2.2 Electron States and Bonding in Molecules

In this section, we will examine briefly how ideas about atomic states and orbitals can be applied to a description of electron states in molecules and bonding within a molecule (i.e. between its atoms) and between molecules.

2.2.1 Atom-Atom Bonding in Molecules

In many ways, electron energy states in molecules are analogous to those in atoms. Only states with certain discrete energies are allowed. The Pauli Principles applies. States are filled with electrons from the bottom up. And so forth.

The major complication with molecules arises from the fact that one has to deal with two or more nuclei, i.e. two or more centers which attract the electrons. This makes the determination of the allowed energies and associated states/orbitals much more difficult.

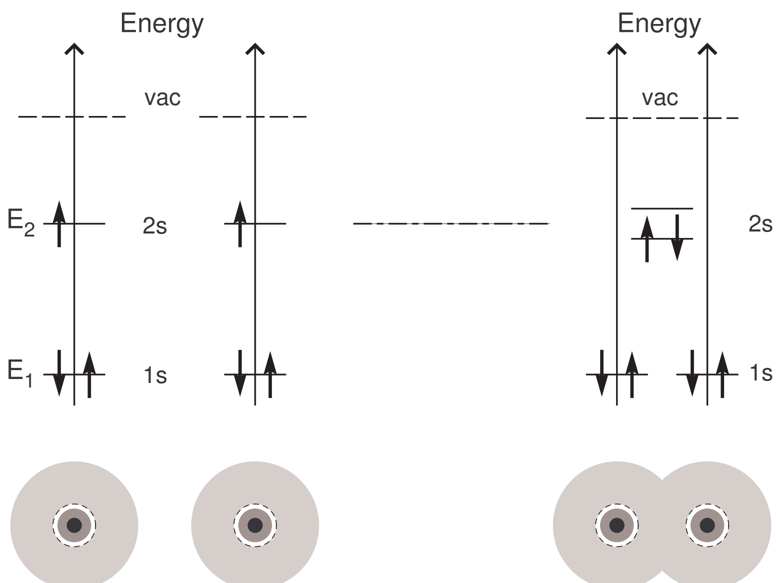

Figure 2.6: Energy states and orbitals of two Li atoms approaching each other

We will try to develop at least a qualitative sense of some of the important parameters and effects by looking at the example of the Li_2 (lithium) molecule. The ground state configuration of a Li atom is $1s^2 2s^1$ (cf. Fig. 2.5). Now observe what happens with the atomic electron energy states as two Li atoms approach each other (Fig. 2.6). The top of the figure shows the energy levels and the bottom the atomic orbitals. The little arrows indicate the electrons with their spin orientation.

As long as the two Li atoms are far apart, all the atomic orbitals are clearly separated. When the Li atoms are close enough, the 2*s* orbitals begin to overlap, and thus interact, while the 1*s* are still separate. This causes the two atomic levels at E_2 to shift up and down slightly. Now, in order to assume the lowest possible energy configuration, the two 2*s* electrons will go into the lower of the two 2*s* states, and you have made yourself a Li_2 molecule.

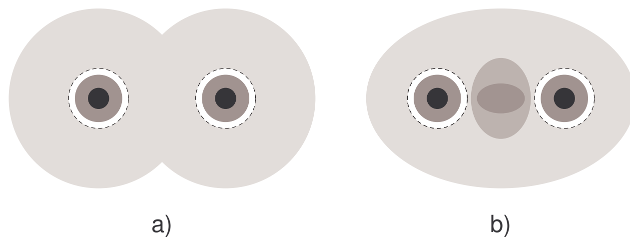

Figure 2.7: Charge distributions for a Li_2 molecule. a) Two overlapping 2*s* atomic orbitals; b) The corresponding molecular orbital. Note the increased charge density in-between the atoms.

As regards the charge distribution in the molecule, Fig. 2.7a with two overlapping atomic orbitals gives a rather inaccurate picture. As noted above, the atom-atom interaction gives rise to the formation of a molecular orbital occupied by two electrons with opposite spins, and with increased charge density between the two atomic centers (Fig. 2.7b). It is in effect this locally enhanced charge which brings about the chemical bonding in the Li_2 molecule. We can say that a **covalent bond** has been formed by two electrons shared by the two Li atoms. Again, be aware that this extra charge, and all charge in general, is distributed continuously, without sharp boundaries.

We will not need to delve into the intricacies of molecular orbitals. The most important orbitals for us will be of the bonding type, i.e. those that allow a pair of electrons to be shared between two atoms while at the same lowering their combined energy. There are also molecular orbitals of the so-called anti-bonding type which, if they were occupied by shared electrons, would raise rather than lower the energy of the electrons. An example is the upper of the two 2*s*-derived orbitals for Li_2 in Fig. 2.6. Furthermore, there may be molecular orbitals which are occupied by one or two electrons coming from the same atom. In the latter case one would speak of a lone pair of electrons.

When it comes to predicting the geometries of more complex molecules, containing three or more atoms, a useful principle to keep in mind is that electric charges generally try to arrange themselves so as to minimize the total energy (i.e. the most stable state is the one with lowest energy. In particular, electrons (or clouds of negative charge) will try to stay away from each other and, at the same, as close as possible to nuclei (positive charges). The same idea will be applicable in discussions of the bonding and structure of solids.

An example for this principle in action would be the geometry of a CH_4 molecule (methane). It is well known that the four covalent C-H bonds are completely equivalent, and the molecule has a tetrahedral geometry: the four H atoms are at the corners of a tetrahedron, with the C atom in the center. The reason for this is that the electrons in the orbitals forming each of the C-H bonds want to be as far from each other as possible.

2.2.2 Bonding between Molecules

In order to round out our discussion of molecules, I wish to make a few remarks about bonding *between* molecules, that is **intermolecular bonding**, as opposed to bonding *within* molecules, or **intramolecular bonding**, the latter having been the theme above for the formation of molecules from atoms.

Although all interactions between electrons and nuclei, between atoms, and between molecules are ultimately electrostatic in nature, as per Coulomb's Law, you should not forget that even entities with no overall net charge can have attractive or repulsive interactions, depending on how close they are. After all, a large number of substances that are gaseous under normal conditions can be liquefied, even solidified, at sufficiently low temperatures, and when they are in the liquid state, they are very hard to compress. We will have much more to say about atom-atom bonding in solids in the next section.

As an aside let us agree that when we talk about **normal** or **standard conditions**, we use the terminology of chemistry, meaning **room temperature**, i.e. 20°C or 293 K, and 1 atmosphere of pressure.

2.3 Atom-Atom Bonding in Solids

Here we will discuss in greater detail the various types of bonding between atoms that are relevant for the formation of solids. For this purpose, our discussions above will have direct applications, but we will also have to deal with a few new types of bonding. These arise due to the very large number of atoms interacting when they come together to form a solid material. We begin with an examination of some generic properties of atom-atom bonding in solids. Then we will focus on the different classes of solids and their associated atomic bonding.

2.3.1 Generic Features of Atom-Atom Bonding in Solids

Perhaps the most universal property of solids, as compared to liquids and gases, is that they maintain their shape or, speaking a bit more like an engineer, they resist deformation. In addition, regardless of how exactly they are deformed, if the deformation is small enough, solids will resume their original dimensions once the deforming force is removed.