Critique of Bohr Theory and of the "Old" Quantum Mechanics

We saw in Chapters 3 and 4 that many phenomena—blackbody radiation, the photoelectric effect, Compton scattering, optical spectra of hydrogen, and the x-ray spectra of many elements—could be "explained" by various ad hoc quantum assumptions. These "theories," a strange mixture of classical theories and quantum assumptions, are now usually referred to as "old" quantum mechanics. Applying this quantum mechanics in the early years of the twentieth century was as much an art as a science, for no one knew exactly what the rules were. The successes of the Bohr theory, however, were substantial and spectacular. The existence of unknown spectral lines was predicted, and subsequently they were observed. Not only was the Rydberg constant explained in terms of known constants, but its slight variation from atom to atom was accurately predicted by the slight variation of the reduced mass. The radius of the first Bohr orbit in hydrogen, 0.0529 nm, corresponded well with the known diameter of the hydrogen molecule, about 0.22 nm. The wavelengths of the characteristic x-ray spectra could be calculated accurately based on Bohr's theory for hydrogenlike atoms.

The failures of Bohr theory and the old quantum mechanics were mainly matters of omission. While the correct H atom transitions were accurately predicted, the theory was silent on the *rate* at which the transitions occurred; that is, there was no way of predicting the relative intensities of the spectral lines. In addition, there was little success in applying the theory to the optical spectra of atoms more complex than hydrogen. Finally, there was the very considerable philosophical problem that the assumptions of the theory lacked physical foundation. For example, why did the accelerating atomic electrons not radiate energy as the extremely well-tested classical electromagnetic theory required? And why were the oscillating molecules in the walls of the blackbody cavity restricted to quantized frequencies? There were no a priori reasons to expect that Coulomb's law would work but the laws of radiation would not or that Newton's laws could be used but only certain values of the angular momentum were allowed. In the 1920s scientists struggled with these difficulties and a systematic theory, now known as *quantum mechanics* or *wave mechanics*, emerged formulated by de Broglie, Schrödinger, Heisenberg, Pauli, Dirac, and many others. Some important aspects of this theory are studied in Chapters 5 and 6 and applied to the study of atoms, nuclei, molecules, and solids in the remaining chapters of the book. As we do so, we will see that, although this theory is much more satisfying from a philosophical point of view, it is somewhat abstract and sometimes difficult to apply in detail to problems. In spite of its shortcomings, the Bohr theory provides a model that is easy to visualize, gives the correct atomic energy levels in hydrogen, and often provides a useful model for visualizing and describing quantum-mechanical calculations.