

Chapter 2

Model problems that form important starting points

The model problems discussed in this chapter form the basis for chemists' understanding of the electronic states of atoms, molecules, clusters, and solids as well as the rotational and vibrational motions of molecules.

2.1 Free electron model of polyenes

The particle-in-a-box problem provides an important model for several relevant chemical situations.

The "particle-in-a-box" model for motion in two dimensions discussed earlier can obviously be extended to three dimensions or to one. For two and three dimensions, it provides a crude but useful picture for electronic states on surfaces or in metallic crystals, respectively. I say metallic crystals because it is in such systems that the outermost valence electrons are reasonably well treated as moving freely. Free motion within a spherical volume gives rise to eigenfunctions that are used in nuclear physics to describe the motions of neutrons and protons in nuclei. In the so-called shell model of nuclei, the neutrons and protons fill separate s, p, d, etc. orbitals with each type of nucleon forced to obey the Pauli principle (i.e., to have no more than two nucleons in each orbital because protons and neutrons are fermions). To remind you, I display in Fig. 2.1 the angular shapes that characterize s, p, and d orbitals.

This same spherical box model has also been used to describe the orbitals of valence electrons in clusters of metal atoms such as Cs_n , Cu_n , Na_n and their positive and negative ions. Because of the metallic nature of these species, their valence electrons are essentially free to roam over the entire spherical volume of the cluster, which renders this simple model rather effective. In this model, one thinks of each electron being free to roam within a sphere of radius R (i.e., having a potential that is uniform within the sphere and infinite outside the sphere). Finally, as noted above, this same spherical box model forms the basis of the so-called shell model of nuclear structure. In this model, one assumes that the protons and neutrons that make up a nucleus, both of which are fermions, occupy