Reese Ch. 27, Part C (pp. 1261-1265)

- Review of Characteristics of the Wave Function
- Quantum-mechanical Operators
- The Schroedinger Equation

Characteristics of the Wavefunction Ψ

- The wavefunction Ψ is complex-valued.
- The absolute square of the wavefunction is the probability per unit distance of detecting the particle.
- The wavefunction is believed to keep track of all information about the particle-wave, but the predictions we can make from it are in general statistical.
- The wavefunction satisfies a linear wave equation that was first written down in 1926 by Erwin Schroedinger.

Quantum-mechanical Operators: I

- In Newtonian mechanics, it is considered possible to precisely know both the position x and the momentum p_x of a particle at a given instant. Other physical quantities (such as energy and angular momentum) are known functions of the position and momentum, so when x and p_x are known, it's easy to find precise values for other physical quantities.
- Because of wave-particle duality and the resultant uncertainty principles, the quantum-mechanical description of nature works from the wave function $\Psi(x,t)$. How do we obtain the values of physical variables and how do we determine the evolution of Ψ? The next few slides set out the answer provided by Schroedinger, Heisenberg, Born, and others.

Quantum-mechanical Operators: II

- Since the basic description of a particle in quantum mechanics is through the wavefunction, the way to learn the values of physical quantities is through acting on the wavefunction with various **operators**.
- Let's look at a specific and important example of this. We have already written down the wavefunction for a particle of definite momentum $p = \hbar k$:

$$\boxed{\Psi(x,t) = Ae^{i(kx-\omega t)}}$$

Notice that if we "operate" on this wavefunction with the "operator" $\frac{\hbar}{i}\frac{\partial}{\partial x}$, the result is pΨ ! **Bingo!**

Quantum-mechanical Operators: III

This illustrates some of the general QM "rules":

- For each physical quantity, there is a quantum-mechanical operator **Q**.
- If the wavefunction describes a QM "state" Ψ_q in which the system has a **definite value** q for a particular physical quantity, then applying the corresponding operator to Ψ results in a new function that is just q times the original function: $\boxed{\mathbf{Q}\Psi_q = q\Psi_q}$
- In a general state Ψ, the physical quantity doesn't have a definite value, but the statistical **expected value** for the quantity is given by

$$\boxed{\overline{q} \equiv \langle Q \rangle = \int_{-\infty}^{\infty} \Psi^*(\mathbf{Q}\Psi)dx}$$

Quantum-mechanical Operators: IV

Let's look at two basic applications of this last rule. We'll suppose that $\Psi(x,t)$ represents a "wave packet" which has a reasonably well-defined location and a reasonably well-defined momentum (but of course obeying the Heisenberg uncertainty principle).

- Expected momentum: $\boxed{\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \left[\left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi \right] dx}$
- Expected position:

$$\boxed{\langle x \rangle = \int_{-\infty}^{\infty} \Psi^* \left[x\Psi \right] dx}$$

- Notice that this latter expression is fully consistent with the idea that $\Psi^*\Psi dx$ represents the probability of detecting the particle in the interval (x, x+dx)

The Schroedinger Equation: I

- In 1926, the Austrian physicist Erwin Schroedinger wrote down an equation that gives the rule for finding how the wavefunction changes with time:

$$\boxed{i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \mathbf{H}\Psi(x,t)}$$

Here the operator **H** is called the Hamiltonian; it is the operator equivalent of the classical total energy. For example, the Hamiltonian for a free particle of mass m is **p²/**2m. (The square of an operator means apply the operator twice in a row.) If a particle is moving under the influence of a potential energy, then **H= p²/**2m + **V**(x).

The Schroedinger Equation: II

- The full name of the equation on the previous slide is the time-dependent Schroedinger equation. What makes Schroedinger famous is the fact that he was able to use his equation to explain the spectrum of hydrogen, and that others have used it ever since to understand the behavior of a huge variety of atoms and molecules.
- The states of definite energy are those states Ψ_E for which $\mathbf{H}\Psi_E = E\Psi_E$. For such states,

$$\boxed{\Psi_E(x,t) = \psi_E(x)e^{-iEt/\hbar}}$$

The Schroedinger Equation: III

- The "stationary-state" function $\psi_E(x)$ satisfies the time-independent Schroedinger equation:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_E(x)=E\psi_E(x)$$

- Schroedinger obtained the spectrum of hydrogen by solving the appropriate 3-D generalization of this equation. From the solutions come not only the allowed energies, but also (using $\psi_E^*\psi_E$) the probability-density clouds shown in chemistry texts. The discovery of the Schroedinger equation was arguably one of the most important events of the twentieth-century intellectual life on planet Earth.