CHAPTER 28

Splitting of Electron Energy Levels

Imagine two atoms that are initially far apart. The two isolated atoms have the same energy levels. As the atoms come closer together, the electron wave functions begin to overlap. This overlap changes the wave functions and their energies—just as the energy levels in multielectron atoms differ from the energy levels in a hydrogen atom due in part to the overlap of the electron wave functions. Each energy level splits into two energy levels. With significant overlap of the wave functions, we can no longer tell which electron "belongs" to which nucleus. Instead of two identical atomic energy levels, there are two energy levels for the system of two atoms. The first levels to split are the higher energy levels, since their wave functions extend farther from the nucleus and thus begin to overlap first as the atoms are brought closer together. As the atoms get closer and closer together, the lower energy levels start to split in order of decreasing energy (Fig. 28.30).

Energy level splitting is the basis of the formation of covalent chemical bonds. Imagine two hydrogen atoms in their ground states, initially far apart. Each has an electron in its 1*s* state. As the atoms are brought closer together, the electron wave functions overlap each other. The interaction modifies the wave functions and the energies—the 1*s* energy levels split. The electron wave function is no longer spherically symmetrical around a single nucleus; now the electrons are attracted by two nuclei. In the lower of the two energy levels that result from the split of the 1*s* atomic level, the electron probability is high in the region between the two protons, where its electric potential energy is low. In the higher of the two energy levels, the electron is less likely to be between the two protons, so it is less tightly bound—its energy is higher. In the ground state, both electrons go into the lower of the two levels, one with spin up and one with spin down.

The equilibrium separation of the protons in the H_2 molecule is that which makes the energy minimum. If the protons are pushed closer together than that, the energy of the molecule rises again, reflecting in part the Coulomb repulsion between the two protons.

Bands of Energy Levels

A solid is an assembly of a huge number *N* of atoms instead of the two atoms in the H_2 molecule. Instead of each atomic energy level splitting into two levels, now they split into *N* levels—one for each atom. *N* might typically be of the order of Avogadro's number, $\approx 10^{24}$. Each atomic energy level becomes a **band** of *N* closely spaced energy levels.

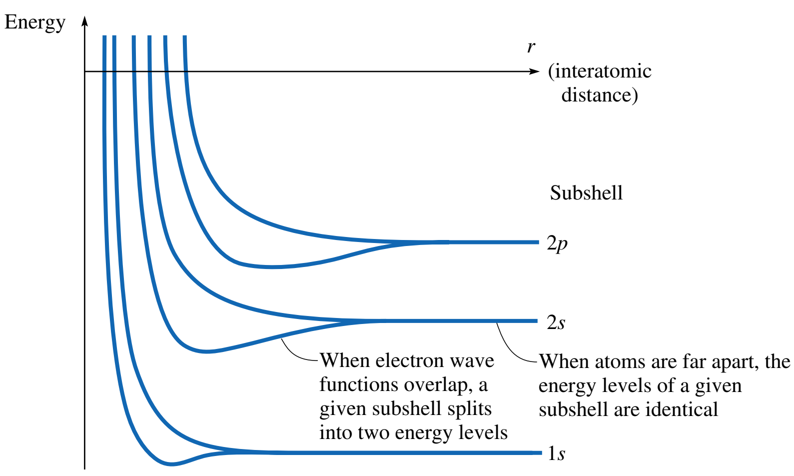

Figure 28.30 Graph showing the energy levels for two lithium atoms as a function of their separation. The ground-state configuration of a single Li atom is $1s^2 2s^1$. When the atoms are far apart, each atom has one electron in the 2*s* subshell; the two have the same energy. The energy level starts to split when the atoms are sufficiently close together that the wave functions begin to overlap. Both 2*s* electrons are in the lowerof the two energy levels (one spin up, the other spin down).

Overlap between the bands associated with adjacent atomic energy levels is common, but there are also **band gaps:** ranges of energy in which there are no electron energy levels.

The crystalline form of carbon known as diamond has a larger band gap (about 5.5 eV) than the semiconductors. It is considered to be an insulator at room temperature. The number of electrons in the conduction band is approximately proportional to $e^{-E_g/(k_B T)}$, so a gap five times larger than that of silicon means that diamond has only $e^{-5} \approx 0.7\%$ as many conduction electrons as silicon and a correspondingly smaller number of holes.

As discussed in Section 18.4, the dependence of resistivity on temperature is opposite for conductors and semiconductors. In a conductor, the effect of higher temperature is largely to make collisions between electrons and ions more likely, since the ions are vibrating with larger amplitudes. Thus, the resistivity of a conductor increases with increasing temperature. In a semiconductor, the main effect of a higher temperature is to excite a larger number of electrons into the conduction band. The greater number of conduction electrons translates into a *decrease* of resistivity with increasing temperature.