VII. INTO THE UNKNOWN

7-1 THE ELECTRON DENSITY

Now we are ready to look at lowest level of engineering structure—the level at which everything else is determined—the relation between the structure of the electron density and properties. Most importantly, we are going to associate a properties with the structure of that thing we have heard of, but never seen—the chemical bond--begining with the moving electron and electron density.

As you know, atomic electrons are in constant motion about the tiny but massive nucleus. An electron's mass is about 1/2000 that of a proton or neutron and it is moving very fast compared to the nucleus. While an electron is traveling at 3 to 10 million meters per second, as we know from the Boltzmann equation, at the temperature that concern us— < 3000K—even a fast nucleus is moving at less than one thousandth this speed— 1000 or so meters per second.

As a mental image, think of an atom as a bee hive. At the center of the hive is the queen bee, which we will take as the location of an atomic nucleus. The electrons are the worker bees, making circuits about the hive. If the beekeeper moves the hive a bit, the circling bees simply move along with the hive—their motion is fast compared to that of the hive. But how fast? Well, the "electron bees" are moving much faster than the ordinary bees of our experience. In one second, an individual electron bee will make between 10^{16} and 10^{17} circuits around the hive. They are moving so fast that to your eye they appear

Fig. 7-1

as a blur, and you cannot specify their location. What you *can* specify is a bee's most probable location. It is more probable that you will find bees where the blur is more opaque. And, as you might imagine, it is more probable that you will run into a bee near the center of the hive than 10 meters away.
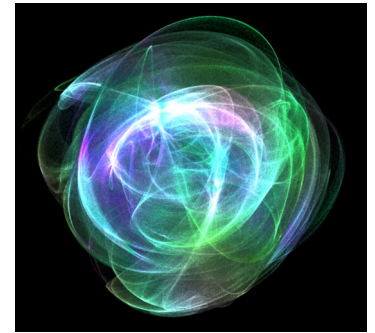
This picture of bees moving about a hive is all well and good, but let's get a little more quantitative and assign numbers to our blur, remembering that we are really talking about the moving electrons around an atom's nucleus. Let's imagine taking a small volume, ΔV, at some distance from the nucleus. Through some process, we count the number of electrons, N, that pass through this volume in, say, a nanosecond (10^{-9} seconds). We will define a quantity ρ (rho) as N (the number of electrons present) divided by the product of the volume and time of our observation:
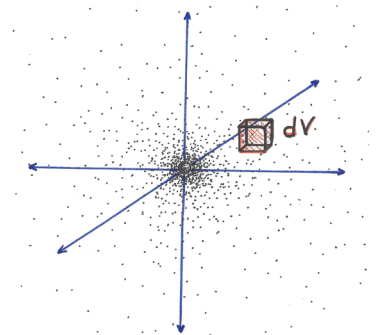

Fig. 7-2

$$\rho = \frac{N}{\Delta V * 10^{-9}}$$

Note that if we double the time of our observation (two nanoseconds) we would expect to find twice as many electrons in this volume:

$$\frac{2\,N}{\Delta V * 2 * 10^{-9}} = \rho$$

Thus, ρ is independent of the time over which the observation is made. ρ is called the **electron density** with units of electrons per volume.

During a chemical reaction the electron density changes. For things that are very reactive, the electron density changes more than for things that are inert and unreactive. When you push or pull on an object, it is the electron density of the atoms within that object that changes. Whether a material is hard or soft depends on the nature of that change. The temperature and pressure at which a substance boils, sublimes or melts is controlled by changes in the electron density. Whether a material is strong or weak, ductile or brittle, red or blue, a conductor or an insulator is determined by its electron density and how it changes when pushed pulled, illuminated, or shocked. If you want to control properties and make new things, ultimately (whether you do it intentionally or not) you will need to control the electron density. So "it is all about the electron density."

7-2 REPRESENTING THE ELECTRON DENSITY

Given how important electron density is, we need ways to represent it and its changes. We are going to use three different representations for the electron density. Here we will use the nitrogen atom to illustrate each of these representations. Atoms are particularly easy because they are spherically symmetric (look the same when viewed from any angle). The utility of the electron density representations will become obvious as we start to look at molecules, none of which have spherical symmetry. (Don't discount what follows even if it seems very simple!)

The first representation we call the *electron fog*. Just as its name implies, the electron density is drawn as a cloud using dots. Where the electron density is the highest, there are more dots. Figure 7-3 is a fog picture of the electron density about a nitrogen atom. Note that the density falls off quickly moving away from the nucleus at the center of the fog.
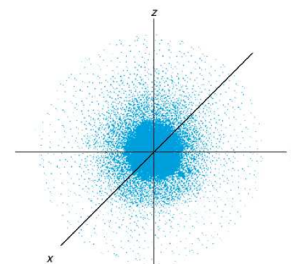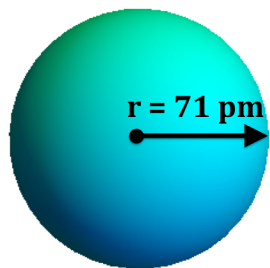

Fig. 7-3

r = 71 pm

Fig. 7-4

The fog representation provides a 3D picture of the electron density, but it is not particularly quantitative. The second model eliminates that problem, but we also lose much of the 3D information. This model is called the *probability surface* or *isosurface* representation. It is depicted as a surface on which the value of the electron density is everywhere the same. For an atom, this will be a sphere (in molecules it's more complicated).

The question is what value of probability should we pick to for the sphere? We generally draw a sphere that contains 90 or 95% of the electrons in the atom or molecule. For example, the 90% surface of nitrogen (with 7 electrons) is shown in Figure 7-4. Each time we look, we would expect to find 6.3 electrons inside the sphere and 0.7 electrons outside the sphere. The radius of this sphere is called the *atomic radius,* and it is this representation that leads to the picture of an atom as spheres. But be careful: atoms and molecules do *not* have hard surfaces inside of which all of the electrons are located! Again we can think of a beehive: the bees are spread out and in constant motion, and there is always some chance that a few bees are far away from the hive.

The isosurface model gives information about the "shape" of a molecule or atom, but it doesn't give us much detail about the distribution of electrons inside or outside of that surface. We could, however, get a lot of useful information with a set of nested isosurfaces with progressively greater probability values, like Figure 7-5. We have sliced through the concentric probability surfaces of nitrogen so we can better see how they are nested.
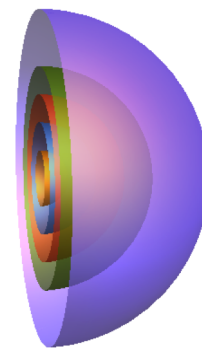
The orange sphere closest to the center is the 10% probability surface—for a sufficiently long measurement, one will always find one electron inside this orange sphere for every nine found outside. The blue, red, green, and purple spheres are respectively the 50, 80, 90 and 95% probability surfaces. While this gives us lots of information, it is very hard to draw and interpret such nested surfaces. To get around this difficulty we pick some plane to slice through these surfaces, and we draw the nested circles formed as the "loops" where an isosurface intersects the cutting the plane. Such plots are called *contour diagrams* and provide information about the shape and distribution of electron density in a specific plane.

Fig. 7-5

As with the probability surface, the contours delineate a region inside which the probability of finding an electron has some particular value, or as a line on which the value of the electron density is everywhere the same. For example, everywhere on the purple contour line, the value of the electron density is 0.05 electrons per unit volume (in this case the volume is a cubic Angstrom: 10^{-30} m^3). This same boundary denotes the intersection of the 95% probability surface with a plane passing through the nucleus.
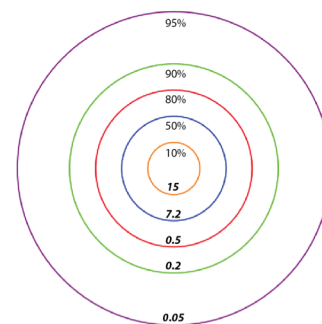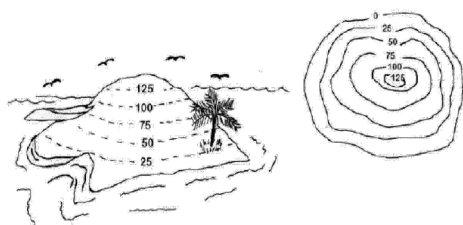

Fig. 7-6

Fig. 7-7

You can think of the electron density contour map as a "topographic map" of the atom. A topographic map relays three-dimensional elevations on a two dimensional plot. Each line represents a line or path with the same elevation. Similarly, the lines on our atomic contour plot represent a line or path with the same electron density.

The force that brings atoms together is the electrostatic force of attraction between the nuclei and electrons. In a molecule, however, there is also a repulsive force between the nuclei of the atoms and between the electrons sitting on the individual atoms of the molecule.

Let's take as a specific example, a hydrogen molecule (H_2). One of the protons in this molecule we will designate as A and the other as B. And we will designate the electrons as (1) and (2). Remember that the charge on the protons is +e and that on the electrons is –e. Now let's say we take a snapshot of the two hydrogen atoms when separated by some distance R as is shown in Figure 7-8. Let's imagine that R~ 2 Å. Then nucleus A will be attracted to electron (2) as well as (1) and similarly nucleus B will attract electron (1) as well as (2). These interactions are indicated by the four solid lines in Figure 7-8.
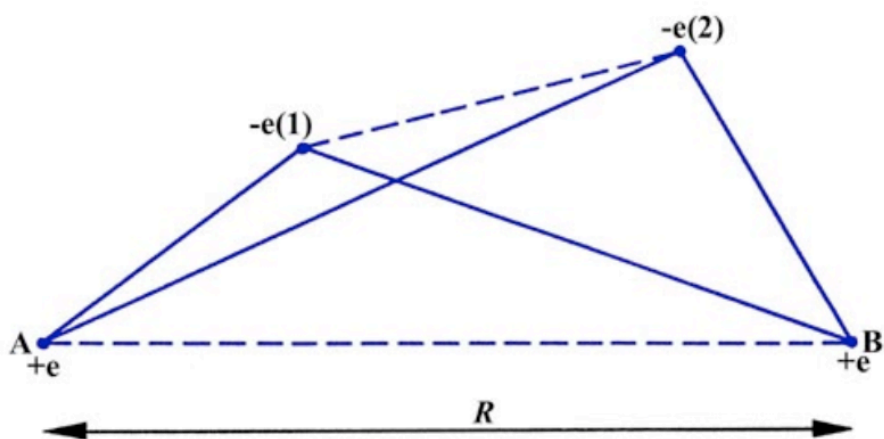

Fig. 7-8. *One possible set of the instantaneous relative positions of the electrons and nuclei in an H_2 molecule. The dashed lines represent the repulsive interactions between like charges and the solid lines indicate the attractive interactions between opposite charges.*

There are also two repulsive interactions, indicated by the dashed lines joining charges of like sign. The two electrons repel one another as do the two nuclei. When the two atoms are close together, the attractive interactions exceed the repulsive ones, but when they get even closer together the repulsive interactions are greater. Why?

To answer this question, we need to take a closer look at the electron distribution around the hydrogen nuclei, which we will represent in the form of a contour map shown in Figure 7-9. Imagine a hydrogen molecule to be cut in half by a plane that contains the nuclei. The amount of electronic charge at every point in space is determined and all points having the same value for the electron density in the plane are joined by a line, a contour line. Also shown is a profile of the contour map along the internuclear axis. A profile illustrates the variation in the charge density along a single axis.

---

[1]*These notes were adapted from Chapter 6 of Bader's, "An Introduction to the Electronic Structure of Atoms and Molecules" which is available at: http://www.chemistry.mcmaster.ca/esam/Chapter_6/intro.html*
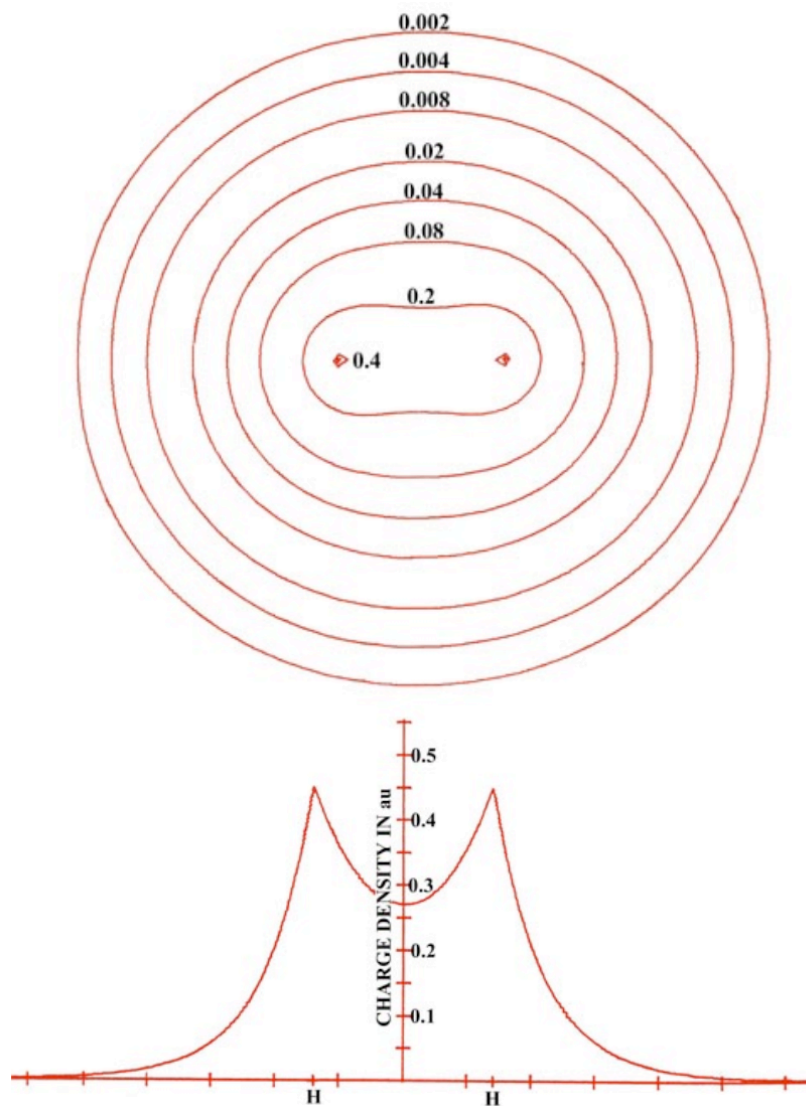
Fig. 7-9 *A contour map of the electron density distribution (or the molecular charge distribution) for H$_2$ in a plane containing the nuclei. Also shown is a profile of the density distribution along the internuclear axis. The internuclear separation is 1.4 au. The values of the contours increase in magnitude from the outermost one inwards towards the nuclei. The values of the contours in this and all succeeding diagrams are given in au; 1 au = e/a_o^3 = 6.749 e/Å^3.*

The electron density contours of highest value are in the region of each nucleus. Thus, the negative charge is concentrated in the region of the nuclei in a molecule as well as in an atom. The next highest concentration of negative charge is found in the region between the nuclei.

The same contour map would be obtained for any plane through the nuclei. Therefore, in three-dimensional space the hydrogen molecule would appear to be an ellipsoidal distribution of negative charge. Most of the electronic charge is concentrated along the internuclear axis and becomes progressively more diffuse at large distances from the center of the molecule. Recall that the addition of all the charge in every small volume element of space equals the total number of electrons, which in the case of the hydrogen molecule is two. The volume of

space enclosed by the outer contour in Figure 7-9 contains over 99% of the total electronic charge of the hydrogen molecule.

7-4 AN ELECTROSTATIC INTERPRETATION OF THE CHEMICAL BOND

With this as background let's return to the question of why at one distance atoms are attractive and at another they are repulsive.
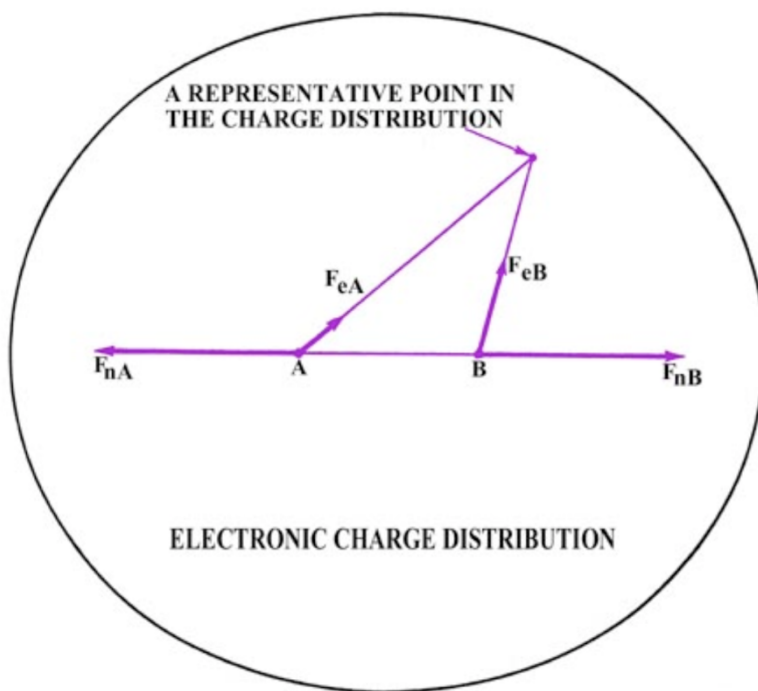
There is a theorem of quantum mechanics that allows us to understand this behavior. This theorem states that the force acting on a nucleus in a molecule may be determined by the methods of classical electrostatics. Which tells us that, using the appropriate units, the force between two charges, q_1 and q_2, separated by a distance R is given by the formula:

$$F = (q_1 q_2)/R^2$$

When applied to the hydrogen molecule of Figure 7-8, the force between the hydrogen nuclei, with a charge of $+e$, is given by:

$$F_{nA} = F_{nB} = +e^2/R^2$$

which acts to push the two nuclei apart as in Figure 7-10.

A REPRESENTATIVE POINT IN
THE CHARGE DISTRIBUTION

F_{eA} F_{eB}

F_{nA} A   B F_{nB}

ELECTRONIC CHARGE DISTRIBUTION

Fig. 7-10. The forces acting on the nuclei in H_2. Only one outer contour of the electron density distribution is shown. Over 99% of the total electronic charge is contained within this contour.

The attractive force that balances this force of repulsion and draws the nuclei together is exerted by the negatively-charged electron density distribution, where each small element of this charge distribution exerts a

force on the nuclei, illustrated in Figure 7-10 for one such small charge point. The forces this small region exerts on the nuclei are labeled Fe_A and Fe_B.

The electronic force of attraction Fe_A or Fe_B may be equated to two components, one along the internuclear axis, and one perpendicular to it. The density distribution is symmetric with respect to the internuclear axis, i.e., for every charge point above the axis there must, by symmetry, be another point of equal charge at the corresponding place beneath the axis. The symmetrically related charge point will exert the same force along the bond, but the component perpendicular to the bond will be in the opposite direction. Thus, the perpendicular forces of attraction exerted on the nuclei are zero (Figure 7-11) and we may confine our attention to the components of the attractive force along the axis.
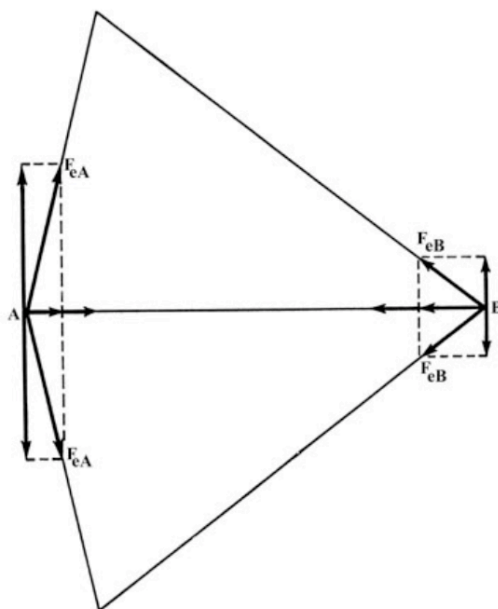
Fig. 7-11. *The two components of force along the bond add together while the two perpendicular components cancel at both A and B.*

All of the charge elements, which are in the general region between the two nuclei will exert forces that draw the two nuclei together. The force exerted by the density in this region acts in opposition to the force of nuclear repulsion and binds the two nuclei together. It is also clear that a charge element in the region behind either nucleus will exert a force that tends to increase the distance between the nuclei Figure 7-12
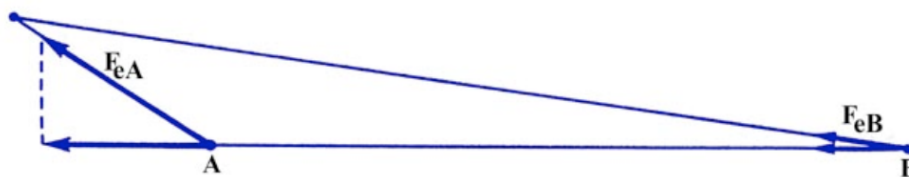

Fig. 7-12. *The component of Fe_A along the bond is greater than the corresponding component of Fe_B.*

7-7

Since the charge element is closer to nucleus A than it is to nucleus B, the component of the force on A along the bond will be greater than the component of the force on B along the bond. And the effect of density in this region will be to separate the molecule into atoms.

There must also be a line on which the density exerts the same force on both nuclei and thus neither increases nor decreases R because the charge density in one region draws the nuclei together and in another draws them apart.

The charge element shown in Figure 7-13 exerts the same force along the bond on both A and B even though it is closer to B than it is to A. Although the total force Fe_B is much larger than Fe_A, Fe_B is directed almost perpendicular to the bond axis and thus its component along the bond is quite small and equal to the component of Fe_A along the bond. Charge density on either of the two curves shown in Figure 7-13 exerts equal forces on both of the nuclei along the bond, and such charge density will not tend to increase or decrease the distance between the nuclei. Thus these two curves (surfaces in three dimensions) divide the space in a molecule into a binding region and an antibinding region. Any charge density between the two boundary curves, in the **binding region**, draws the two nuclei together while any charge density in the hatched region behind either curve, the **antibinding region**, exerts unequal forces on the nuclei and separates the molecule into atoms.
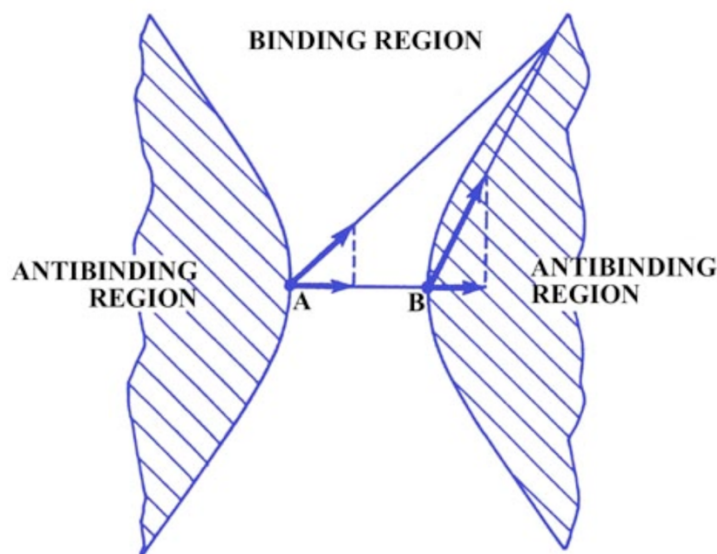
Fig. 7-13. *The boundary curves which separate the binding from the antibinding regions in a homonuclear diatomic molecule.*

A chemical bond is the result of the accumulation of negative charge density in the region between the nuclei to an extent sufficient to balance the nuclear forces of repulsion. This corresponds to a state of electrostatic equilibrium, as the net force acting on each nucleus is zero for this one particular value of the internuclear distance.

If the distance between the nuclei is increased from the equilibrium value, the nuclear force of repulsion is decreased. At the same time the force of attraction exerted by the electron density distribution is increased as the binding region is increased in size. Thus, when R is increased from its equilibrium value there are net forces of attraction acting on the nuclei which pull the two nuclei together again.

Similarly, if the value of R is decreased from its equilibrium value, the force of nuclear repulsion is increased over its equilibrium value. At the same time, the attractive force exerted by the electron density is decreased, because the binding region is decreased in size. In this case, there will be a net force of repulsion pushing the two nuclei apart and back to their equilibrium separation. There is thus one value of R for which the forces on the nuclei are zero and the whole molecule is in a state of electrostatic equilibrium.

The division of the space around a molecule into a binding and an antibinding region shows where charge density must be concentrated in order to obtain a stable chemical bond.

7-5 LOOKING AT CHEMICAL BONDS

What does a bond look like? To answer this question, let's return to the general shape of the charge density between two bound atoms. As we have shown, if one were to "walk" from one atom to another bound to it, one would start at a high density and proceed to some minimum before ascending again. At the minimum point along this bond direction the charge density is a maximum in the perpendicular directions (see Figure 7-14) A point of this sort is called a saddle point. Standing at this point the charge density is curved in the 3 direction—x, y, and z—two of these curvatures are concave down, i.e. negative curvature, and one is concave up, i.e. positive curvature. A critical point (CP) of this type is called a saddle point and through every such point there passes a charge density ridge. This ridge is called a bond path—you know those things we draw as lines. In essence, given a sufficiently powerful microscope we could look at the charge density of a molecule to determine where the bonds are and which atoms are connected by these bonds. As an example, the picture below shows the charge density in a H_2 molecule. The height indicates the amount of charge density.
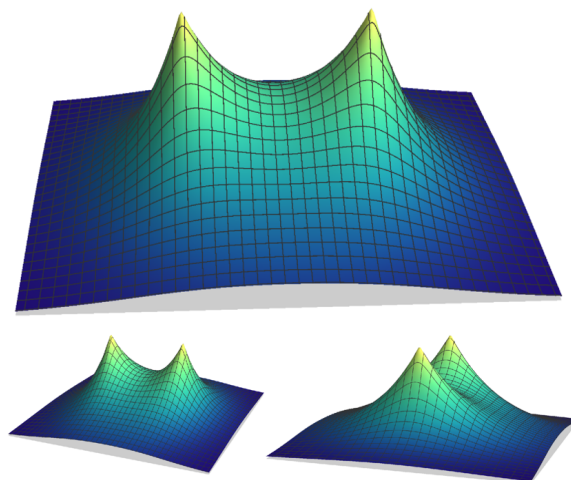

Fig. 7-14 The charge density in one plane of an H_2 molecule

The peaks show the locations of the atomic nuclei. Note how there is a single ridge connecting the two peaks in the above images. This ridge corresponds to the bond (path) between the two hydrogen atoms.

Figure 7-15 shows the charge density in the molecular plane of benzene (C_6H_6). See if you can figure which peaks correspond to hydrogen and which to carbon. You may notice that the carbon atoms appear to have flat "summits", but they really don't. The charge density has just been truncated because there is so much charge density near the carbon nuclei that if it wasn't truncated we could only see six peaks. Then we could not, for instance, make out the ridges connecting the atoms, and those ridges are very important. Each ridge that passes from one atom to another is a **bond** (path). Note that each bond must pass through a saddle point (one of which is shown with a blue circle). Count the bonds in this molecule; you should get 12: 6 carbon-carbon bonds and 6 carbon-hydrogen bonds.
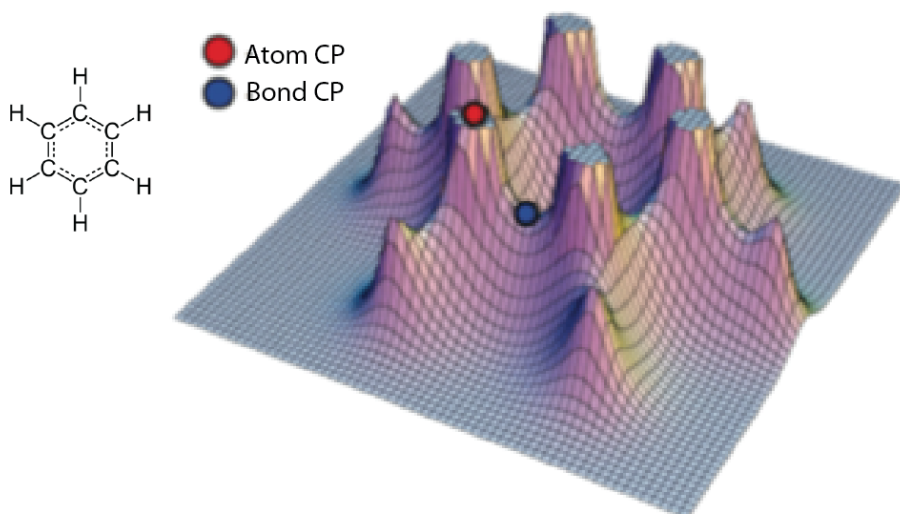

Fig. 7-15 The charge density structure of benzene (typical chemical structure shown at left).

One will always see a saddle point in the charge density when two atoms are bound, no matter what type of bond it is—ionic, covalent, metallic, polar covalent, van der Waals —there will always be a saddle point. (Can you explain why this should be the case?)

What will change is the amount of curvature in the direction parallel to the bond and in the perpendicular directions. And that is just what is shown in the Figures 7-16 and 7-17. Figure 7-16 provide a pictorial representation of the parallel curvature in the charge density for the BeO bond and the N_2 bond.
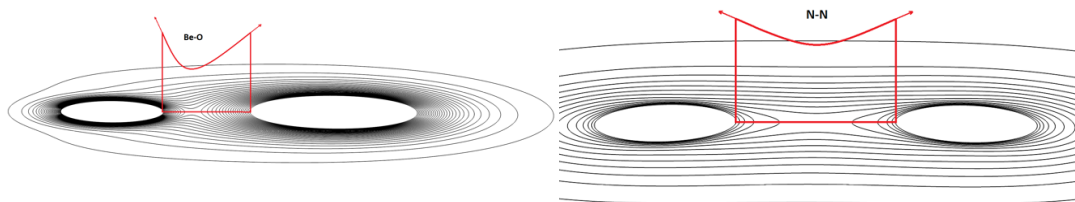

Fig 7-16 The different shapes of an ionic bond (left) and a covalent bond (right).

In Figure 7-17, "rho par" (rho parallel) shows the charge density parallel to the bond path and "rho perp" (rho perpendicular) shows the charge density perpendicular to the bond path. N_2 is what we would call a covalent bond, LiF is ionic, Cu_2 is a metallic bond, and He_2 is a Van der Waals bond.
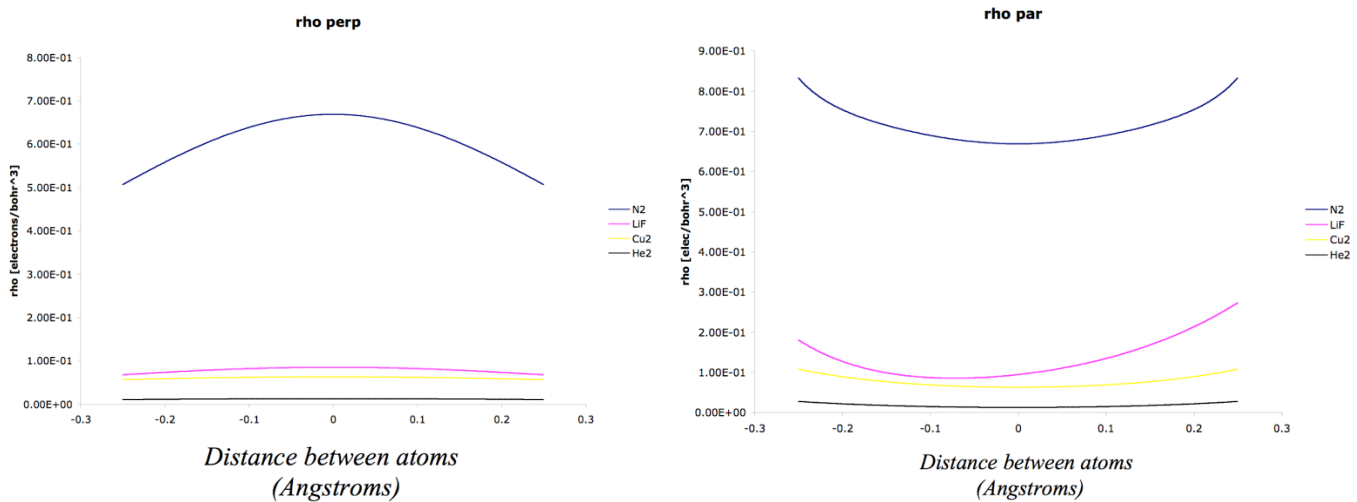

Fig. 7-17

Note that there is more charge density at the saddle point for N_2 than any other bond and that N_2 and LiF curve along the bond. In the perpendicular direction, N_2 is the most curved.

We see that **a ridge of charge density connecting atoms causes the 4 types of bonds. In fact, ALL bonds are caused by a ridge of charge density connecting atoms!** It is the amount of charge in this ridge that determines whether these bonds will be called ionic, covalent, etc. But in more important than what we call it, is to understand what causes atoms to be bound.

7-6 PROBLEMS FOR THE CURIOUS

1) Speculate on the location of the bond CPs in BCC and FCC metallic crystals.

2) For the close packed planes draw a diagram showing the bond paths in BCC and FCC crystals. How many bond paths do you find in the plane. How many bond paths are there connecting neighboring close packed plane?

3) Speculate as to why dislocations move most easily along close packed planes and directions.