the elements beyond krypton, although a complete table of electron configurations could be given, as it usually is, without further explanation. At this point, the standard "rules" governing electron configurations (number of subshells in a shell equals n, maximum number of electrons in a shell equals 2n², etc.) may be presented.

Summary

We have shown that the shell model, the concept of energy levels, and simple electron configurations, can be easily and satisfactorily developed from experimental data such as that summarized in the periodic table and/or in a table of ionization energies. These electron arrangements can then be refined, when and if necessary, to full electron configurations by a more detailed discussion of ionization energies. In our opinion this is a better pedagogical approach for the introductory course than the conventional treatment in terms of quantum numbers introduced as "magic numbers" that arise by a mysterious process from quantum mechanics, that is, from the solutions to the Schrödinger equation, an equation that students do not understand. Students will have seen how the principal quantum number arises simply from the shell model and they will be prepared for the azimuthal quantum number as an alternative description of s, p, d, ..., subshells. When they subsequently encounter quantum numbers, these numbers will have already lost some of their air of mystery.

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Demystifying Introductory Chemistry

Part 2. Bonding and Molecular Geometry Without Orbitals — The Electron Domain Model

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One of the most difficult parts of an introductory chemistry course for most students, and one of the most difficult to teach in a satisfactory way, is the concept of covalent bonding in terms of the conventional valence bond (overlap of atomic or hybrid orbitals) method. The simplest approach to bonding is in terms of Lewis diagrams and the concept of the shared electron pair. This is as far as this topic needs to be taken in the most elementary introductions. Commonly the next step is to use the VSEPR model (1, 2) to predict basic geometries from the Lewis diagram on the basis that the electron pairs in the valence shell (both bonding and nonbonding) keep as far apart as possible. Then the valence bond model is usually introduced using the VSEPR predicted geometry as a basis for choosing an appropriate set of hybrid orbitals. The purpose of this article is to present an alternative approach to bonding and geometry—the electron domain model—that avoids some of the problems with the conventional approach and presents fewer difficulties for the student, while providing a physical basis for the VSEPR model and a link to the valence bond model. It is not intended that this model should necessarily replace the valence bond and molecular orbital models, but rather that it could serve as a simple introduction to bonding that would precede the discussion of these approaches. For the many general chemistry students who do not take further chemistry courses, the electron domain model alone might be adequate. In order to make the advantages of the electron domain model clearer, we first review some of the difficulties associated with presenting the orbital model.

Difficulties with the Orbital Model at the Introductory Level

1. The atomic orbitals used in the valence bond method are the wave functions ψ that are the solutions to the Schrödinger equation for a hydrogen-like atom. Because the Schrödinger equation and its solutions are not presented at the introductory level, the concept of an orbital can have little meaning for the beginning student, and the forms of the orbitals (including the nodes and the change of sign at the nodes) can be something of a mystery.

2. These difficulties are frequently avoided by moving directly to the square of the wave function, which, for a hydrogen-like atom, gives the probability of finding the electron at any point in space. This probability is usually expressed as the shape and density of a corresponding electron charge cloud, which is a concept that can be visualized and that the student can begin to understand. That this electron density distribution is often (somewhat inaccurately) called an orbital is partly responsible for some of the difficulties encountered with the valence bond approach. As no justification can be given for these shapes at the introductory level, they have to be memorized by the student. Moreover, the shapes of these "orbitals" (electron density distributions) are often portrayed in a stylized and very approximate manner that can be very misleading for students, who often accept them as having the exact form with which they are depicted. Consequently, any subsequent use of these orbital shapes may be misunderstood by the student.

3. Little use is, in fact, made of these orbital shapes in the introductory course. Almost their only use is to pro-
provide a justification for the angular shape of the H₂O molecule and the pyramidal shape of the NH₃ molecule. They are also customarily used in the crystal field or ligand field treatment of transition metal complexes, but the theoretical treatment of transition metal complexes is too advanced for most introductory courses. In either case, however, these discussions are pedagogically unsound as they are based on orbital shapes the origin and meaning of which are not clear to the student, even if they are correctly depicted.

4. In order to discuss many simple molecules such as CH₄ and BF₃ in the valence bond approach the concept of hybrid orbitals must be introduced. The forms of these hybrid orbitals cannot be derived at the introductory level; the student has to accept that the apparently mysterious process of mixing (hybridizing) of atomic orbitals leads to new orbitals that have directional properties consistent with the observed geometry of these molecules. Even a qualitative discussion of the origin of hybrid orbital shapes is only possible if the form of the wave function with its appropriate signs has been given. When the approximate shapes of hybrid orbitals are depicted in the customary fashion students get the distinct, but incorrect, impression that hybridization causes a change in the electron density distribution and that it therefore is a phenomenon rather than a mathematical operation. Moreover, these hybrid orbital sets do not provide an explanation of molecular geometry, but merely a description of the bonding in terms of the valence bond method, although not infrequently the student gets the impression that geometry is somehow “explained” by hybrid orbitals.

**Electron Spin and the Pauli Exclusion Principle**

The concepts of electron spin and the Pauli exclusion principle are essential for understanding the electronic structure of atoms and molecules, whatever bonding model is used. The experimental evidence that an electron has a magnetic moment comes from atomic spectra and the Stern–Gerlach experiment, which showed that a beam of silver atoms (or other atoms with one valence electron) splits into two beams in an inhomogeneous magnetic field. This magnetic moment is customarily accounted for in terms of a model that pictures the electron as a spherical, negatively charged particle that can spin in either a clockwise or an anticlockwise direction about its own axis. Because a moving charge produces a magnetic field, this model allows us to “understand” that an electron has a magnetic moment, which can be oriented in only two directions in an external magnetic field. It is important to emphasize that the experimentally determined magnetic moment is an intrinsic property of an electron, whereas the concept of spin is a model that has been proposed to “explain” the magnetic moment. Another important property of electrons associated with their spin is that they obey the Pauli principle, which is normally stated in terms of the orbital model in the form:

- No orbital can accommodate more than two electrons, which must have opposite spins.

But the Pauli exclusion principle is more fundamental than the orbital model and it can be stated in a more general form that is independent of the orbital model (3), namely that:

- The total wave function for an atom or molecule must be antisymmetric to electron interchange.

This statement will not mean anything to the beginning student—but we do not need to state the principle in this form. The physical consequence of the Pauli exclusion principle is that (4):

- Electrons with the same spin have a low probability of being close together and a high probability of being far apart, whereas there is no restriction on electrons of opposite spin, which may come close together.

That an electron has spin, which can have only one of two values, and that the Pauli principle describes the behavior of a system of two or more electrons are fundamental properties of electrons. These properties cannot be “explained”—at least not at an introductory level—any more than we can explain the mass and charge of an electron. The more general form of the Pauli exclusion principle may be difficult for a student to accept at first, but no more difficult than the statement that an orbital can “contain” no more than two electrons and these must be of opposite spin.

The importance of the Pauli principle in determining molecular geometry can be clearly seen if we consider the valence shell of an atom that obeys the octet rule so that there are eight electrons in its valence shell—four of α spin and four of β spin. As a consequence of the Pauli principle there is a high probability that the four electrons of α spin will have a mutually tetrahedral arrangement and a high probability that the four β electrons will also have a tetrahedral arrangement (Fig. 1), but there is no restriction on the relative positions of the α and β electrons. If, for the moment, we neglect electrostatic repulsion, we may say that electrons of opposite spin behave as if they do not recognize each other’s presence. In other words there is no correlation between the two tetrahedral sets of electrons. However, electrostatic repulsion not only reinforces the tendency of each set of electrons to adopt a tetrahedral arrangement but also tends to keep the two tetrahedra apart. In a free atom such as the neon atom there is no external force restraining the free movement of the two tetrahedral sets of electrons, resulting in an overall spherical total electron density. In contrast, in a molecule, the positive cores of one or more ligand atoms attract the valence shell electrons of the central atom. In accordance with the Pauli principle, a ligand core may attract two electrons into the same region to form a bond if they have opposite spins. If A is the central atom with a tetrahedral arrangement of α spin electrons and a tetrahedral arrangement of β spin electrons in its valence shell, then the formation of two A–H (or two A–X bonds) brings the tetrahedron of α spin electrons into approximate coincidence with the tetrahedron of β spin electrons forming four electron pairs—two bonding pairs and two nonbonding (lone) pairs, as shown in Figure 1. Each pair of electrons is approximately localized in a part of the valence shell of A, one pair in each of two bonding regions and one pair in each of two nonbonding regions.

![Figure 1](image_url)

**Figure 1.** (a) The most probable arrangement of four α spin electrons is tetrahedral. (b) The most probable arrangement of four β spin electrons is tetrahedral. (c) In an A₄H₄ molecule the two tetrahedra are brought into approximate coincidence forming two bonding pairs and two nonbonding (lone) pairs.
Electron Pair Domains

We call the region of space in the valence shell in which an electron pair is most probably to be found an electron pair domain. Thus a valence shell containing four electron pairs may be thought of as divided into four tetrahedrally arranged regions or domains, in each of which there is a high probability of finding an electron pair. As a first approximation we may consider that the domains are spherical and that the domains are nonoverlapping, as first proposed by Bent in his tangent sphere model (4). We will see later that this assumption is not as crude as it might at first seem to be. Because these spherical domains are attracted by the core, they adopt those arrangements that allow them to get as close as possible to the core. Four spheres pack as closely as possible around the core by adopting a tetrahedral arrangement, demonstrating in a simple way that four domains are expected to have a tetrahedral arrangement (Fig. 2). In the methane molecule, or any other AX₄ molecule, there are four bonding domains and so the molecule has a tetrahedral shape. In an AX₃L molecule, where L is a lone pair, there are a lone pair domain and three bonding domains, so the molecule has a triangular pyramidal shape. In an angular AX₃L₂ molecule there are two bonding domains and two nonbonding domains. Similarly, two spheres representing two electron pair domains adopt a linear arrangement, so that an AX₂ molecule such as BeCl₂ is linear; three spheres adopt a planar triangular arrangement, as in an AX₃ molecule such as BF₃. It is also easily shown that five spheres adopt a trigonal bipyramidal arrangement and six spheres an octahedral arrangement. These arrangements are the basis of the structures of molecules such as PF₅, SF₅Cl, CIF₅, SF₆, and BrF₅ (1, 2). The arrangements of two to six spherical electron pair domains may be readily illustrated using Styrofoam spheres connected by elastic bands or by toy balloons joined together (5).

Nonequivalent Domains

Because the domain of a nonbonding or lone pair of electrons is under the influence of only one core, it tends to spread out around this core as much as possible and its shape can be better represented as in Figure 3. In contrast, a bonding domain is more confined to the space between the two bonded cores and so is less spread out in the valence shell of A and can be approximately represented as in Figure 3. In general a nonbonding domain takes up more space in the valence shell than a bonding domain. Therefore the bond angles in AX₃L and AX₃L₂ molecules are smaller than the ideal tetrahedral angle. In the original version of the VSEPR model this nonequivalence of bonding and nonbonding pairs was expressed in terms of the assumption that lone pairs (lp) repel more strongly than bond pairs (bp); in other words; the repulsions between electron pairs decrease in the order lp > lpbp > bpbp (6). The equivalent statement that:

The bonding domains in a given valence shell are smaller than the nonbonding domains

is simpler and easier to apply.

Multiple Bonds

The bonding in ethene (ethylene, C₂H₄) can be readily described and its planar geometry can be predicted by the bond model on the basis of the tetrahedral arrangement of four electron pair domains in the valence shell of each carbon atom. Of these four domains, two form the CH bonds and two form carbon–carbon bonds resulting

Figure 2. Four spherical electron pair domains have a tetrahedral arrangement so an AX₄ molecule has a tetrahedral shape, an AX₃L molecule a triangular pyramidal shape, and an AX₃L₂ molecule an angular shape. S is a single bond domain and L is a lone pair domain.

Figure 3. Approximate shapes of the lone pair (L) and single bond domains (S) in an AX₃L molecule.

Figure 4. (a) Bent-bond model of ethene. (b) Domain model of ethene based on single electron pair domains. (c) Merging the two single electron pair domains representing the double bond forms an ellipsoidal double bond (four electron) domain. (d) Domain model of ethene showing the single bond (S) and double bond (D) domains.

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in an overall planar geometry for the molecule as shown in Figure 4. This description of the ethene molecule corresponds to the classical bent-bond model and to the original VSEPR model. However, we can improve on the description of the double bond as consisting of two adjacent nonoverlapping spherical domains; since both domains are attracted toward the same internuclear region they will in fact overlap to a considerable extent, giving a total electron density with a maximum along the internuclear axis and an approximately ellipsoidal shape (7). We describe this as a four-electron, double-bond domain. This description is consistent with the known total electron density of the CC double bond that has an elliptical cross section and a maximum along the CC axis. According to this description there are three domains in the valence shell of each carbon atom—two single bond domains and a double bond domain—which adopt a planar AX$_3$ geometry.

In the sulfur dioxide molecule, SO$_2$, the sulfur atom has three domains in its valence shell—two double bonded domains and a lone pair domain. These domains have a trigonal, planar AX$_3$L arrangement so that the molecule is angular, with a bond angle of approximately 120° (Fig. 5).

Similarly, the three single bond domains forming a triple bond can be merged to give a single six-electron

**Table 1. Bond Angles in Some X,C=CX, and X,C=O Molecules**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XCX</td>
</tr>
<tr>
<td>H$_2$C=CH$_2$</td>
<td>116.2</td>
</tr>
<tr>
<td>F$_2$C=CF$_2$</td>
<td>112.4</td>
</tr>
<tr>
<td>Cl$_2$C=CCl$_2$</td>
<td>116.6</td>
</tr>
<tr>
<td>(CH$_3$)$_2$C=C(CH$_3$)$_2$</td>
<td>118.2</td>
</tr>
<tr>
<td>H$_2$C=O</td>
<td>116.5</td>
</tr>
<tr>
<td>F$_2$C=O</td>
<td>107.7</td>
</tr>
<tr>
<td>Cl$_2$C=O</td>
<td>111.8</td>
</tr>
<tr>
<td>Br$_2$C=O</td>
<td>112.3</td>
</tr>
<tr>
<td>(CH$_3$)$_2$C=O</td>
<td>116.7</td>
</tr>
</tbody>
</table>

**Figure 6.** (a) Bent-bond model of ethyne. (b) Domain model of ethyne based on single electron pair domains. (c) Merging three single electron pair domains to form a triple bond (six electron) domain. (d) Domain model of ethyne showing the single bond (S) and triple bond (T) domains.

A triple-bond domain that is, overall, cylindrically symmetrical. On this basis each carbon atom in the ethyne (acetylene, C$_2$H$_2$) molecule has two domains in its valence shell—a triple bond domain and a single bond domain—and therefore each carbon atom has a linear AX$_2$ geometry (Fig. 6). Further examples of the shapes of molecules containing multiple bonds that can be predicted in this way are given in Figure 7. It is reasonable to suppose that in a given valence shell the sizes of domains will decrease in the order: triple bond domain > double bond domain >

**AX$_2$**  
O=C=O  
H-CoN

**AX$_3$**  
Cl-C=O  
O=O

**AX$_2$L**  
O=O  
*O=O

**AX$_4$**  
Cl-O  
Cl  
Cl  
Cl

**AX$_3$L**  
*O=Cl

**AX$_2$L$_2$**  
*O=Cl

**Figure 7.** The structures of some molecules containing double and triple bonds.
single bond domain. For this reason the bond angles in molecules containing multiple bonds deviate from the ideal angles. Angles between single and double bonds are expected to be larger than those between single bonds, and those between triple bonds and single bonds are expected to be larger still. Examples of some AX₃ molecules containing a CO or CC double bond are given in Table 1. In each case the single-bond-double-bond angles are larger than the angles between single bonds. Further examples are given in references 7 and 2.

Many rather subtle features of the shapes of molecules can be accounted for if both the size and shape of electron pair domains is taken into account, as is illustrated by a recent paper discussing the bond angles in the SF₄, O$_{2}$S=O, H$_{2}$O, and H$_{2}$O$_{2}$ molecules (8).

It is customary to describe double and triple bonds in terms of the σ-π model. But it is important to realize that although this model has many useful applications it does not explain molecular geometry, for example, the planar shape of ethene. We must know that the molecule has a planar geometry before the bonding can be described in terms of bonds formed from a planar set of sp₂ hybrid orbitals and a π bond.

The bent bonds in the bent-bond models of double and triple bonds can be described in terms of the valence bond theory as being formed by the overlap of two sp³ hybrid orbitals. There has been considerable discussion in the literature regarding the relative merits of the σ-π and bent-bond models for double bonds (9), but they are essentially equivalent and we may use whichever is more convenient for a particular purpose. For the discussion of spectroscopic properties and for delocalized systems, for example, the σ-π model is more useful; but for the discussion of the geometry of localized systems, the valence bond model (or the equivalent electron pair domain model) is more convenient and useful. The bent-bond model is sometimes unjustifiably criticized on the grounds that it appears to show that there is no electron density along the bond axis. But this false impression is simply a consequence of taking the bond lines too literally or of using approximate representations of sp³ orbitals. The σ-π model, the valence bond model, and the domain model are all consistent with a maximum electron density along the bond axis in a double bond as is observed experimentally and found by ab initio calculations. Although a molecular orbital description is ultimately to be preferred for delocalized systems, it is not generally possible to give anything but a very incomplete and inadequate treatment at the introductory level. A simple resonance description is, however, quite adequate and in our opinion is to be preferred at the introductory level.

Origins of the Domain Model

The ideas on which the domain model are based are not new. They owe a great deal to the work of N. V. Sidgwick, whose classical paper with H. E. Powell (10) was the starting point for the development of the VSEPR model; to H. A. Bent, whose tangent-sphere model (4) gave birth to the idea of electron pair domains; and to J. W. Linnett, whose book The Electronic Structure of Molecules (11) emphasized in a clear and convincing manner the importance of the Pauli principle as a basis for understanding bonding and molecular geometry. One of us has previously discussed the concept of electron domains (1, 2), but it has not previously been proposed as an alternative to the atomic orbital model for the discussion of bonding and molecular geometry in the introductory course.

Justification of the Electron Domain Model

It might be argued that the domain model is far too crude to be useful because electrons are not nearly so localized as the model assumes. One justification of the model is that it provides a good basis for a simple description of the chemical bond and an understanding of molecular geometry at an elementary level. In other words, it is useful. It is well-known that the total electron density of a molecule gives little evidence for the localized bond pairs and lone pairs depicted in Lewis structures or in the domain model. However, recent work on the analysis of the electron density of atoms and molecules by means of the Laplacian of the electron density (12, 13) shows that, in the valence shell of an atom in a molecule, there are regions in which the electron density is more concentrated than in the surrounding regions. In the majority of molecules studied there is an electron density concentration corresponding to each of the bond pairs and to each of the lone pairs in the valence shell of each atom. These electron density concentrations have the same relative positions and sizes and shapes as postulated for the corresponding electron pair domains, so despite the crudity of the model it appears to rather accurately reflect real features of the electron density distribution in a molecule.

Advantages of the Electron Domain Model

- The electron domain model provides a simple introduction to the covalent bond for beginning students and leads directly to the VSEPR model for molecular geometry.
- The model emphasizes that the Pauli principle is the reason for the importance of the electron pair in chemistry and that it is fundamental to understanding the chemical bond and molecular geometry. It shows that the charge of an electron is not the only property to be taken into account when describing the distribution of the electrons in an atom or molecule, and that it is not correct to regard VSEPR as a “classical” electrostatic model. Rather, the VSEPR model is based on the tendency of each electron in a valence shell to take up as much space as possible—that is, to occupy as large a domain as possible and to keep other electrons of the same spin out of its domain.
- The electron domain model leads easily and directly to an approximate description of the electron density distribution in a molecule in terms of localized bonds and lone pairs that is essentially the same as that arrived at by the valence bond method, but the difficulties associated with the description of bonding in terms of the overlap of atomic and hybrid orbitals are avoided. Because the terms sp, sp², and sp³ have become such an important part of the language of chemistry, however, we could use them to denote the linear, triangular, and tetrahedral arrangements of domains just as we use the terms s, p, and d to describe atomic orbitals, although these terms have only a historical significance.
- Molecules in which there are five- and six-electron pair domains with a trigonal bipyramidal and octahedral arrangement, respectively, are very easily dealt with using the domain model, whereas the description of these molecules (sometimes called hypervalent molecules) in terms of the valence bond model is controversial. Originally the domains in these molecules were described in terms of sp³d and sp³d hybrid or-
bital, but the extent to which d orbitals are needed in the description of the bonding has been shown by ab initio calculations to be considerably less than is implied by these hybrid orbital descriptions (14).

The domain model is proposed as an alternative model for use primarily in the introductory course as it provides a quicker, simpler, and (to the student) less mysterious route to an understanding of bonding and molecular geometry. It is not meant to replace the valence bond and molecular orbital models, and in chemistry courses beyond the introductory level students will have to become very familiar with those models. However, once students have learned about the arrangements of the domains of two, three, and four electron pairs it will be much easier for them to accept the concepts of sp, sp^2, and sp^3 orbitals. This would make for an easy transition to the orbital model and the concept of hybridization.

The electron domain model is not only easier for students to understand, requiring less comprehending memorization, but its presentation also takes considerably less time than the conventional approach. This time can be devoted to less theoretical but no less important aspects of chemistry, such as environmental, materials, and polymer chemistry, which may also be of greater interest to students, and to introducing students to areas of chemistry where major advances are being made today.

The extent to which bonding is treated in any particular course will depend on the level of the course, the needs of the students, and the interests of the instructor. The simplest treatment would use only Lewis structures. This could be followed by a simple empirical treatment of VSEPR, which might be far enough for some students.

But for many students one could proceed directly to the electron domain model and a more complete discussion of VSEPR. In our opinion this would be far enough for many students in an introductory chemistry course. The next logical step would be a discussion of the valence bond and molecular orbital models, although these discussions could be left to subsequent inorganic and organic chemistry courses when they could be treated more rigorously and in greater depth. By proceeding from a very simple model to the more sophisticated valence bond and molecular orbital models, students will learn to recognize them for what they are—simply models—and to understand that they all have both uses and disadvantages.

Literature Cited


