points each representing a valence-shell electron pair are confined to the surface of a sphere and between which there is a repulsive potential of the form:

$$V_{ij} = kr_{ij}^{-s}$$

where k is a constant and r_{ij} is the distance between any pair of points i and j and s is a constant where small values of s correspond to a soft repulsion and values of $s \geq \sim 10$ correspond to a hard repulsion. For an AX_n molecule the predicted arrangement of n points where $n \leq 6$ are independent of the value of s, and are the equilateral triangle, the tetrahedron, the trigonal bipyramid and the octahedron. For $n > 6$ the predicted arrangement depends on the value of s. However, the trigonal bipyramid structure with equal bond lengths is not the equilibrium structure if the five particles are not constrained to a sphere. In this case the equilibrium structure is a trigonal bipyramid with longer axial than equatorial bonds [6,7].

It was emphasized in the original 1957 paper that electron pairs in a valence shell behave *as if* they repel each other and that this behavior is a consequence of the Pauli principle and not of electrostatic repulsion. The great importance of the Pauli principle in determining molecular geometry was not widely appreciated at the time although the Cambridge theoretician Lennard-Jones had stated in 1954: “The effect of the Pauli principle is much more powerful than that of electrostatic force. It does more to determine the shapes of molecules than any other single factor. Its all pervading influence does not seem to have been fully realized by chemists, but it is safe to say that ultimately it will be regarded as the most important property to be learned by those concerned with molecular structure” [8].

Lewis [4] first conceived three key ideas: valence-shell electrons are normally found in pairs, a covalent bond could be represented by a pair of electrons shared between the two bonded atom, and four pairs of electrons constitute a stable valence shell. In this way he could account for the formulas of a very large number of molecules and could write consistent structures for them. But he did not understand why electrons in molecules appeared to be found in pairs which did not seem to be consistent with the electrostatic repulsion between electrons. The understanding of why electrons in molecules are found in pairs only came after the discovery of electron spin in 1926 and the later formulation of the Pauli principle. It is a consequence of the Pauli principle that two electrons of the same spin have a zero probability of being found at the same location and a maximum probability of being found as far apart as possible. Consequently, in an octet valence-shell four electrons of the same spin are most probably located at the vertices of a tetrahedron so that there is a set of α spin electrons and a set of β spin electrons each of which has a most probable tetrahedral geometry. These two sets are not correlated with each other unless in a molecule the attraction exerted by the ligands on the valence-shell electrons, if it is sufficiently strong, draws the two tetrahedra into approximate coincidence giving four localized pairs of bonding and nonbonding electrons with a tetrahedral geometry [6,9]. The strength of the attraction exerted by the ligands depends on the relative electronegativities of the ligands and the central atom. If their electronegativities are similar, or if the ligands have a higher electronegativity than the central atom, the valence-shell electrons are well localized in pairs, but if they have a significantly lower electronegativity then the valence-shell electrons will not be well localized. This leads to some exceptions to the VSEPR which will be discussed later.

The great popularity of the valence bond model in the 1950s and 1960s tended to obscure the great importance of the Pauli principle in determining geometry. This model is based on the directional character of atomic or hybrid orbitals and only incorporates the Pauli principle in the form of the Pauli exclusion principle which states that an orbital can be occupied by at most two electrons which must be of opposite spin, and for which no explanation was offered in introductory texts.

Of course the simplest possible explanation of molecular geometry is that it is determined simply by repulsions between the ligands which adopt the arrangement that minimizes the repulsion energy. In other words the ligands pack around the central atom so as to minimize the repulsion between them giving the obvious tetrahedral geometry for four ligands and the equilateral planar geometry for three ligands. However, the NH_3 molecule is not planar triangular and the SF_4 molecule is not tetrahedral. Clearly the ligand–ligand repulsion model is not adequate and the VSEPR model is superior. The most important feature of the VSEPR model is the dominating influence of non-bonding or lone pairs of electrons in the valence shell of the central atom which determines, for example, that the water molecule is angular not linear and the BrF_5 molecule has a square pyramidal rather than a triangular bipyramidal shape. There are only a very few molecules of only just two types for which the Lewis structure has one or more lone pairs in the valence shell of the central atom that appear to have no effect on the geometry of the molecule: (1) the BrF_6^- molecule and several molecules of the types $SnX6^{4-}$, SbX_6^{3-}, and SeX_6^{2-}, where X = Cl, Br or I which have octahedral geometries, and not a geometry based on a valence shell of seven electron pairs so that in these molecules the lone-pair appears to play no role in determining the geometry. (2) The molecule $N(SiH_3)_3$ which is planar and not pyramidal like NH_3 and many other NX_3 molecules. These molecules are discussed later (Section 6).

Although there are very few molecules in which lone pairs do not appear to play any role in determining the geometry there are many in which the bond angles deviate significantly from the regular polyhedral shapes that are predicted, assuming that lone pairs and bond pairs are equivalent. These include many such as NH_3 and H_2O in which the bond angles are smaller than tetrahedral and many others such as BrF_5 in which the bond angles are smaller than 90°. In the original 1957 article I accounted qualitatively for these deviations of the geometry of many molecules from the regular polyhedral shapes by means of three simple rules:

(1) The strength of the repulsions between the electron pairs in a valence-shell decrease in the order: lone pair–lone pair > lone pair–bond pair > bond pair–bond pair. In other words lone pairs and bond pairs are not equivalent but lone pairs exert a greater effect on bond angles than bond pairs.
(2) The strengths of the repulsions between bonds of different multiplicity decreases in the order triple–double > double–double > double–single > single–single.
(3) The strength of the repulsion between single bonds decreases with increasing electronegativity of the ligand and/or decreasing electronegativity of the central atom.

These rules were based on the concept of the electron-pair domain. Electrons in molecules are found as opposite-spin pairs each of which is most probably found at a particular location and with decreasing probability from this location of greatest probability. When an opposite-spin electron pair is sufficiently well localized in a particular region it is a useful approximation to assume that it almost completely excludes any other electrons from this space. This space is called an electron-pair domain which is a qualitative, and incompletely defined, but nevertheless very useful, concept. The three rules above can be restated as follows:

(1) Lone pairs are only under the influence of a single core and so they tend to spread out round this core occupying as much angular space in the valence shell as is allowed by the other pairs in the valence shell. In contrast bonding pairs are under the influence of two cores and tend to be concentrated in the region between the two cores. In other words lone-pair domains occupy a greater angular space in the valence shell than do bonding pair domains (Fig. 1). But it is important to note that lone-pair domains do not stick out from the core of the central atom like “rabbit ears”, as they are so often depicted, rather they are more spread out around, and on average closer to, the central atom core than the bonding electrons. So the angles between bonds are smaller than the angles between lone-pairs and bonds as illustrated in Fig. 1. Accordingly the bond angles adjacent to a lone pair are smaller than the ideal angles of 90°, 109.5° and 120° associated with regular polyhedra. Many examples are given in Refs. [5,6].
(2) Multiple bonds are composed of two or three electron-pair domains so that together they take up more angular

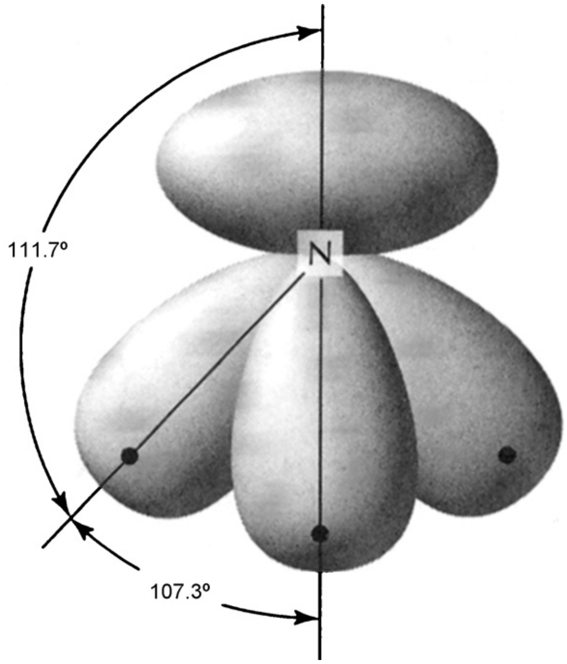

Fig. 1. Representation of the bonding and nonbonding electron-pair domains in the NH_3 molecule showing the greater angular spread of the lone-pair domain compared to the non-bonding (lone pair) domains.

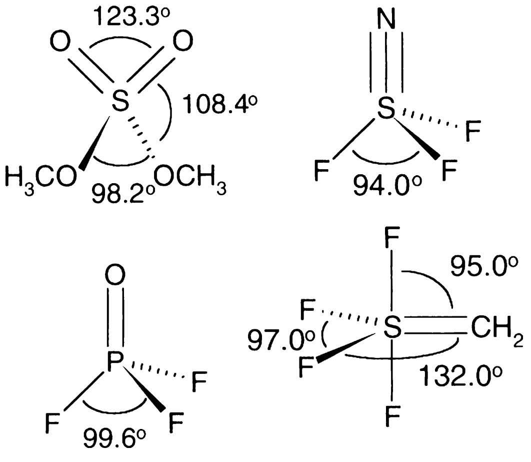

Fig. 2. Bond angles in some multiply bonded molecules showing that bond angles decrease in the order: multiple bond–multiple bond > multiple bond–single bond > single bond–single bond.

space than a bonding pair domain, in other words bond angles decrease in the order multiple bond–multiple bond > multiple bond–single bond > single bond–single bond as illustrated in Fig. 2.

(3) The strengths of the repulsions between single bonds, and therefore the angles between the single bonds, decrease with increasing ligand electronegativity because a bonding pair domain decreases in size with increasing electronegativity of the ligand as more of the bonding electron density is transferred to the ligand. For example, bond angles, decrease in the series PI_3 102°, PBr_3 101°, PCl_3 100°, PF_3 98° as the electronegativity of the ligand increases. Many other examples can be found in Refs. [5,6]. However, the expected bond angle dependence on ligand electronegativity is often obscured by ligand–ligand repulsions as we discuss later, consequently rule 3 is not a rule that can be relied upon for all molecules.

3. Force constants and the VSEPR model

Although the VSEPR model has been widely used for predicting molecular structures it has been much less used for predicting and understanding the potential energy surface implied by the structure. Bartell [10] and Bartell and Barshad [11] have shown how the potential energy surface for a molecule can be obtained by means of the points-a-sphere (POS) version of the VSEPR model and therefore how bending force constants can be determined. Good agreement was obtained between the calculated POS quadratic and cubic bending force constants and the extended Huckel molecular orbital theory calculated values for SiF_4, CF_4, CCl_4, and SF_6 providing support for the validity of the potential energy surface calculated from the POS model.

An interesting and important application of the POS calculation of molecular force fields has been to trigonal bipyramidal AX_5 molecules for which there were found to be two possible assignments of the bending modes for PF_5. Assignment A [ν(equatorial in-plane-bend) > ν(axial bend)] and assignment B [ν(eq) < ν(ax)]. Assignment A was believed to be supported by the observation that the axial bonds are longer than the equatorial bonds and therefore have lower stretching force constants than equatorial bonds and the expectation that the axial bending frequencies would also be lower that the equatorial bending frequencies. However, according to the VSEPR model the axial bonds are repelled and constrained by three close (90°) equatorial bonds while the equatorial bonds are constrained by only two close (90°) axial bonds and, much more weakly, by two remote (120°) bonds. Consequently, axial bending modes and out-of-plane equatorial bending modes are severely restricted while allowing more freedom of motion for equatorial in-plane modes consistent with assignment B [12].

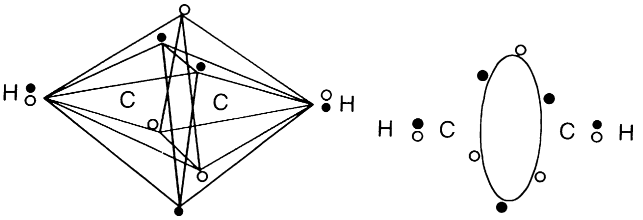

Fig. 3. Linnet double quartet description of the triple bond in ethyne showing that there is only one localized pair of electrons in the valence shell of each carbon atom.

4. Linnett's double quartet model

There a few molecules with an even number of electrons in which, contrary to the assumption made by Lewis and by the VSEPR and valence bond models, the electrons are not present in pairs. These are linear molecules, in which as Linnett pointed out in 1960 [13], electrons that are not on the molecular axis are not present as opposite-spin pairs, but rather have their most probable locations equally spaced in a ring around the molecular axis. In such cases an octet of electrons is not attracted by the ligands into four localized pairs but in linear molecules the ligands only cause the formation of one pair leaving the remaining electrons in tetrahedra that only coincide at one point and hence can be described as a double quartet. This does not affect the VSEPR prediction of a linear geometry as shown for ethyne in Fig. 3 but simply gives a different, but more correct, picture of the bonding in which the three electron-pair domains surrounding the molecular axis envisaged by Lewis and the VSEPR model are replaced by a single toroidal domain containing three α spin electrons and three β spin electrons with their most probable locations alternately and equally spaced around the molecular axis. This description is also slightly different from, and more accurate than, that provided by the molecular orbital σ–π description which considers that the six bonding electrons are distributed in pairs in the σ and two π orbitals.

5. Exceptions to the VSEPR model, ligand–ligand repulsion and the ligand close packing (LCP) model

Over the years some failures of the VSEPR model to give a correct qualitative explanation of the deviations of bond angles from the polyhedral angles of 90°, 109.5° and 120° have been used as a basis for claims that the model does not have a sound physical basis, but, as we have shown, the model is, indeed, soundly based on the Pauli principle. Nevertheless, there are a significant number of exceptions to the VSEPR model. It has been realized in recent year that these exceptions are primarily due to the neglect of ligand–ligand repulsions by the VSEPR model. The importance of vicinal ligand interactions in determining geometry and reaction rates has been recognized for many years but it was not generally appreciated that the interactions between geminal ligands can also be of importance as we now discuss.

Bartell [14] provided some strong evidence as early as 1960 of the importance of repulsions between geminal ligands in determining bond lengths and bond angles in molecules with a central carbon atom. But because the geometry of these molecules was at the time was interpreted by most chemists, and in particular organic chemists, by means of the VB theory and hybridization Bartell's work did not have much impact and was not much referred to. Unfortunately I did not become aware of Bartell's work until several years later and was too much influenced by the success of the VSEPR model to seriously take account of the possible importance of geminal ligand repulsion which the VSEPR model ignored. And I continued to do so after later further suggestions by Istvan and Magdolna Hargittai [15,16] that, at least in some molecules, they appeared to be important. Moreover my preoccupation with my principal fields of research—super acid solvents, and fluorine and noble gas chemistry—did not allow me much time for looking more deeply into the VSEPR model, and caused me to continue to ignore the importance of ligand–ligand repulsions. However, several failures of the model were becoming more frequently referred to in the literature and it was clear that ligand–ligand interactions could probably no longer be ignored.

The importance of ligand repulsions was finally impressed upon me when in 1997 Peter Robinson and I were analyzing bond lengths to fluorine we found clear evidence of the importance of ligand–ligand interactions. We noticed that ligand–ligand distances in a large number of molecular fluorides of the period 2 elements are essentially constant for a given central atom, independently of the coordination number and the presence of other ligands [17], as Bartell had already found in 1960 for molecules with a central carbon [14]. These results suggested strongly that the ligands in these molecules may be regarded as close packed, in other words that ligand–ligand repulsions must be of considerable importance in determining the geometry of these molecules and probably other molecules too. Accordingly we went on to study ligand–ligand distances in molecules with other ligands such as Cl, Br, and CH_3, and found that interligand distances for these ligands bonded to a period 2 central atom are also essentially constant [18,19]. From this data, and the assumption that the ligands can, to a reasonable approximation can be regarded as hard spheres, it was possible to derive ligand radii from the F–F, Cl–Cl, etc., distances [17,18]. These ligand radii are listed in Table 1. We then showed that they are additive to give values for X···Y distances in molecules with two or more different distances in good agreement with experiment, just as Bartell had done for a more limited number of molecules of carbon. For the molecules of the larger period 3 elements close packing of the ligands is less likely and only the octahedral MX_6, MX_5E, MX_4E_2 molecules have been found to have close packed ligands with constant interligand distances and these are very largely fluorides [20]. The ligand radii determined from the interligand distances in these period 3 molecules are consistent with those given in Table 1. The four coordinated molecules of the elements of period 3 and higher periods are not close-packed, nevertheless ligand–ligand repulsions may still be of importance in influencing the geometry of a molecule.

Table 1
Ligand radii (pm)

Ligand	Be	B	C	N	Si	P	S
Central atom							
H		110	90	82	–	–	–
C		137	125	120	–	–	–
N	144	124	119	–	–	–	–
O_t[a]	133	119	114	–	–	–	–
F	128	113	108	108	127	120	118
Cl	168	151	144	142	160	156	155

[a] Terminal oxygen atom.

The concept of the close packing of nearly spherical ligands with a fixed radius that depends only on the nature of the central atom constitutes what Robinson and I called the ligand close packing (LCP) model [18,19]. The radius of a ligand depends on the nature of the central atom, because with decreasing electronegativity of the central atom electron density is transferred to the ligand so that it has a larger negative charge and its size increases accordingly. Indeed there is a good correlation between the ligand radius and the atomic charge [20]. (Table 2). That a ligand radius varies with the nature of the central atom and therefore on the ligand charge had not been previously realized and was responsible for the lack of success of attempts to use Bartell's radii for molecules with other central atoms which in turn was a reason for the continued lack of interest in Bartell's work.

The recognition of the importance of ligand–ligand repulsions enables almost all the failures of the VSEPR model for the main group elements to be easily explained. For example, although chlorine is more electronegative than hydrogen the ClOCl angle in Cl_2O (111.2°) is larger than the HOH angle

Table 2
Atomic charges and ligand radii[a]

	q (A)	q (F,Cl)	r (F,Cl) (pm)
LiF	0.92	−0.92	–
BeF_2	1.75	−0.88	128
BF_3	2.43	−0.81	113
CF_4	2.45	−0.61	108
NF_3	0.83	−0.28	106
OF_2	0.26	−0.13	–
LiCl	0.91	−0.91	–
$BeCl_2$	1.77	−0.84	168
BCl_3	1.93	−0.64	151
CCl_4	0.35	−0.03	144
NCl_3	−0.24	0.08	142
OCl_2	−0.46	0.23	–

[a] QTAIM calculated charges [27,28].

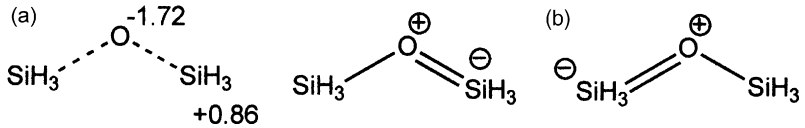

Fig. 4. Bonding in disiloxane. (a) Recently proposed structure involving strong, predominately ionic, bonds resulting from the large charges on the Si and O atoms. (b) Earlier proposed resonance structures showing double bond character for the strong SiO bonds.

(104.5°) in H_2O because the large size of the Cl ligand prevents the Cl ligands from being pushed any closer together by the lone pair. Indeed the ClOCl bond angle is larger than the tetrahedral angle which cannot be explained by the VSEPR model alone. Similarly the bond angle in PH_3 (93.8°) is significantly smaller than the bond angles in both PF_3 (97.8°) and in PCl_3 (100.3°) despite the fact that F and Cl are both more electronegative than H. The reason for these deviations from the VSEPR rules is now obvious: hydrogen is much smaller than any other ligand with a ligand radius decreasing from 102 pm on boron to 82 pm on nitrogen so that $H\cdots H$ repulsions only become important at smaller ligand–ligand distances and smaller bond angles than in comparable molecules with other ligands [21]. Because of the large size of the Cl ligands the lone pairs in Cl_2O are unable to push the ligands closer together than 111.2° and similarly the lone pair in PCl_3 (100°) and PF_3 (98°) cannot push these ligands as close together as in PH_3 (94°) [21]. The early success of the electronegativity rule in fact obscured the importance of ligand–ligand repulsions in many molecules. For example, the bond angle increase in the series PF_3 (98°), PCl_3 (100°), PBr_3 (101°) is consistent with the decreasing electronegativity of the ligand but it is also consistent with the increasing size of the ligand. Overall ligand size explains those bond angles that are not consistent with the electronegativity rule but also those that are consistent with the rule, so it is reasonable to replace the electronegativity rule of the original VSEPR model with the rule that bond angles increase with ligand size. Since bond angles can be predicted from the ligand radii in close-packed AX_2E_2 and AX_3E molecules where the bonds are all the same length and can be calculated if the bond lengths in $AXYE_2$ and AXYZE molecules are known the LCP model adds a semi-quantitative aspect to the VSEPR model.

As we mentioned earlier there are a few molecules in which lone pairs appear to have no effect on the geometry such as the triangular planar $N(SiH_3)$ molecule which has 120° bond angles, considerably larger than the tetrahedral angle of 109.5° Here the ligands are large and only weakly electronegative so ligand–ligand repulsions are strong while the nitrogen lone pair is not well localized. Consequently ligand–ligand repulsions dominate the geometry. The closely related molecule $O(SiH_3)_2$ has an even larger bond angle of 144° as a consequence of having only two ligands rather than three. This angle is much larger than 109.5° the largest angle consistent with the VSEPR model again because the SiH_3 group is only weakly electronegative and the ligand is large [6]. There is no experimental evidence for the alternative and widely accepted explanation of the delocalization of the Si lone pairs into the antibonding orbitals of the O–H bonds which can be represented by resonance structures such as that given in Fig. 4. The other type of molecule in which a lone-pair appears to have no effect on the geometry is AX_6E molecules such as BrF_6^- and $SbCl_6^{3-}$ which are octahedral although their Lewis structures have seven electron pairs in the valence shell of the central atom. Robinson and I suggested that this is because the six ligands in these molecules are close-packed leaving no room in the valence shell for a lone pair [22,23]. So there is, in fact, no lone pair in these molecules–the two non-bonding electrons are forced to remain associated with the core forming a spherical shell around the inner core, that is a Br^{4+} or Sb^{3+} core, for example. Evidence that this is indeed the case is provided by SeF_6^{2-}, IF_6^-, and XeF_6 where, because the central atom is larger than the Br atom the fluorine ligands are not quite close-packed, allowing room for some of the non-bonding electron density to move into the valence shell to form what has been called a partial or weak lone pair, resulting in a small C_{3v} distortion of the octahedral structure observed for BrF_6^- [23] (Fig. 5). Because of the close, or near close, packing of the ligands none of these molecules has a structure based on a pentagonal bipyramidal valence shell of seven electrons with a fully active lone pair, such as that found for the IF_7 molecule. It is interesting to point out that on the basis of the VSEPR model I predicted in 1962 [24] that the XeF_6 molecule would not be found to be octahedral contradicting the claims by theoreticians based on qualitative MO theory, that it would have a regular octahedral geometry. When my prediction was later ver-

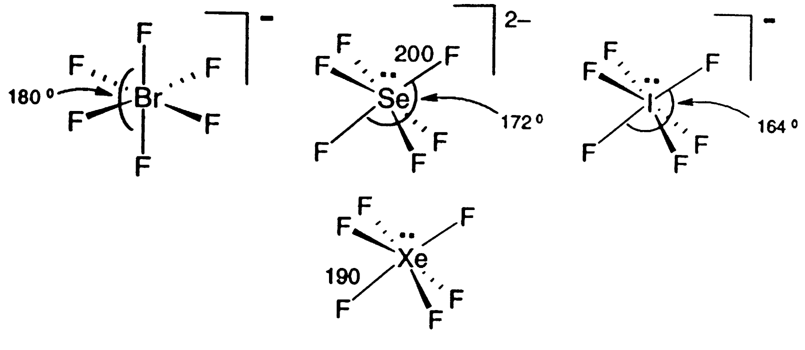

Fig. 5. The octahedral (O_h) structure of BrF_6^- and the C_{3v} distorted octahedral structures of SeF_6^{2-}, IF_6^-, and XeF_6 caused by the presence of a "weak" lone pair.

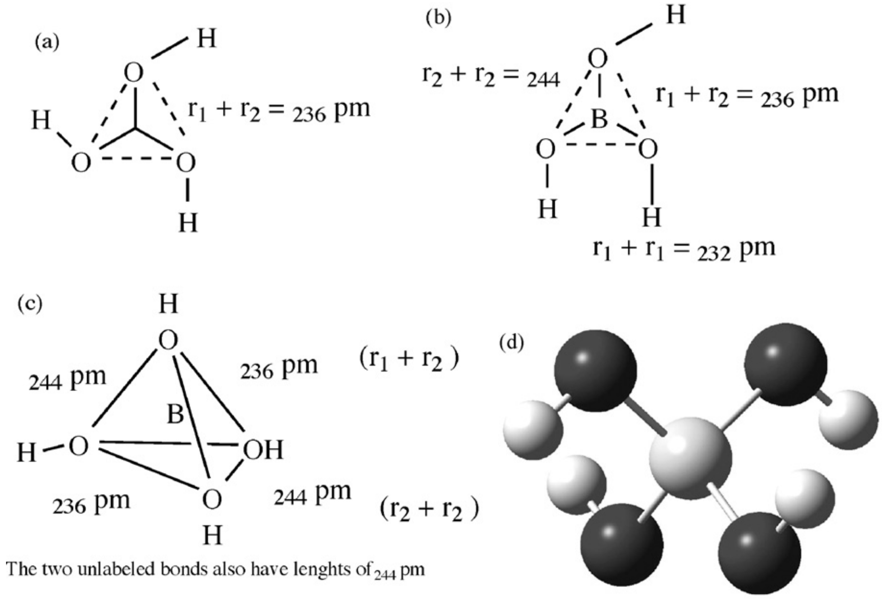

Fig. 6. The non-tetrahedral D_2 geometry of $B(OH)_4^-$ and related molecules. (a) The three interligand distances in D_{3h} $B(OH)_3$ are all equal and equal to the sum of the two radii of the oxygen atom. (b) The calculated structure of the higher energy C_s form has three unequal interligand distances and three correspondingly different bond angles equal to the three possible sums of the two radii of the oxygen atom. (c) Simplified diagram of the $B(OH)_4^-$ molecule showing only the six interligand distances. There are two shorter interligand distances corresponding to a bond angle of 106.2° and four longer distances corresponding to a bond angle of 111.4°. (d) Three-dimensional view of the D_{2d} structure of $B(OH)_4^-$.

ified by the determination of the structure by Bartell and Gavin [25] who found it to have a C_{3v} distorted octahedral structure it significantly increased interest in the VSEPR model.

A very interesting application of the ligand close packing model is its use to explain the geometries of molecules with diatomic ligands such as OH and OMe. [6,26] It was found that the oxygen atom in these molecules could not satisfactorily be assigned a single ligand radius because the electron density around the oxygen is not spherical because there are two lone pairs and two bonding pairs in the valence shell of the central atom. This is clear from the structure of the less stable C_s isomer of $B(OH)_3$ in which there are three different bond angles and correspondingly three different $O\cdots O$ distances in contrast to the single O–O distance in the C_3 isomer. Fig. 6a and b shows that these unequal interligand distances can be accounted for by assigning two different ligand radii to the oxygen atom: r_1 in the direction between the assumed positions of the lone pairs and r_2 in the opposite direction, to take account of the non-spherical nature of the electron density. Fig. 6c shows that these same radii provide a simple explanation for the D_{2d} symmetry of the $B(OH)_4^-$ molecule. In this molecule the interligand distances cannot all be the same as in a truly tetrahedral (T_d) molecule because there are two different types of contacts leading to two different interligand distances: two of one type ($r_1 + r_2$) and four of another type ($r_2 + r_2$). So the molecule has D_{2d} symmetry.

Similar arguments can be used to explain the non tetrahedral bond angles of other similar four coordinated molecules which have S_4 or D_2 symmetry, such as $C(OMe)_4$, $B(OSO_2Cl)_4^-$, $C(C_2H_5)_4$ and $Ti(NMe_2)_4$ rather than the tetrahedral T_d symmetry predicted by the VSEPR model. These non-tetrahedral bond angles are a direct consequence of the unsymmetrical electron density of the ligand atom bonded to the central atom, such as the O atom in OH. It is worth while emphasizing again that the two lone pairs on the central atom do not "stick out like rabbit ears: the ligand radius in the direction of the lone pairs (r_1) is smaller than the radius in the opposite direction (r_2). In other word, ligand atoms have closer contacts in the direction of the lone pairs than in the opposite direction because the lone pairs are more spread out and closer to the core than the bonding electrons.

6. Analysis of the electron density

In the preceding section we have mentioned how the distribution of the electron density around an atom in a molecule can affect its geometry. In recent years interest in the electron density distribution in molecules has been growing as it has been determined in an increasing number of molecules and with increasing accuracy by ab initio calculations and by X-ray crystallography. These electron densities have provided important information about the bonding in molecules and at the same time provided strong support for, and a better understanding of, the VSEPR model.

The electron density of a molecule can be analyzed by the QTAIM theory [27,28] to partition the density of a molecule into regions surrounding each nucleus. Each of these regions, called atomic basins, represents the atom as it exists in the molecule. Various properties of an atomic basin, such as its volume and electron population and hence its charge can be obtained by numerical integration of the electron density. However, there are no features of the electron density that can be associated with either bonding, or non-bonding, electron pairs. This is not surprising as there are no fully localized pairs, only regions, called electron-pair domains in the VSEPR model, in which there is a higher probability of finding an opposite spin electron pair than in other regions of the valence shell. Although the VSEPR domains are not directly observable in the electron density certain functions of the electron density can reveal the presence of opposite-spin electron pairs as we shall see.

My interest in the VSEPR model was revived and heightened by the discovery by my colleague Richard Bader that the negative of the Laplacian of the electron density ($-\nabla^2\rho$) exhibits maxima which indicate the presence of localized concentrations of electronic charge in the valence shell of an atom which equal in number the domains of the VSEPR model, and have the same angular distribution as these domains [29]. It seemed that the analysis of the electron density might be able to provide a better understanding of the VSEPR model and of the geometry of molecules that appear to be exceptions to the VSEPR model. At this time my program of experimental work was drawing to a close and I slowly transformed myself from an experimentalist to an amateur theoretician with the aim of trying to further understand the VSEPR model and its limitations. This work has continued to provide an interesting and stimulating occupation during my "retirement" and has indeed led to a much better understanding of the VSEPR model and of its exceptions including the development of the LCP model.

Richard Bader's discovery led to a very fruitful collaboration with him and his graduate student Preston MacDougall that started with the publication of a paper in 1988 in which we studied the Laplacian of the $O=ClF_3$ molecule [30]. Again we found that the Laplacian maxima are the same in number and angular geometry as the VSEPR domains. As a result of this work and the earlier work [29] we concluded that the Laplacian of the charge density appears to provide a physical basis for the VSEPR model [30]. Examples of the charge concentrations observed in the Laplacian of some simple molecules are given in Fig. 7. They have the number and general geometry expected for the domains of the VSEPR model, that is as expected as a consequence of the Pauli principle, although these domains are not precisely defined their angular distribution is the same as predicted by the Pauli principle. Nevertheless it is not certain that the volume and exact position of these charge concentrations can be regarded as a quantitative description of the VSEPR domains. Indeed, the relationship between the Laplacian charge concentrations and the domains of the VSEPR model appears to be essentially empirical. As we discuss later, in some molecules the charge concentrations do not have the same number and geometry as expected for the domains of the VSEPR model. Nevertheless, studies of the Laplacian of the electron density have provided additional understanding of the geometry of some molecules. For example, in a Laplacian study of molecules of the type $(SiH_3)_2O$ it was found that the localization of the charge concentrations in the valence shell of the oxygen was much weaker than in $(CH_3)_2O$ molecule consistent with the explanation that this, together with the larger size of Si than C, is responsible for the large bond angle of 144° in $(SiH_3)_2)O$ (Fig. 8) [31], confirming the explanation proposed in Section 4 and Fig. 4.

More direct and more certain support for the VSEPR model is provided by other functions of the electron density which depend more directly on the probability of finding an electron pair at a particular location such as the electron localization function (ELF) [32–34]. So it seemed like a good idea to see what further understanding of the VSEPR model and its limitations could be obtained from studies of the ELF (η) and for these studies I benefited from a fruitful collaboration with Bernard Silvi. The ELF partitions a molecule not into atomic basins, or regions of charge concentration, but into basins within which the probability of finding of finding same spin electrons is minimized. Such regions are therefore usually dominated by the presence of a single opposite spin pair. Each basin has a maximal value of η at which point the local perfect opposite spin pair character is high. At low values of η the corresponding basin encompasses the whole molecule but with increasing values of η this basin splits into separate basins that are considered to correspond to core electrons, bonding pairs and non-bonding pairs, in other words to the domains of the VSEPR model. Some examples are given in Fig. 9. A particularly interesting case is that of ethene (Fig. 10) which shows two maxima situated on opposite sides of the CC axis corresponding to the VSEPR and Lewis models of ethene. In contrast the Laplacian for this molecule has two maxima along the CC axis. Similar differences between the Laplacian and the ELF descriptions are found

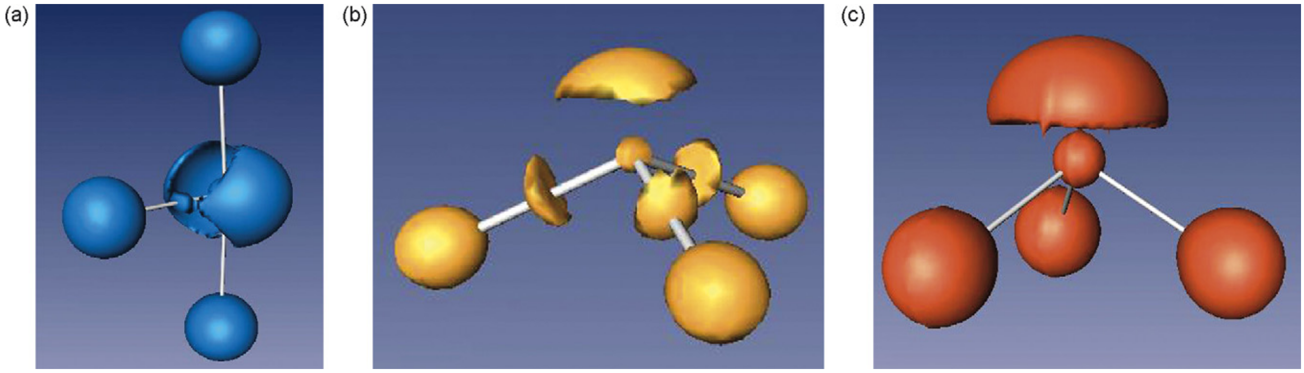

Fig. 7. Isosurfaces for a given value of ($-\nabla^2\rho$) showing the locations of the charge concentrations. (a) ClF_3 – showing the charge concentrations corresponding to the three F atoms and the two charge concentrations corresponding to the two lone pairs in the valence shell of the central Cl atom. (b) NH_3 – showing the nitrogen lone pair, three bonding pairs and the three H atoms. (c) PF_3 – showing the phosphorus lone pair and the three F atoms – no bonding charge concentrations are observed because of the large difference in electronegativity between P and F.

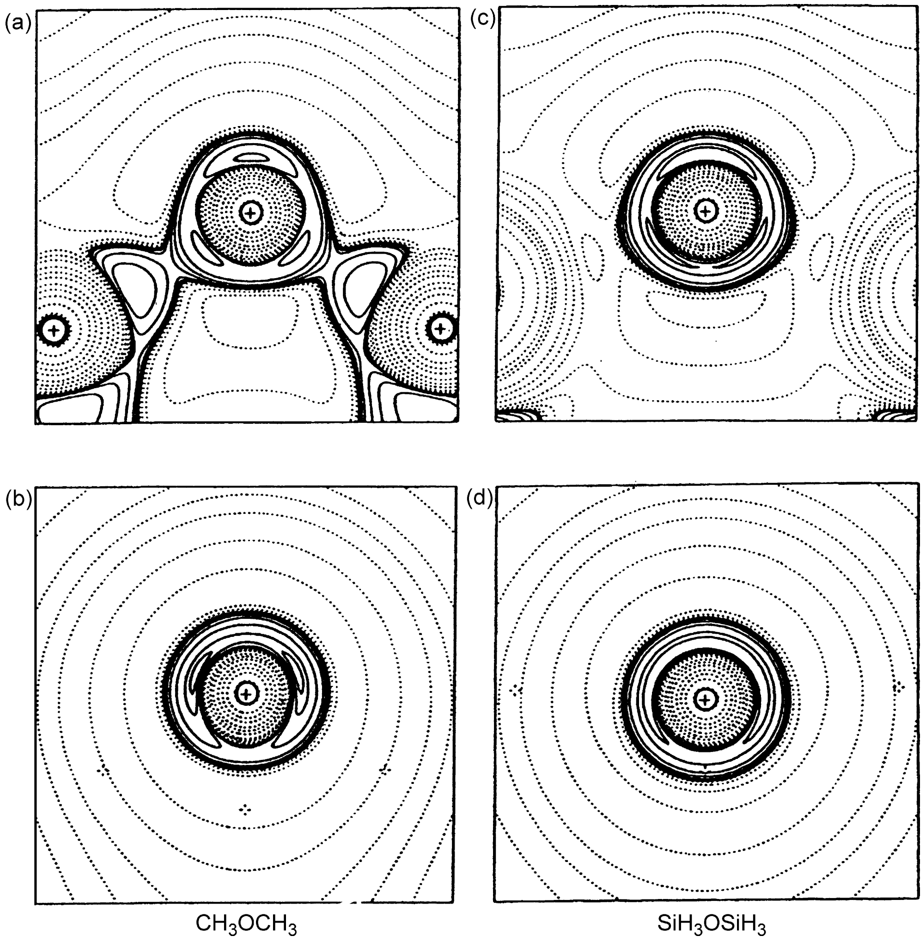

Fig. 8. Two-dimensional plots of the Laplacian for the dimethyl ether and disiloxane molecules. (a) In the COC plane and (b) in the perpendicular plane through the oxygen (c) in the SiOSi plane (d) in the perpendicular plane through the oxygen atom. Comparison of (a) and (b) with (c) and (d) shows that the oxygen valence-shell electrons are much more poorly localized in disiloxane that in dimethly ether, so that ligand–ligand repulsions are much more important in disiloxane than in dimethyl ether causing the SiOSi bond angle to increase to 144°.

for a CC triple bond. The Laplacian shows two maxima along the CC bond whereas the ELF has a toroidal basin surrounding the CC axis in accord with the Linnett double quartet model [13].

An ELF study of AX_6E molecules has provided strong support for the LCP explanation (Section 5) of the unexpected octahedral O_h and C_{3v} distorted octahedral geometry of molecules of this type [35]. Fig. 11 shows the ELF basins

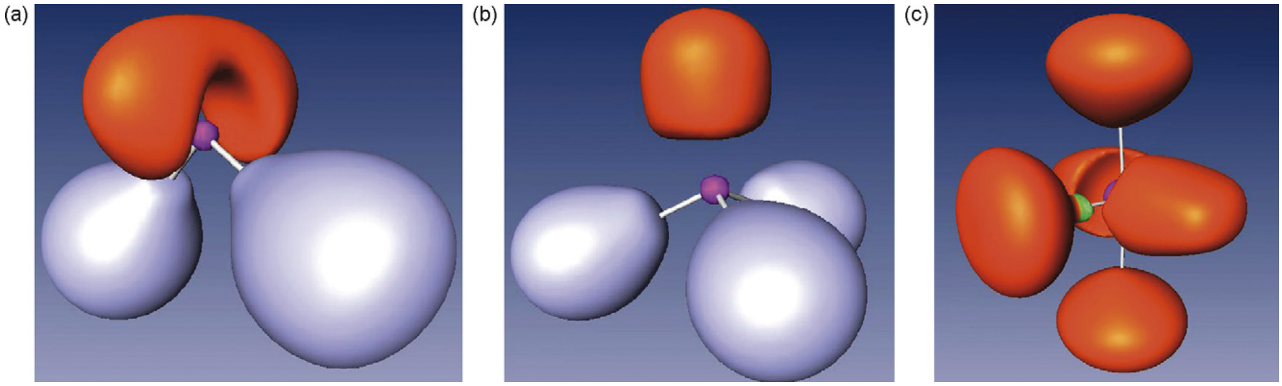

Fig. 9. Isosurfaces of the ELF for a given value of η for (a) H_2O showing the two oxygen lone pairs (brown), the two hydrogen bonding – nonbonding localization basins (blue) and the oxygen core (mauve) (b) NH_3 showing the nitrogen lone-pair localization basin (brown), the three hydrogen bonding-nonbonding basins (blue) and the nitrogen core (mauve) (c) ClF_3 showing the two localization basins corresponding to the lone pairs and the three F atoms (brown), a bonding pair (green) and the Cl core (mauve).

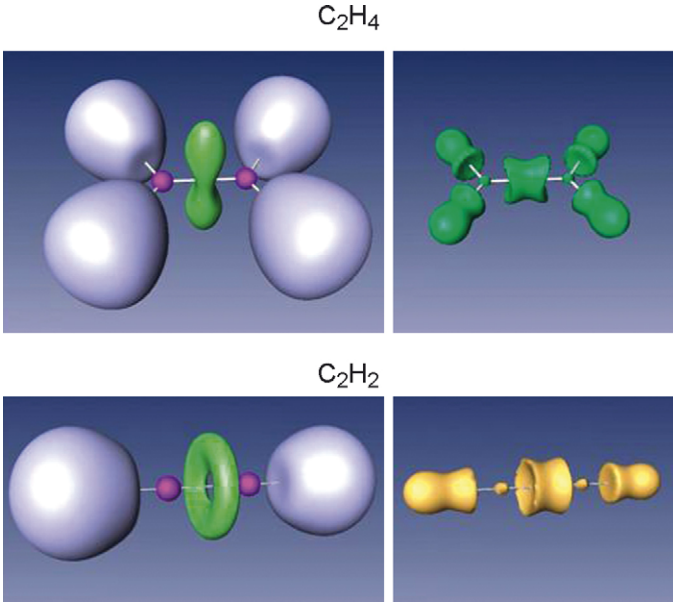

Fig. 10. Comparison of the ELF and Laplacian isosurfaces for (a) C_2H_4 ELF (left) and Laplacian (right). ELF shows two maxima between the C atoms located one on each side of the molecular plane in accordance with the VSEPR and Lewis models for these molecules. In contrast the Laplacian shows two maxima along the CC axis. (b) C_2H_2 ELF (left) and Laplacian (right). ELF shows a bonding torus around the mid point of the CC axis in accordance with Linnett's double quartet model while the Laplacian shows two incompletely resolved tori one on each side of the mid point of the CC axis.

of BrF_6^-, SeF_6^{2-} and XeF_6. It can be seen that there is no basin corresponding to a lone pair in the BrF_6^- molecule consistent with its strictly octahedral geometry. In contrast the other molecules show the presence of a non-bonding (partial lone pair) basin in the valence shell causing the C_{3v} distortion.

The molecules R_2SiSiR_2 and RSiSiR and their Sn and Ge analogues are examples of molecules which according to their Lewis structures have double and triple bonds respectively and no lone pairs in the valence shell, yet, unlike their carbon analogues, ethene and ethyne, they have angular structures as if each Si or Ge atom has a lone pair in its valence shell. The basic reason for the difference in the structures of ethene and ethyne and the corresponding silicon and germanium analogues is that silicon and germanium are not sufficiently electronegative to be able to attract six electrons into the bonding region because of the strong electrostatic repulsion between these six electrons. Fig. 12a and b show the results of an ELF study [36] of HSiSiH and HGeGeH where it can be seen that there are six localization basins that form a torus surrounding the SiSi or GeGe axis. These are single electron localization basins. There are four basins (orange and yellow) that have both a bonding and a nonbonding character occupying both the bonding region and the lone-pair region, indicating that these electrons that in C_2H_2 are bonding electrons are only partially bonding and partially nonbonding electrons in Si_2H_2 and Ge_2H_2. In addition there are two localization basins (green) that can be regarded as bonding basins but they are not well localized into an opposite spin pair. The torus of localization basins strongly resembles the toridal localization basin in ethene that is nicely described by the Linnett double quartet, but for silyne and germyne the toroidal localization basin is tipped away from its position vertical to the CC axis as shown in Fig. 12c and splits into six single electron basins. Two of the electrons are closer to one Si atom and two more are closer to the other Si atom giving their basins some partial lone-pair character. The other two electrons are bonding electrons. These partially lone-pair electrons are responsible for the angular shapes of the molecules. Similar ELF studies were also made on H_2SiSiH_2 and H_2GeGeH_2 and on the methyl derivatives of all these molecules and gave similar results. The bonding in these molecules can be approximately described by the resonance structures in Fig. 12d. Corresponding Laplacian studies of a related molecule have also given similar results [37].

An advantage of the ELF is that the number of electrons associated with a given ELF basin can be obtained by integration of the electron density over a bonding, non-bonding or core basin. Silvi and I made use of this property in our study of hypervalent

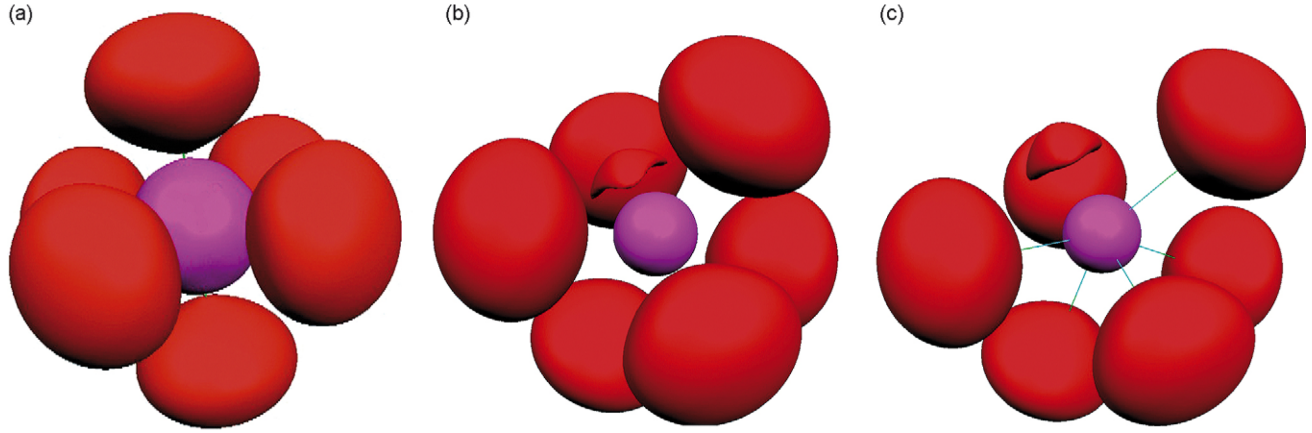

Fig. 11. Isosurfaces of the ELF showing localization basins for some AF_6E molecules. Nonbonding basins are brown and the central core is mauve. (a) BrF_6^- is octahedral (O_h) and there is no nonbonding lone pair in the valence shell of the Br atom. The Br core is large because it incorporates the non bonding pair. (b) IF_6^- has a C_{3v} distorted octahedral geometry because of the weak or partial lone pair that is evident in the valence shell of iodine. The iodine core in IF_6^- is smaller than the bromine core in BrF_6^- because electron density is lost from the I core to form the partial lone pair. (c) XeF_6 has a larger lone pair and the molecule is more distorted from octahedral symmetry because of the larger size of the Xe atom and the consequent increased distances between the ligands.

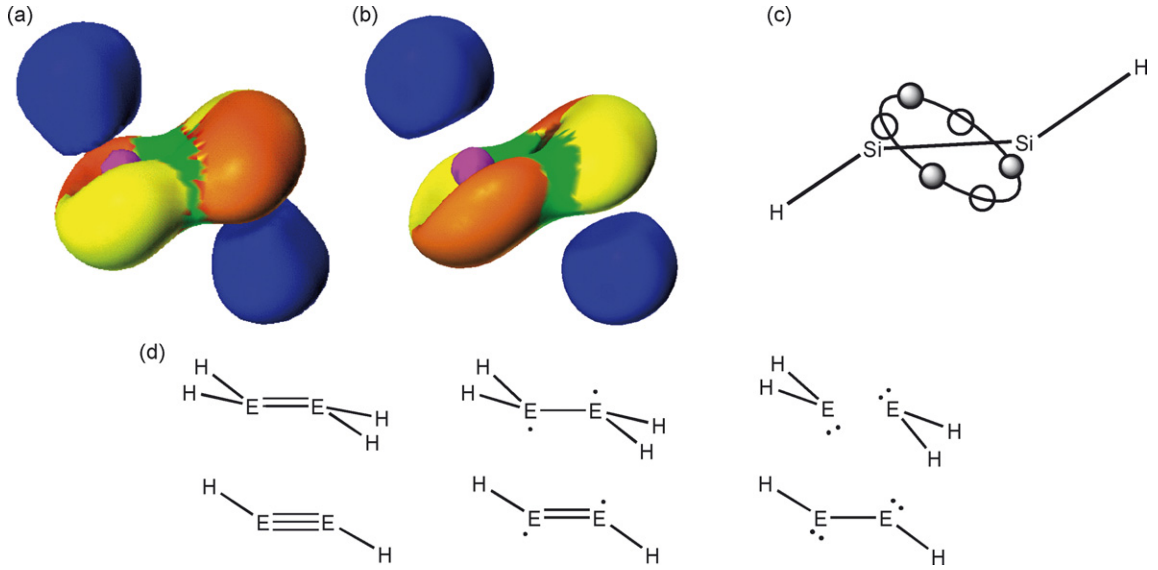

Fig. 12. (a) ELF basins for Si_2H_2, (b) ELF basins for Ge_2H_2, (c) Linnet Double Quartet Model for HSiSiH and HGeGeH. (d) Approximate representation of the bonding in HSiSiH, H_2SiSiH_2 and analogous molecules by means of resonance structures.

molecules [38,39]. It has often been claimed that hypervalent molecules, although having 10, 12 or even more electrons in the valence shell of the central atom in their Lewis structures, in fact obey the octet rule, because the electronegativity of the ligands in most hypervalent molecules attracts much of the electron density out of the valence shell of the central atom [40]. However, we showed by integration of the electron density in each of the six Te-C bonding basins that in $Te(CH_3)_6$ there are a total of 11.6 electrons in the valence shell of the central atom. And in other similar molecules there are many more than eight electrons in thee valence shell [39]. We concluded that these molecules do not therefore obey the octet rule, that the bonds are not any different from the bonds in other non-hypervalent molecules, and that the term hypervalence no longer has any useful significance.

It is clear that the Laplacian of the electron density and the ELF have been very helpful in providing support for, and for furthering our understanding of, the VSEPR model, including the important role of lone pairs and the dependence of molecular geometry on the Pauli principle. However, both functions and their role in providing support for, and further understanding of the VSEPR model, have been the subject of some controversial discussion. Overall, it appears that the ELF is more consistent with the VSEPR model than is the Laplacian.

7. Molecules of the transition metals

Sidgwick and Powell noticed that the exceptions to their model were almost all among the molecules of the transition metal [3]. Because a large number of transition metal compounds exist only in the crystalline state, rather than as discrete molecules, models such as the crystal field theory were developed to explain their geometry at about the same time as the VSEPR model was proposed and relatively little has been done to propose alternative models that might be more relevant for discrete molecules. All the molecules we discuss in this section are isolated molecules whose structures have been determined in the gas phase or by ab initio calculations. Transition metals differ in an important way from the main group elements in that they do not have any lone pairs in the valence shell of the central metal atom: any non-bonding electrons are in the

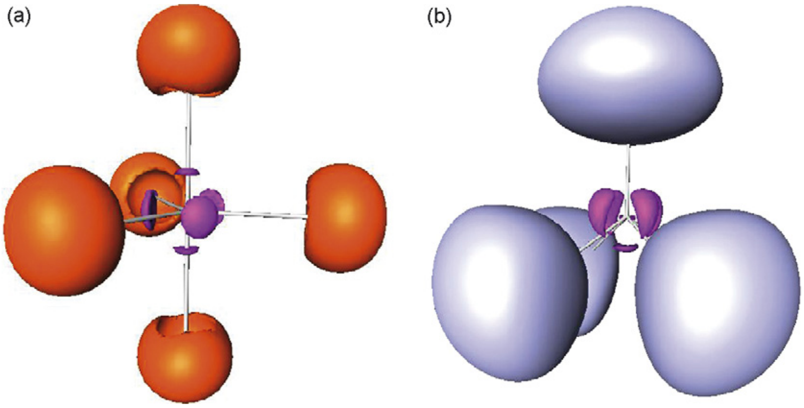

Fig. 13. ELF localization basins for (a) VF_5 and (b) VH_5.

outer sub-shell of the underlying core, the d sub-shell according to the LCAO-MO model. So, assuming that the core is spherical, it would be expected that their geometries should be simply those predicted by ligand–ligand repulsion or the VSEPR model for molecules without lone pairs – AX_3 equilateral triangular, AX_4 tetrahedral etc. However, even molecules in which there are formally no nonbonding electrons in the d shell – so called d^0 molecules – do not always have these predicted shapes. For example, CaF_2 and CaH_2 are angular, not linear, ScH_3 is pyramidal while ScF_3 has the expected trigonal planar geometry, and VH_5 is square pyramidal, while VF_5 has the expected trigonal bipyramidal shape, and CrH_6 and $CrMe_6$ have C_{3v} distorted trigonal prism shapes while CrF_6 has the expected octahedral shape [41,42]. Some of these molecules and a few other related molecules have been studied by both the Laplacian [41] and by ELF [42] and there is qualitative agreement between the positions of the Laplacian charge concentrations and the ELF basins. According to the quantitative analysis of the ELF for these molecules the population of the M shell is larger than the conventional value of 18 because in the LCAO-MO scheme the 3d basis functions centered on the metal contribute noticeably to the electron density within the core. Under the influence of the ligands these electrons the core loses its spherical symmetry by forming localization basins which in turn influence the geometry of the ligands if they interact with the core sufficiently strongly. Fig. 13a shows the localization basins for VF_5 and Fig. 13b those for VH_5. The bonding localization basins for VF_5, have a trigonal bipyramidal geometry, just as they do in PF_5, presumably because, the interaction of the F ligands with the core is weak and the core is very little distorted from a spherical shape. In contrast VH_5 has a square pyramidal geometry because the interaction of the H ligands with the core is strong. This strong interaction produces core localization basins which appear in locations on the opposite side of the core from the ligands. The ligands take up positions which minimize their interaction with these localization basins. The analogy between the main group molecules in which the interaction of the ligands with a spherical core causes the formation of localized lone-pair domains, which in turn affect the geometry of the ligands is clear. However, the number and angular location of the core localization basins in ELF or the core charge concentrations in the Laplacian cannot yet be easily predicted so a model for the geometry of the AX_n molecules of the transition elements analogous to the VSEPR model for the main group molecules has not yet been proposed. Further studies of additional d^0 molecules, and also those with d^1 to d^{10} configurations are required before such a model could be developed.

8. Teaching the VSEPR model

The success of the VSEPR model and its widespread acceptance has, undoubtedly, been very largely due to its great usefulness in teaching molecular geometry in introductory courses, particularly because it avoids any consideration of orbitals which have proven, for beginning students, to be a difficult and much misunderstood concept. The first presentation of the model can be simply as a set of empirical rules following immediately after Lewis structures. These rules concerning the relative sizes of the domains of lone pairs, bond pairs and multiple bonds can then be used to account qualitatively for deviations from the regular polyhedral angles. The relationship between the VSEPR model and the Pauli principle can then be introduced, either in the first course or in subsequent courses, as seems appropriate. The discussion of exceptions to the VSEPR model might then be based on ligand–ligand repulsions and the LCP model. Moreover, there are many opportunities to discuss the geometry of molecules from the point of view of the VSEPR and LCP models during any later discussions of molecule structure in both inorganic and organic chemistry courses. This is not to say that chemistry students, beyond the first year course should not also be familiar with both the Valence Bond and Molecular Orbital theories. Indeed by comparison of the treatments of particular molecules by both the VSEPR model, the LCP and orbital models they can learn to appreciate the advantages and limitations of each of them.

9. Summary and conclusions

Not surprisingly the VSEPR model has not survived 50 years without undergoing some changes. Investigation of exceptions to the model has been particularly fruitful in providing new understanding of these exceptions and in revealing the role of factors not considered in the original version of the VSEPR model such as ligand–ligand repulsion. Nevertheless, the original VSEPR model remains extremely useful, not only for teaching, but also for anyone interested in molecular structure, as a type of “back of the envelope” method for quickly predicting the qualitative geometry of a molecule. Almost all the exceptions to the bond angles predicted by the VSEPR model can be understood by means of the LCP theory, including the D_{2d} geometry of $B(OH)_4^-$. Recent work on functions of the electron density such as the Laplacian of the density and the ELF has further enhanced our understanding of the VSEPR model, including in particular the important role of lone pairs, and has confirmed proposed explanations for unexpected geometries such as those of AX_6E molecules and molecules such as RSiSiR and R_2SiSi_2. A combination of the VSEPR and LCP models now provides a very satisfactory explanation for the qualitative geometry of a vast number of main group molecules with very few exceptions. Much work remains to be done on the meaning of, and the relationship between, various functions of the electron density, and on the molecules of the transition metals.

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