Understanding and Interpreting Molecular Electron Density Distributions

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Advances in the power and speed of computers have made ab initio and density functional theory (DFT) calculations an almost routine procedure on a PC (1). From these calculations the equilibrium geometry, the energy, and the wave function of a molecule can be determined. From the wave function one can obtain all the properties of the molecule, including the distribution of electronic charge, or electron density. However, the electron density is often not calculated or discussed, perhaps because it is not widely realized that very useful information on bonding and geometry can be obtained from it. It seems particularly important to discuss electron densities in introductory chemistry courses because students can grasp the concept of electron density much more readily than the abstract mathematical concept of an orbital. It is also not as widely understood as it should be that orbitals are not physical observables but only mathematical constructs that cannot be determined by experiment (2). In contrast, the electron density distribution in a molecule or crystal can be observed by electron diffraction and X-ray crystallography (3); and it can also, and often more readily, be obtained from ab initio and density functional theory calculations.

This article gives a simple introduction to the electron densities of molecules and how they can be analyzed to obtain information on bonding and geometry. More detailed discussions can be found in the books by Bader (4), Popelier (5), and Gillespie and Popelier (6). Computational details to reproduce the results presented in this paper are presented in Appendix 1.

The Electron Density

Quantum mechanics allows the determination of the probability of finding an electron in an infinitesimal volume surrounding any particular point in space \((x,y,z)\); that is, the probability density at this point. Since we can assign a probability density to any point in space, the probability density defines a scalar field, which is known as the probability density distribution. When the probability density distribution is multiplied by the total number of electrons in the molecule, \(N\), it becomes what is known as the electron density distribution or simply the electron density and is given the symbol \(\rho(x,y,z)\). It represents the probability of finding any one of the \(N\) electrons in an infinitesimal volume of space surrounding the point \((x,y,z)\), and therefore it yields the total number of electrons when integrated over all space. The electron density can be conveniently thought of as a cloud or gas of negative charge that varies in density throughout the molecule. Such a charge cloud, or an approximate representation of it, is often used in introductory texts to represent the electron density \(\psi^2\) of an atomic orbital. It is also often used incorrectly to depict the orbital \(\psi\) itself. In a multielectron atom or molecule only the total electron density can be experimentally observed or calculated, and it is this total density with which we are concerned in this paper. A more formal discussion of electron density is presented in Appendix 2.

The electron density is key to the bonding and geometry of a molecule because the forces holding the nuclei together in a molecule are the attractive forces between the electrons and the nuclei. These attractive forces are opposed by the repulsions between the electrons and the repulsions between the nuclei. In the equilibrium geometry of a molecule these electrostatic forces just balance. The fundamentally important Hellman–Feynman theorem (4–7) states that the force on a nucleus in a molecule is the sum of the Coulombic forces exerted by the other nuclei and by the electron density distribution \(\rho\). This means that the energy of interaction of the electrons with the nuclei can be found by a consideration of the classical electrostatic forces between the nuclei and the electronic charge cloud. There are no mysterious quantum mechanical forces, and no other force, such as the gravitational force, is of any importance in holding the atoms in a molecule together. The atoms are held together by the electrostatic force exerted by the electronic charge on the nuclei. But it is quantum mechanics, and particularly the Pauli principle, that determines the distribution of electronic charge, as we shall see.

The Representation of the Electron Density

The electron density \(\rho\) varies in three dimensions (i.e., it is a function of the three spatial coordinates \([x,y,z]\)), so a full description of how \(\rho\) varies with position requires a fourth dimension. A common solution to this problem is to show how \(\rho\) varies in one or more particular planes of the molecule. Figure 1a shows a relief map of the electron density, \(\rho\), of the \(\text{SCl}_2\) molecule in the \(\sigma,(xz)\) plane. The most striking features of this figure are that \(\rho\) is very large in an almost spherical region around each nucleus while assuming relatively very small values, and at first sight featureless topology, between these nuclear regions. The high electron density in the nearly spherical region around each nucleus arises from the tightly held core electrons; the relatively very small and more diffuse density between these regions arises from the more weakly held bonding electrons. In fact, it was necessary to truncate the very high maxima in Figure 1a (at \(\rho = 2.00\) au) to make it possible to show the features of the electron density distribution between the nuclei. 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 \(3.123 \times 10^3\) and \(2.589 \times 10^3\) au at the S and Cl nuclei, respectively, but a value of only \(1.662 \times 10^{-1}\) 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 bonding region that is responsible for pulling the nuclei together. Along a line at 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 (4–6, 10). The point of minimum electron density along the bond path is called the bond critical point.

Figure 1b shows a relief map of the electron density of the water molecule. Its features are similar to those of the density map for SCl₂, but 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 × 10⁻² au, whereas that at the hydrogen nucleus is only 4.341 × 10⁻³ au, which is only slightly greater than the value of 3.963 × 10⁻¹ au at the minimum at the bond critical point. The very small electron density surrounding the hydrogen nucleus is due to 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 way to represent the electron density distribution is as a contour map, analogous to a topographic contour map representing the relief of a part of the earth's surface. Figure 2a shows a contour map of the electron density of the SCl₂ molecule in the \( \sigma_{xz} \) plane. The outer contour has a value of 0.001 au, and successive contours have values of \( 2 \times 10^{-n}, 4 \times 10^{-n}, 8 \times 10^{-n} \) au; \( n \) starts at 3 and increases in steps of unity. Figure 2b shows a corresponding map for the H₂O molecule. Again we clearly see the large concentration of density around each nucleus. The outer contour is arbitrary because the density of a hypothetical isolated molecule extends to infinity. However, the 0.001 au contour corresponds rather well to the size of the molecule in the gas phase, as measured by its van der Waals radius, and the corresponding isodensity surface in three dimensions usually encloses more than 99% of the electron population. 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. We see more clearly here that the bond paths (the lines along the top of the density ridges between the nuclei) coincide with the bonds as they are normally drawn.

Figure 3 shows the electron density contour maps for the period 2 fluorides LiF, BF₃, CF₄, OF₂, and for the isolated B atom. In LiF each atom is almost spherical, consistent with the usual model of this molecule as consisting of the ions Li⁺ and F⁻. The volume of the lithium atom is much smaller than that of the F atom, again consistent with the ionic model. We will see later that we can also obtain the atomic charges from the electron density and that the charges on the two atoms are almost \( \pm 1 \), again consistent with the representation of these atoms as ions. Moreover, there is a very small distortion of the almost spherical density of each atom toward its neighbor, giving a very low ridge of density between the two nuclei indicating that the amount of electronic charge in the bonding region is very small. Thus the bonding in this molecule is close to the hypothetical purely ionic model, which would describe the molecule as consisting of two spherical ions held together by the electrostatic force between their opposite charges.

As we proceed across period 2 the electron density of the core of each atom remains very nearly spherical but the
outer regions of the atom become increasingly distorted from a spherical shape, stretching out toward the neighboring atom to give an increased electron density at the bond critical point ($\rho_b$) (see Table 1). Figure 4 shows the electron density plots for some chlorides of period 2. We see similar changes in the electron density distribution for these molecules as we saw for the fluorides.

For a three-dimensional picture of the electron density distribution we can easily show a particular isodensity envelope (i.e., a three dimensional surface corresponding to a given value of the electron density). The 0.001-au envelope gives a picture of the overall shape of the molecule as shown by the examples in Figure 5. Making the outer 0.001-au envelope transparent as in Figure 5 reveals an inner envelope, but showing additional envelopes becomes increasingly difficult. The particular inner surface shown in Figure 5 corresponds to the bond critical-point isodensity envelope ($\rho_b$ envelope), the single envelope just encompassing all the nuclei. All isodensity envelopes with $\rho_b < \rho$ will form a continuous sheath of density surrounding all the nuclei in the molecule, and all isodensity envelopes with $\rho > \rho_b$ will form a discontinuous surface surrounding each nucleus separately. Thus the $\rho_b$ envelope is just about to break into separate surfaces, one surrounding each atom, at higher values of $\rho$.

The $\rho_b$ envelopes are also shown for some period 2 fluorides and chlorides in Figure 6. These surfaces show the distortion of the electron density from a spherical shape even more clearly than the contour maps in Figures 3 and 4. For example, in Figure 6 one can see the distinctly tetrahedral shape assumed by the part of the $\rho_b$ envelope surrounding the carbon atom in CCl$_4$ owing to the distortion of the electron density.
density in the four tetrahedral directions. In addition to the distortion of the electron density toward each neighboring atom we can see other changes. Proceeding across period 2 the ligand atoms have an increasingly squashed "onion" shape, flattened on the opposite side from the central atom. These changes can be understood in the light of the Pauli principle, which is an important factor in determining the shape of the electronic charge cloud. The Pauli principle is discussed below and more formally in Appendix 3.

**The Pauli Principle**

The many-electron wave function ($\Psi$) of any system is a function of the spatial coordinates of all the electrons and of their spins. The two possible values of the spin angular momentum of an electron—spin up and spin down—are described respectively by two spin functions denoted as $\alpha(\omega)$ and $\beta(\omega)$, where $\omega$ is a spin degree of freedom or "spin coordinate". All electrons are identical and therefore indistinguishable from one another. It follows that the interchange of the positions and the spins (spin coordinates) of any two electrons in a system must leave the observable properties of the system unchanged. In particular, the electron density must remain unchanged. In other words, $\Psi^2$ must not be altered when the space and spin coordinates of any two electrons are interchanged.

This requirement places a restriction on the many-electron wave function itself. Either $\Psi$ remains unchanged or it must only change sign. We say that $\Psi$ must be either symmetric or antisymmetric with respect to electron interchange. In fact, only antisymmetric wave functions represent the behavior of an ensemble of electrons. That the many-electron wave function must be antisymmetric to electron interchange ($\Psi \rightarrow -\Psi$ on electron interchange) is a fundamental nonclassical property of electrons. They share this property with other elementary particles with half-integral spin such as protons, neutrons, and positrons, which are collectively called fermions. Ensembles of other particles, such as the $\alpha$ particle and the photon, have symmetric many-particle wave functions ($\Psi \rightarrow \Psi$ on particle interchange) and are called bosons.

The requirement that electrons (and fermions in general) have antisymmetric many-particle wave functions is called the Pauli principle, which can be stated as follows:

A many-electron wave function must be antisymmetric to the interchange of any pair of electrons.

No theoretical proof of the Pauli principle was given originally. It was injected into electronic structure theory as an empirical working tool. The theoretical foundation of spin was subsequently discovered by Dirac. Spin arises naturally in the solution of Dirac’s equation, the relativistic version of Schrödinger’s equation.

A corollary of the Pauli principle is that no two electrons with the same spin can ever simultaneously be at the same point in space. If two electrons with the same spin were at the same point in space simultaneously, then on interchanging these two electrons, the wave function should change sign as required by the Pauli principle ($\Psi \rightarrow -\Psi$). Since in this case the two electrons have the same space and spin coordinates (i.e.,
The most probable distribution of the four \( \alpha \) electrons—the distribution that keeps them as far apart as possible—is at the vertices of a tetrahedron (Fig. 7a). The most probable arrangement of the four \( \beta \) electrons is also at the vertices of a tetrahedron (Fig. 7b). In a free atom these two tetrahedra are independent, so they can have any relative orientation giving, an overall spherical density.

In a molecule, electrons are attracted toward a neighboring nucleus but only electrons of opposite spin can be attracted close to each other. In the valence shell of any singly bonded ligand, not all the electrons are formed into pairs, as was first pointed out by Linnett (11) and discussed in refs 6 and 7. Thus in a diatomic molecule such as HF or ClF the two tetrahedra of \( \alpha \)- and \( \beta \)-spin electrons on each atom are brought into approximate coincidence at one vertex, forming a bonding pair of electrons and increasing the electron density in this region (Fig. 8).

Figure 8 shows only the most probable position of the electrons, not their actual position. The increase in the probability of finding an electron in the bonding region depends on the attractive force exerted by the neighboring atom—that is, on its electronegativity. Thus the extent to which two electrons of opposite spin are localized in the bonding region varies from molecule to molecule, with the electronegativities of the atoms. In diatomic molecules the two tetrahedra on each atom are still free to rotate around this shared vertex, so that the six nonbonding electrons are most probably distributed in a circle around the direction of the bond and on the opposite side from the bond, forming a torus of increased density. This leaves a region of relatively depleted electron density at the back of the atom opposite the bond, which accounts for the flattening of the surface of constant electron density in this nonbonding region (Fig. 6). In the Cl\(_2\) molecule, for example, the distance to the outer 0.001-au contour from a Cl nucleus in a direction perpendicular to the bond is 210 pm, but in the direction opposite to the bond it has the appreciably smaller value of 185 pm. This characteristic shape is found for any singly bonded atom whose electron density is deformed toward a neighboring atom. It can also be clearly seen in the contour maps in Figures 3 and 4.

**Electron Density and the VSEPR Model**

When there are two ligands, as in H\(_2\)O, Cl\(_2\), OF\(_2\), or any other AX\(_2\)E\(_2\) molecule, the two tetrahedra (Figs. 7a and 7b) of same-spin electrons lose their independence of one another and are brought into approximate coincidence at all four vertices (Fig. 7c). This results in the formation of two partially localized bonding pairs (one to each of the two ligands X) and two partially localized nonbonding pairs (E); the four pairs adopt an approximately tetrahedral geometry (Fig. 7c). There is therefore a concentration of electron density in the bonding regions, which we observe as the distortion of the spherical electron density distribution in the bonding directions as seen in the \( \sigma_v \) plane of Cl\(_2\) and H\(_2\)O (Fig. 2) and OF\(_2\) (Fig. 3). The increased electron density due to the two localized lone pairs is seen as bulges in the electron density in the \( \sigma_v \) plane of OF\(_2\) (Fig. 3) and Cl\(_2\) (Fig. 4). In OF\(_2\) the distance to the outer 0.001 au contours from an F nucleus in a direction perpendicular to the bond pointing toward the open side of the molecule in the \( \sigma_v \) plane is 166 pm, but in the direction opposite to the bond it is 155 pm. In Cl\(_2\) those
values are 212 and 186 pm, respectively. In the \( \sigma_{v}^{(xz)} \) plane of the NCl \(_3\) molecule (Fig. 4) we see the distortion of the electron density toward the chlorine ligand and a bulge in the electron density in the lone pair region. The influence of the Pauli principle on the distribution of electrons in a valence shell provides the physical basis for the VSEPR model (6, 12), according to which the electrons in the valence shell of an atom are in pairs, either bonding or nonbonding, that stay as far apart as possible.

The Atoms in Molecules Theory

So far we have considered the shape of the electron density of a limited inner region of each atom but not of the complete atom. How do we find the shape of the complete atom? In other words, how do we find the interatomic surfaces that separate one atom from another and define the size and shape of each atom? The atoms in molecules (AIM) theory developed by Bader and coworkers (4) provides a method for doing this.

The AIM theory, which is solidly based on quantum mechanics, differs from orbital-based theories in that it is based directly on the electron density and interprets this density to provide information on bonding. The density may be obtained experimentally or from theoretical electronic structure calculation. Experimental densities of sufficient quality to be analyzed by the AIM theory can be obtained from low-temperature X-ray diffraction experiments using the nonspherical multipolar refinement procedure pioneered by Coppens (3). Theoretical densities must be calculated by high-level ab initio or DFT methods (see Appendix 1). It has been consistently shown that the numerical results based on AIM converge to limiting values as the size of the basis set used in the calculation increases.

For a homonuclear diatomic molecule such as Cl\(_2\) the interatomic surface is clearly a plane passing through the midpoint between the two nuclei—in other words, the point of minimum density. The plane cuts the surface of the electron density relief map in a line that follows the two valleys leading up to the saddle at the midpoint of the ridge between the two peaks of density at the nuclei. This is a line of steepest ascent in the density on the two-dimensional contour map for the Cl\(_2\) molecule (Fig. 9).

In all molecules other than homodiatomic the interatomic surfaces are not planar, as seen in Figure 9 for CO and FCl. These surfaces can be found by computing the gradient paths of the electron density. In a relief map of the density in a particular plane these are the paths of steepest ascent starting at infinity and leading up to the maximum or peak at each nucleus. Gradient paths are always orthogonal to the contours of constant electron density and they never cross each other. Figure 10 shows two gradient paths up an idealized mountain. These are two of the infinite number of steepest paths up the mountain. Throughout their length they are perpendicular to the circular contours of equal height. Figure 10 also shows a longer, less steep path that is not perpendicular to the contours. It not is not a gradient path.

The collection of all the gradient paths of the electron density constitutes the gradient vector field of the molecular electron density. Figure 11 shows the gradient vector field of the electron density of the BCl\(_3\) molecule in the \( \sigma_{h} \) plane. The collection of gradient paths that terminate at a given nucleus defines a discrete region of space surrounding each nucleus that is called the atomic basin. These basins define the atoms as they exist in the molecule. Among the gradient
into separate nonoverlapping atoms (atomic basins), which according to the AIM theory.

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paths that constitute the gradient vector field are two sets of unique paths: those that start at infinity but terminate at the point of minimum density on the ridge of electron density (the bond critical point) between two nuclei, and those that start at this point and terminate at a nucleus. The complete set of the gradient paths in three dimensions that terminate at a bond critical point constitute the surface between the atoms, the interatomic surface. This is also called a zero-flux surface because no gradient paths cross it.

Figure 11 shows a few of the infinite number of gradient paths that lie in the \( \sigma_h \) plane. The set of two gradient paths that terminate at a bond critical point indicate the intersection of the interatomic surfaces with this plane. In Figure 11 there are six gradient paths that start at the bond critical point and terminate at a nucleus. The two that start at the same bond critical point trace a bond path between the boron atom and a fluorine atom. Bond paths are found between every pair of atoms in a molecule that we usually consider to be bonded to each other, and not between atoms that are not bonded together. The existence of a bond path between the nuclei of two atoms that share an interatomic surface constitutes a clear and rigorous definition of a bond between the two atoms according to the AIM theory.

The interatomic (zero-flux) surfaces partition the molecule into separate nonoverlapping atoms (atomic basins), which extend to infinity on the open side of any exterior atom. For the purpose of representing the electron density as a contour map or an isosurface, or for determining the atomic volume, it is convenient to take the 0.001-au envelope of constant density as the practical representation of the surface of an atom on its open (nonbonded) side. Normally, the outer 0.001-au isodensity envelope encloses more than 99% of the electron population of the molecule (4). Integrating any property density, such as the electron population, energy, or volume, over the atomic basin yields the contribution of this atom to the corresponding molecular property. The sum of these atomic properties gives the corresponding molecular property with high accuracy. For example, the sum of the charges is accurately zero for a neutral molecule and the sum of the atomic populations is accurately equal to the total number of electrons. Moreover the properties of atoms or functional groups, as defined by AIM, are often almost constant (i.e., transferable) when their immediate surrounding is similar as is the case in homologous series for example. Therefore, these atoms and groups contribute constant additive amounts to every molecular property in a molecule, and they have been shown to recover the empirical additivity schemes for several experimental quantities, the heat of formation being an example (13). An impressive recent example of using the transferability and additivity of the properties of atoms and functional groups is the calculation of the properties of a very complex biological molecule, an opioid, from the properties of a number of smaller fragments (14).

**AIM Atomic Charges and Dipoles**

The charge on each atom is the difference between the total electron population, obtained by integrating the electron density over the volume occupied by the atom, the atomic volume, and the nuclear charge. The atomic charges for the fluorides and chlorides of the period 2 elements are given in Table 1. The charge on the fluorine ligand decreases across the period from a value of nearly \(-1\) in LiF to zero in F\(_2\). The charge on the chlorine ligand similarly decreases from a value of nearly \(-1\) in LiCl to almost zero in Cl\(_2\) and then becomes increasingly positive from NC\(_3\) to FCl. Figure 12 shows that the fluorine and chlorine charges correlate well with the electronegativity of the elements (15), bearing in mind the approximate nature of the electronegativity values. For example, the charge on each of the atoms in ClF\(_3\) is nearly zero, consistent with the very similar values of their electronegativity (Cl, 2.8; C, 2.5). The charge on the central atom increases across period 2 with the increasing number of ligands to a maximum at carbon for the fluorides and at boron for the chlorides.

It is important to understand that the atomic charges refer to atoms that are not spherical. Consequently the centroid of electronic charge of an atom does not in general coincide with the nucleus, and each atom therefore has an electric dipole moment—or, more generally, an electric dipolar polarization (since only the dipole moment of electrically neutral atoms is origin independent).

The total dipole moment of a molecule is the resultant of the vector sum of the atomic dipolar polarization \( \mu_{ap} \) of all the atoms in the molecule and of all the charge transfer dipoles arising from the transfer of charge between bonded...
and the atomic polarization terms. Even though the atoms bear significant charges consistent with their respective electronegativities (C\textsuperscript{+1.170}, F\textsuperscript{-1.170}), when these charges are used to calculate the \( \mu_{c.t.} \) terms and are added to the \( \mu_{ap} \) terms they recover the magnitude and direction of the observed molecular dipole. The dipole moment of any molecule can be expressed and recovered from group contributions calculated in this manner \( (16) \) using available Windows-based software \( (17) \).

**Comparison between AIM Theory and Conventional Models for Describing Bonding**

We now compare how the atoms in a molecule and the bonds between them are defined in the AIM theory and in conventional bonding models.

**Atoms**

There is no clear rigorous definition of an atom in a molecule in conventional bonding models. In the Lewis model an atom in a molecule is defined as consisting of its core (nucleus and inner-shell electrons) and the valence shell electrons. But some of the valence shell electrons of each atom are considered to be shared with another atom, and how these electrons should be partitioned between the two atoms so as to describe the atoms as they exist in the molecule is not defined.

Conventionally, the bonding electrons are arbitrarily divided in two ways. One is to assume that the bonds are fully ionic, which gives atomic charges that are called oxidation numbers; the other is to assume that the bonds are fully covalent, which gives charges that are called formal charges. Although both of these concepts have proved useful they do not give real atomic charges. For molecules with polar bonds there is no clearly defined method for partitioning the bonding electrons between the bonded atoms that reflects the unequal sharing of electrons or partial electron transfer. In localized

**Figure 12.** Electron negativity difference between the halogen atom \( X \) and the atom to which it is bonded \( A \) in the halides of period 2 \( \{A,X\} \) as a function of the atomic charge of the halogen atom \( q(X) \). \( \text{a) } X = Cl; \text{b) } X = F \). Atom A of the halide is shown in the figures. Charges were obtained at the DFT level using the B3LYP functional and a 6-311+G(2d,p) basis set.

**Figure 13.** Contour plot of the electron density of CO, showing the magnitudes and directions of atomic and charge transfer dipoles (arrow length is proportional to magnitude). Arrow heads point to the negative end. The molecular dipole moment is given by the vector sum of charge transfer terms \( \{\mu_{c.t.}\} \) and the atomic polarization terms \( \{\mu_{ap}\} \). Values were obtained at the DFT level using the B3LYP functional and the 6-311+G(3df) basis set. The SCF molecular dipole = 0.096 D; the computed molecular dipole \( \{\mu_{c.t.}[O] + \mu_{ap}[O] + \mu_{c.t.}[C] + \mu_{ap}[C]\} = 0.038 \text{ au} = 0.096 \text{ D}, close to the experimental value of 0.110 D \( (15) \).
orbital models such as the valence bond model, a free atom is defined in terms of the atomic orbitals used to describe it; but in molecule formation some of the orbitals are considered to overlap with those of a neighboring atom to give bonding orbitals, so again the atoms in the molecule are not clearly defined. In the molecular orbital model the whole molecule is described in terms of molecular orbitals and no attempt is made to define the individual atoms.

In contrast, the AIM theory provides a clear definition of an atom in a molecule as a space-filling object, from which all its properties can be obtained. The properties of these atoms are additive to give the corresponding molecular property.

Bonds

According to the Lewis model, a covalent bond consists of a pair of shared electrons—that is, a pair of electrons that belongs to the valence shell of each of the bonded atoms. In other words the two valence shells are considered to overlap. The electrostatic attraction of this pair of electrons for the two nuclei is considered to provide the attractive force holding the two nuclei together. According to the ionic model, two ions (charged atoms) are held together by the Coulombic attraction between their opposite charges. In other words, an ionic bond is the electrostatic attraction between two ions (charged atoms) with opposite charges.

These definitions are clear, but they do not apply to the vast majority of real molecules in which the bonds are neither purely ionic nor purely covalent. Lewis recognized that a pair of electrons is generally not shared equally between two electrons because the atoms generally have different powers of attracting electrons, that is, they have different electronegativities, giving charges to both atoms. Such bonds are considered to have some covalent character and some ionic character and are known as polar bonds.

Polar bonds range from bonds between atoms that have large but slightly less than integral charges and are therefore close to the ionic limit to pure covalent bonds between atoms of equal electronegativity such as the C–C bond in ethane. Almost all bonds are polar. A pure ionic bond is an ideal concept that is never observed; and pure covalent bonds are very rare, inasmuch as the atoms in the vast majority of molecules have different electronegativities and therefore have nonzero charges. The attractive force in a polar bond can be thought of as being due to both the shared electrons and the atomic charges. In other words, a polar bond has both covalent and ionic character. However, these terms have not been clearly defined, so it is not possible to quantitatively evaluate the covalent and ionic character of any given polar bond. A proposed method for doing this based on determining atomic charges from the dipole moment of a diatomic molecule is not valid because it assumes that atoms are spherical and ignores atomic dipoles. In short, the widely used terms ionic character and covalent character cannot be clearly defined and therefore cannot be measured, so they have only a rather vague and approximate meaning.

In contrast, the AIM theory provides clear, unambiguous values for the charges on atoms, which at first sight appear to give us a clear definition of the ionic character of a bond. However, considering the atomic charges of the period 2 fluorides we see that, although the charge on fluorine decreases across the period, the charge on the central atom first increases up to CF₄ before decreasing. The decreasing charge on the ligand might be interpreted as showing that the bonds are becoming less ionic, but the increasing charge on the central atom could be interpreted as showing that the bonds are becoming more ionic. Clearly, a knowledge of the atomic charges does not enable us to define ionic character. All that we know with certainty is the atomic charges, which, it seems reasonable to assume, make a contribution to the strength of the bonding in proportion to their product.

In addition to the attractive force provided by opposite atomic charges, the electronic charge accumulated between the nuclei of the two bonded atoms must also contribute to the attraction between the two atoms. But because the region in which charge is accumulated is not sharply defined, the amount of the accumulated charge is not known. The AIM theory does, however, provide a value of the electron density at the bond critical point, ρₜ. We see in Table 1 that ρₜ for the period 2 fluorides increases up to CF₄ and then becomes essentially constant. The value of ρₜ is an indication, but not a quantitative measure, of the amount of electronic charge in the bonding region and so can only be regarded as a rough measure of the covalent character of a bond—which, as we have said, has not been precisely defined.

Clearly the concepts of ionic and covalent character have only an approximate qualitative significance. They cannot be defined and therefore measured in any quantitative way. Although they are widely used terms and have some qualitative usefulness if used carefully they have caused considerable misunderstanding and controversy. The AIM theory does, however, provide properties that we can use to characterize a bond quantitatively, such as the bond critical point density and the atomic charges. It seems reasonable to assume that the strength of a bond depends on both these quantities, increasing as ρₜ and the product of the atomic charges increase.

These assumptions are consistent with the very large bond strength of the BF bond in BF₃, which is larger than that of any other single bond. It has a bond dissociation enthalpy...
of 613 kJ mol$^{-1}$, compared, for example, to the C–C bond dissociation enthalpy of only 348 kJ mol$^{-1}$. Even though $\rho_b$ for the BF bond (0.217 au) is little smaller than that for the C–C bond in ethane (0.249 au), the atomic charges on B and F are +2.43 and −0.81, respectively, whereas the charges on carbon in ethane are almost zero and of the same sign. Although it is not consistent with current usage, the BF bond can be described as having both a large covalent character and a large ionic character, as has been pointed out in two recent papers in this *Journal* (18, 19).

Bond paths are observed between bonded atoms in a molecule and only between these atoms. They are usually consistent with the bonds as defined by the Lewis structure and by experiment. There are, however, differences. There is consistent with the bonds as defined by the Lewis structure molecule and only between these atoms. They are usually dissociation enthalpy of only 348 kJ mol$^{-1}$.

The AIM theory provides a clear and rigorous definition of a bond. It is defined as a shared electron pair. In the valence bond model it is defined as a bonding orbital formed by the overlap of two atomic orbitals. In the AIM theory a bonding interaction is one in which the atoms are connected by a bond path and share an interatomic surface.

9. Bond paths are normally found in cases in which there is a bond as defined by Lewis. There is only one bond path for a multiple bond irrespective of the bond order. The bond order is, however, reflected in the value of $\rho_{bcp}$. Bond paths are also found in molecules for which a single Lewis structure cannot be written.

10. The concepts of ionic and covalent character of a bond are vague and ill defined. The well-defined AIM-derived quantities such as the integrated atomic charges and the bond critical point density provide a quantitative characterization of bonding.

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### Notes

1. The abbreviation au stands for “atomic units”, which 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 Planck’s constant. By setting these three quantities equal to unity one gets simpler equations. The au system has a simple relation to the SI and Gaussian (cgs) systems of units. For example, 1 au of length $= a_0$ (Bohr radius) = 5.29 $\times$ 10$^{-10}$ cm = 0.529 Å; 1 au of charge $= e = 1.602 \times 10^{-19}$ C = 4.803 $\times$ 10$^{-10}$ esu; 1 au of charge density $= e a_0^3 = 6.748$ eÅ$^3 = 1.081 \times 10^{-12}$ C m$^{-3}$. For a formal discussion of how the au system of units naturally arises in quantum chemistry, see refs 8 and 9.

2. The experimental value for the magnitude of the C_O$^+$ dipole is 0.110 D.

### Literature Cited

21–24 are all parts of the suite of programs known as AIMPAC (GRIDVEC, and CONTOR were used to obtain the plots. These the atomic properties up to the zero-flux surfaces, and GRIDV, to locate the critical points. PROAIM was then used to integrate the resulting densities were analyzed using the program Extreme density function, commonly known as the electron density, and if we multiply the latter integral by \( \psi_i(r) \) weighted by the total number of electrons in the system. This is written:

\[
\rho(r) = N |\Psi(r_1, r_2, \ldots, r_N)|^2 \, dr_1 \ldots dr_N 
\]

This is the probability of finding a single electron, no matter which, at \( r \) (i.e., at the specific spatial position \( x,y,z \) and having the specific spin \( j \)) weighted by the total number of electrons in the system. Integrating eq 2.1, the density, over all space with respect to the coordinates of electron \( n_i \) is

\[
\int \rho(r) \, dr_i = N |\Psi(r_1, r_2, \ldots, r_N)|^2 \, dr_1 \ldots dr_N 
\]

That is, the integral of the density over all space yields the total number of electrons in the molecule.

**Appendix 3. The Pauli Principle**

The Pauli exclusion principle requires that no two electrons can occupy the same spin-orbital is a consequence of the more general Pauli antisymmetry principle:

Any many-electron wave function must be antisymmetric to the interchange of the spacial coordinates and spin (collectively referred to as the vector \( \mathbf{q} \)) of any pair of electrons \( i \) and \( j \).

This is written:

\[
\Psi(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_j, \ldots, \mathbf{q}_n) = -\Psi(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_i, \ldots, \mathbf{q}_n) 
\]

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

\[
\Psi(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_i, \ldots, \mathbf{q}_n) = -\Psi(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_i, \ldots, \mathbf{q}_n) 
\]

This implies that the wave function is equal to its negative. Re-arranging gives 2\( N |\Psi(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_n)|^2 = 0 \), or simply \( \Psi = 0 \).
The physical consequence of this is that two electrons of the same spin have zero probability of occupying the same position in space; that is, two same-spin electrons exclude each other in space. Since $\Psi$ is continuous, there is only a small probability of finding two electrons of the same spin close to each other in space; that is, the Pauli antisymmetry requirement forces them to avoid each other as much as possible and as a result two electrons of the same spin tend to maximize their separation in space. In other words, the motion of two electrons of the same spin is not independent but correlated, a correlation known as Fermi correlation, which is a direct consequence of the Pauli principle.