1　The Motivation for Quantum Mechanics

Physicists at the end of the nineteenth century believed that most of the fundamental physical laws had been worked out. They expected only minor refinements to get "an extra decimal place" of accuracy. As it turns out, the field of physics was transformed profoundly in the early twentieth century by Einstein's discovery of relativity and by the development of quantum mechanics. While relativity has had fairly little impact on chemistry, all of theoretical chemistry is founded upon quantum mechanics.

The development of quantum mechanics was initially motivated by two observations which demonstrated the inadeqacy of classical physics. These are the "ultraviolet catastrophe" and the photoelectric effect.

1.1　The Ultraviolet Catastrophe

A *blackbody* is an idealized object which absorbs and emits all frequencies. Classical physics can be used to derive an equation which describes the intensity of blackbody radiation as a function of frequency for a fixed temperature—the result is known as the Rayleigh-Jeans law. Although the Rayleigh-Jeans law works for low frequencies, it diverges as ν^2; this divergence for high frequencies is called the ultraviolet catastrophe.

Max Planck explained the blackbody radiation in 1900 by assuming that the energies of the oscillations of electrons which gave rise to the radiation must be proportional to integral multiples of the frequency, i.e.,

$$E = nh\nu \tag{1}$$

Using statistical mechanics, Planck derived an equation similar to the Rayleigh-Jeans equation, but with the adjustable parameter h. Planck found that for $h = 6.626 \times 10^{-34}$ J s, the experimental data could be reproduced. Nevertheless, Planck could not offer a good justification for his assumption of energy quantization.

Physicicsts did not take this energy quantization idea seriously until Einstein invoked a similar assumption to explain the photoelectric effect.

1.2   The Photoelectric Effect

In 1886 and 1887, Heinrich Hertz discovered that ultraviolet light can cause electrons to be ejected from a metal surface. According to the classical wave theory of light, the intensity of the light determines the amplitude of the wave, and so a greater light intensity should cause the electrons on the metal to oscillate more violently and to be ejected with a greater kinetic energy. In contrast, the experiment showed that the kinetic energy of the ejected electrons depends on the *frequency* of the light. The light intensity affects only the number of ejected electrons and not their kinetic energies.

Einstein tackled the problem of the photoelectric effect in 1905. Instead of assuming that the electronic oscillators had energies given by Planck's formula (1), Einstein assumed that the radiation itself consisted of packets of energy $E = h\nu$, which are now called photons. Einstein successfully explained the photoelectric effect using this assumption, and he calculated a value of h close to that obtained by Planck.

Two years later, Einstein showed that not only is light quantized, but so are atomic vibrations. Classical physics predicts that the molar heat capacity at constant volume (C_v) of a crystal is $3R$, where R is the molar gas constant. This works well for high temperatures, but for low temperatures C_v actually falls to zero. Einstein was able to explain this result by assuming that the oscillations of atoms about their equilibrium positions are quantized according to $E = nh\nu$, Planck's quantization condition for electronic oscillators. This demonstrated that the energy quantization concept was important even for a system of atoms in a crystal, which should be well-modeled by a system of masses and springs (i.e., by classical mechanics).

1.3   Quantization of Electronic Angular Momentum

Rutherford proposed that electrons orbit about the nucleus of an atom. One problem with this model is that, classically, orbiting electrons experience a centripetal acceleration, and accelerating charges lose energy by radiating; a stable electronic orbit is classically forbidden. Bohr nevertheless assumed stable electronic orbits with the electronic angular momentum quantized as

$$l = mvr = n\hbar \tag{2}$$

Quantization of angular momentum means that the radius of the orbit and the energy will be quantized as well. Bohr assumed that the discrete lines seen in the spectrum of the hydrogen atom were due to transitions of an electron from one allowed orbit/energy to another. He further assumed that the energy for a transition is acquired or released in the form of a photon as proposed by Einstein, so that

$$\Delta E = h\nu \tag{3}$$

This is known as the *Bohr frequency condition.* This condition, along with Bohr's expression for the allowed energy levels, gives a good match to the observed hydrogen atom spectrum. However, it works only for atoms with one electron.

1.4   Wave-Particle Duality

Einstein had shown that the momentum of a photon is

$$p = \frac{h}{\lambda} \tag{4}$$

This can be easily shown as follows. Assuming $E = h\nu$ for a photon and $\lambda\nu = c$ for an electromagnetic wave, we obtain

$$E = \frac{hc}{\lambda} \tag{5}$$

Now we use Einstein's relativity result $E = mc^2$ to find

$$\lambda = \frac{h}{mc} \tag{6}$$

which is equivalent to equation (4). Note that m refers to the relativistic mass, not the rest mass, since the rest mass of a photon is zero. Since light can behave both as a wave (it can be diffracted, and it has a wavelength), and as a particle (it contains packets of energy $h\nu$), de Broglie reasoned in 1924 that matter also can exhibit this *wave-particle duality*. He further reasoned that matter would obey the same equation (4) as light. In 1927, Davisson and Germer observed diffraction patterns by bombarding metals with electrons, confirming de Broglie's proposition.

de Broglie's equation offers a justification for Bohr's assumption (2). If we think of an electron as a wave, then for the electron orbit to be stable the wave must complete an integral number of wavelengths during its orbit. Otherwise, it would interfere destructively with itself. This condition may be written as

$$2\pi r = n\lambda \tag{7}$$

If we use the de Broglie relation (4), this can be rewritten as

$$mvr = n\hbar \tag{8}$$

which is identical to Bohr's equation (2).

Although de Broglie's equation justifies Bohr's quantization assumption, it also demonstrates a deficiency of Bohr's model. Heisenberg showed that the wave-particle duality leads to the famous uncertainty principle

$$\Delta x \Delta p \approx h \tag{9}$$

One result of the uncertainty principle is that if the orbital radius of an electron in an atom r is known exactly, then the angular momentum must be completely unknown. The problem with Bohr's model is that it specifies r exactly and it also specifies that the orbital angular momentum must be an integral multiple of $\hbar$. Thus the stage was set for a new quantum theory which was consistent with the uncertainty principle.

2 The Schrödinger Equation

In 1925, Erwin Schrödinger and Werner Heisenberg independently developed the new quantum theory. Schrödinger's method involves partial differential equations, whereas Heisenberg's method employs matrices; however, a year later the two methods were shown to be mathematically equivalent. Most textbooks begin with Schrödinger's equation, since it seems to have a better physical interpretation via the classical wave equation. Indeed, the Schrödinger equation can be viewed as a form of the wave equation applied to matter waves.

2.1 The Time-Independent Schrödinger Equation

Here we follow the treatment of McQuarrie [1], Section 3-1. We start with the one-dimensional classical wave equation,

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2} \tag{10}$$

By introducing the separation of variables

$$u(x,t) = \psi(x)f(t) \tag{11}$$

we obtain

$$f(t)\frac{d^2\psi(x)}{dx^2} = \frac{1}{v^2}\psi(x)\frac{d^2 f(t)}{dt^2} \tag{12}$$

If we introduce one of the standard wave equation solutions for $f(t)$ such as $e^{i\omega t}$ (the constant can be taken care of later in the normalization), we obtain

$$\frac{d^2\psi(x)}{dx^2} = \frac{-\omega^2}{v^2}\psi(x) \tag{13}$$

Now we have an ordinary differential equation describing the spatial amplitude of the matter wave as a function of position. The energy of a particle is the sum of kinetic and potential parts

$$E = \frac{p^2}{2m} + V(x) \tag{14}$$

which can be solved for the momentum, p, to obtain

$$p = \{2m[E - V(x)]\}^{1/2} \tag{15}$$

Now we can use the de Broglie formula (4) to get an expression for the wavelength

$$\lambda = \frac{h}{p} = \frac{h}{\{2m[E - V(x)]\}^{1/2}} \tag{16}$$

The term ω^2/v^2 in equation (13) can be rewritten in terms of λ if we recall that $\omega = 2\pi\nu$ and $\nu\lambda = v$.

$$\frac{\omega^2}{v^2} = \frac{4\pi^2\nu^2}{v^2} = \frac{4\pi^2}{\lambda^2} = \frac{2m[E - V(x)]}{\hbar^2} \tag{17}$$

When this result is substituted into equation (13) we obtain the famous *time-independent Schrödinger equation*

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0 \tag{18}$$

which is almost always written in the form

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{19}$$

This single-particle one-dimensional equation can easily be extended to the case of three dimensions, where it becomes

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{20}$$

A two-body problem can also be treated by this equation if the mass m is replaced with a reduced mass μ.

It is important to point out that this analogy with the classical wave equation only goes so far. We cannot, for instance, derive the time-*dependent* Schrödinger equation in an analogous fashion (for instance, that equation involves the partial first derivative with respect to time instead of the partial second derivative). In fact, Schrödinger presented his time-independent equation first, and then went back and postulated the more general time-dependent equation.