

## Chemical Bonding and Electronic Structure of Buckminsterfullerene

As is well-known  $C_{60}$  resembles an American soccerball, containing 12 pentagons and 20 hexagons (see Figure 1). Removing the leather, but keeping the seams, leaves 60 vertices for the carbon atoms and 90 covalent bonds between them, 60 single bonds and 30 double bonds.

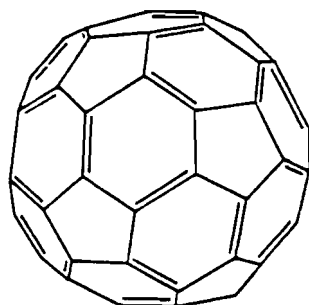


Figure 1

Actually  $C_{60}$  is a truncated icosahedron, the construction of which is shown in Figure 2. Curly and Smalley (see *Scientific American*, October 1991, pp 54-63) have described it as the "roundest molecule that can possible exist."

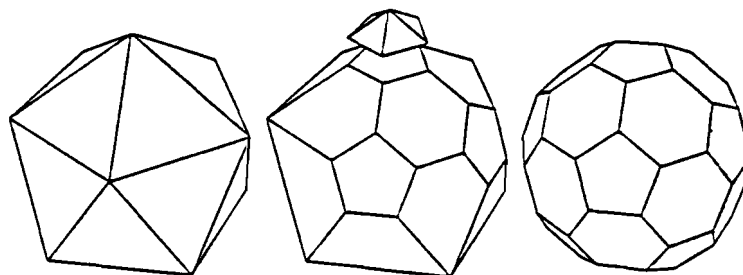


Figure 2

Therefore, we will begin by assuming that  $C_{60}$  is a perfect sphere. Looking at Figure 1 we note that all of the carbon atoms are equivalent. Each carbon is part of one pentagon and two hexagons, each has two single bonds and one double bond for the traditional carbon valence of four. Heeding the principles of the VSEPR theory as presented in Chapter 8 of Zumdahl, we would say that each carbon has  $sp^2$  hybridization with the remaining p-orbital available for  $\pi$ -bonding with one of the adjacent carbon atoms. To summarize, each carbon forms three  $\sigma$ -bonds with its  $sp^2$  hybrid orbitals and one  $\pi$ -bond with the remaining p-orbital. This description is consistent with the Lewis structure shown in Figure 1.

However, we should note that the actual bonding in  $C_{60}$  is somewhat more complex. The reason for this is that  $sp^2$  hybrid orbitals all lie in the same plane, but inspection of any model of buckminsterfullerene clearly shows that the environment at each carbon is not planar. So the hybridization at each carbon cannot be pure  $sp^2$ , and current research indicates that the actual hybridization is  $sp^{2.3}$ . Since we are trying to develop a simple, but serviceable, model of the bonding and electronic structure of  $C_{60}$ , we will assume  $sp^2$  hybridization as a first approximation. It might be a good idea at this point to review what Zumdahl has to say

about models on pages 362 to 364 in his textbook.

In chapter 8 we spent a fair amount of time drawing resonance structures for molecules and ions that had more than one correct Lewis structure.  $C_{60}$  is such a molecule and, as a matter of fact, it has 12,500 resonance structures! Try drawing at least two resonance structures, one in which all double bonds are in the hexagons, and one in which the pentagons have double bonds.

Associated with the concept of resonance is the idea of delocalization of electrons. For example, for a molecule with two resonance structures of equal plausibility (review formal charge arguments) we would say that the molecule's electronic structure is not correctly represented by either one or the other, but an average of the two (see Zumdahl's discussion of resonance in section 8.12). The fact that more than one Lewis structure can be written for a molecule is an indication of weakness in the Lewis' localized electron pair model of chemical bonding, because the existence of resonance structures actually delocalizes the  $\pi$ -electrons over the molecule as a whole. Benzene is, perhaps, the best example of this. Rather than writing structures A or B below, we write C and think Figure 9.48b in Zumdahl.

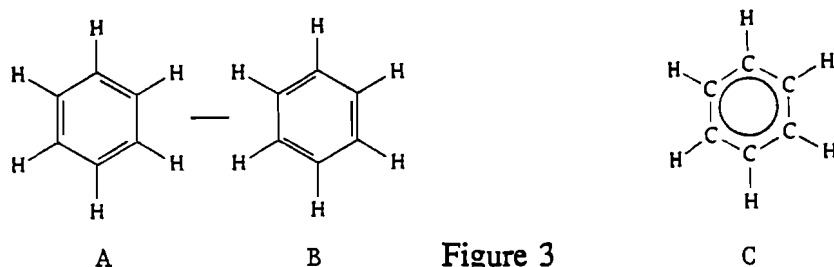


Figure 3

Since  $C_{60}$  has 12,500 resonance structures involving its 60  $\pi$ -electrons we may profitably consider the  $\pi$ -electrons to be particles delocalized over a sphere. The solution of Schrödinger's equation for a particle on a sphere is well known. Since a particle on a sphere is restricted to move in two directions, in spherical polar coordinates its position can be described by two angles,  $\theta$  and  $\phi$ . Thus, two spatial quantum numbers are required and they are the old familiar  $l$  and  $m_l$  of Chapter 7 of Zumdahl. Since the particles in question are electrons, the spin quantum number,  $m_s$ , is also required. The rules for the quantum numbers are as stated in Chapter 7:  $l$  can have integer values starting with 0;  $m_l$  can have integer values ranging from  $-l$  to  $+l$ ;  $m_s$  can have the values of  $\pm 1/2$ .

Using the rules for the  $l$  and  $m_l$  quantum numbers makes it possible to construct an energy level diagram for an electron on a sphere. This is shown in Figure 4.

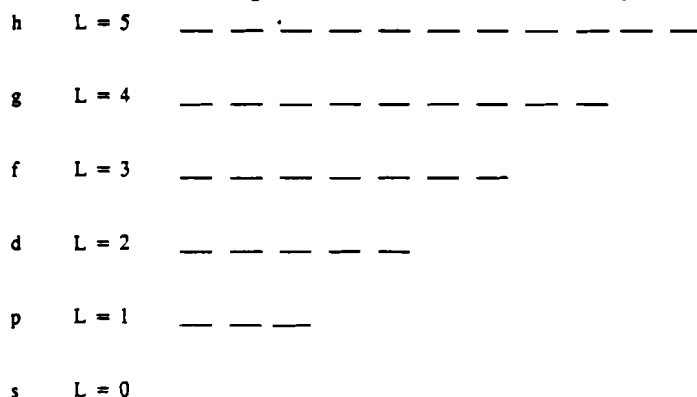


Figure 4

So our model for electronic structure of  $C_{60}$  is that three of the carbon atom's valence electrons are used to form three  $\sigma$ -bonds using  $sp^2$  hybrid orbitals, while the remaining valence electron is delocalized over the surface of the spherical molecule. This remaining electron can, to a first approximation, be treated as if it were a particle on a sphere with the energy levels shown in Figure 4 available. Placing 60 electrons in the available energy levels consistent with the Pauli exclusion principle gives the electronic structure shown in Figure 5.

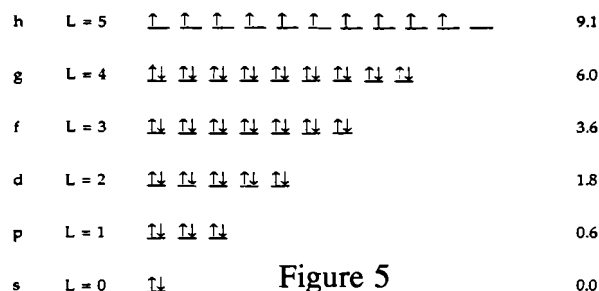


Figure 5

This figure shows 10 unpaired electrons (Hund's Rule) in the highest occupied energy level. This would suggest that  $C_{60}$  is paramagnetic and perhaps a conductor of electricity. In fact  $C_{60}$  is diamagnetic (no unpaired electrons) and does not conduct electricity. Thus, this initial model for the bonding and electronic structure of  $C_{60}$  is not correct.

A way out of this difficulty is to recall that  $C_{60}$  is not a sphere, but a truncated icosohedron. The symmetry of the truncated icosohedron is high, but not as high as a perfect sphere. The main consequence of this is that the degeneracies of some of the higher energy levels are split by the lower icosahedral symmetry. You will see more of this in CHEM 234 when we study transition metal complexes and crystal field theory. Figure 6 shows what happens to the energy levels under icosahedral symmetry and how they are filled with 60 electrons.

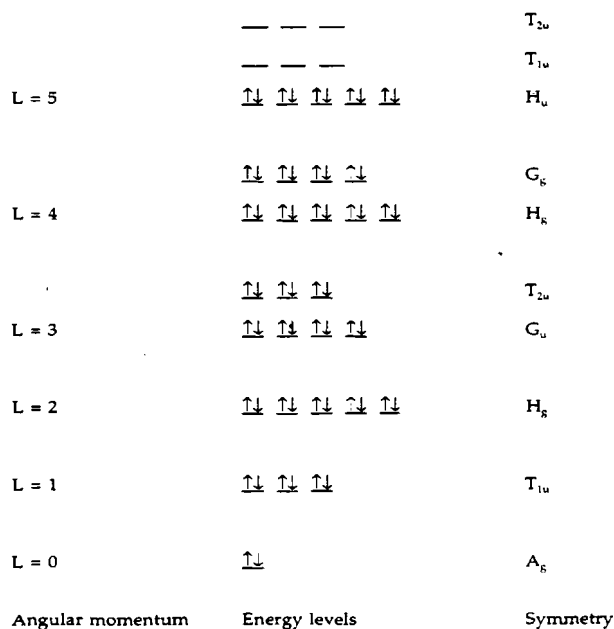


Figure 6

Note that this energy level diagram is in agreement with the basic facts about  $C_{60}$ . It is a non-conductor and diamagnetic. In addition, it suggests that  $C_{60}$  might have a fairly high electron affinity because it has a low-lying unoccupied energy level with room for six electrons. This is consistent with the fact that  $K_3C_{60}$  is known and is a conductor and passes into a super-conducting state at low temperature. The electro-positive potassium atoms supply three electrons which half-fill the lowest unoccupied energy level.  $K_6C_{60}$  is also known and is a non-conductor. This too is consistent with the model as the potassiums supply six valence electrons completely filling the  $C_{60}$ 's lowest unoccupied energy level.

In Chapter 10 we will see that the crystal structures of solid  $C_{60}$ ,  $K_3C_{60}$ , and  $K_6C_{60}$  can be describe using the same concepts as are used to describe the more familiar structures of NaCl,  $CsCl_2$ , and  $CaF_2$ . For now we can say, for example, that solid buckminsterfullerene consists of a face-centered cubic packing of spherical  $C_{60}$  molecules (see Figures 10.15 and 10.17 in Zumdahl).  $K_3C_{60}$  can be described as face-centered cubic  $C_{60}^{3-}$  ions with  $K^+$  ions in all the tetrahedral and octahedral holes (see Figure 10.33 in Zumdahl for an illustration of tetrahedral and octahedral holes). You should confirm that this structure gives the correct stoichiometric ratios for the ions. By contrast  $K_6C_{60}$  is body centered  $C_{60}^{3-}$  ions with four  $K^+$  ions in each of the six cube faces as shown in Figure 7 below. Again you should confirm that this structure gives the correct ratio of the stoichiometric coefficients.

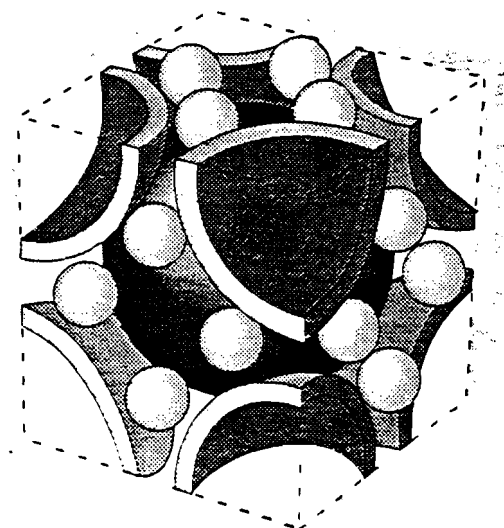


Figure 7

While it is not possible to go into detail at this point, it is also the case that the model presented here for the bonding and electronic structure of buckminsterfullerene is consistent with the absorption spectra of  $C_{60}$  in the ultraviolet, visible, and infrared regions of the electromagnetic spectrum.