Review of Quantum Mechanics

The basic principle underlying quantum mechanics is that everything is both a wave and a particle (wave-particle duality). That means that if you look for wave behavior (in the right wavelength regime), you will find it. Similarly, if you look for particle-like behavior (in the right units or quanta) you will also find it.

We are familiar with the behavior of macroscopic objects (particles), so a way to bring these seemingly contradictory ideas together is to generate a wave equation that gives us Newtonian mechanics at the macroscopic scale.

Start with classical mechanics with $\mathbf{p}$ representing momentum and $\mathbf{r}$ location. The basic laws of motion can be described simply in terms of a Hamiltonian $H(\mathbf{p}, \mathbf{r})$:

$$\frac{d\mathbf{r}}{dt} = \nabla_{\mathbf{p}} H(\mathbf{p}, \mathbf{r}) \tag{1}$$

$$\frac{d\mathbf{p}}{dt} = -\nabla_{\mathbf{r}} H(\mathbf{p}, \mathbf{r}) \tag{2}$$

The classical Hamiltonian is:

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) = \mathrm{KE} + \mathrm{PE} = E \tag{3}$$

Substituting above, we get:

$$\frac{d\mathbf{r}}{dt} = \nabla_{\mathbf{p}} H(\mathbf{p}, \mathbf{r}) = \frac{\mathbf{p}}{m} = \mathbf{v} \tag{4}$$

and

$$\frac{d\mathbf{p}}{dt} = -\nabla_{\mathbf{r}} H(\mathbf{p}, \mathbf{r}) = -\nabla_{\mathbf{r}} V(\mathbf{r}) = \mathbf{F}, \tag{5}$$

which are just the definition of momentum and Newton's second law ($F = ma$).

We can transfer these same ideas to quantum mechanics. Consider a simple plane wave:

$$\Psi = A \cdot \exp\left[i(\mathbf{k} \cdot \mathbf{r} - \omega t)\right] \tag{6}$$

Based on work of Planck, Eistein and de Broglie, for particle as wave (e.g., photon, free electron), $E = \hbar\omega$, $\mathbf{p} = \hbar\mathbf{k}$. We can extract this information from a general wave (superposition of plane waves) by using operators. Specifically, the momentum operator is given by $(\hbar/i)\nabla$, and energy is an operator given by $E = (i\hbar)\partial/\partial t$. We can easily test that these work for the simple plane wave.

If we use these operators in $H = E$ (or $H\Psi = E\Psi$), we get the time-dependent Schrödinger Equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}. \tag{7}$$

$$\Psi(\mathbf{r},t): \text{ state function, solution to S}'\text{s equation}$$

$$|\Psi(\mathbf{r},t)|^2: \text{ probability of finding electron at } \mathbf{r} \text{ at time } t$$

$$\hbar = \frac{h}{2\pi}$$

If we assume that $\Psi(\mathbf{r},t) = \psi(\mathbf{r})\phi(t)$, then we can separate Eq. (7) into

$$i\hbar\frac{\partial\phi(t)}{\partial t} = E\phi(t) \tag{8}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r},t) = E\psi(\mathbf{r}) \tag{9}$$

This simplification is valid whenever E is a constant (independent of time). Equation (8) has the simple solution $\phi(t) = A \cdot \exp(-iEt/\hbar) = A \cdot \exp(-i\omega t)$. Equation (9) is the Time-independent or Stationary Schrödinger Equation, and knowledge of the potential, V, is required in order to solve.

For simplicity, look at 1D. For $V = V_0$, $E > V_0$($= 0$ for free electron) with

$$k^2 = (2m/\hbar^2)(E - V_0),$$

then (1) reduces to:

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0, \tag{10}$$

which has solutions of the form:

$$\psi(r) = A \exp(jkr) + B \exp(-jkr) \tag{11}$$

This solution is in the form of traveling waves in the positive and negative direction, with constant amplitude everywhere (the electron is equally likely to be anywhere). k is the wavenumber (the wavevector in 3D, $\mathbf{k} = (\mathbf{k_x}, \mathbf{k_y}, \mathbf{k_z})$).

$$k = \frac{2\pi}{\lambda} \tag{12}$$

$$E - V_0 = \text{Kinetic Energy} = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} \tag{13}$$

$$p = \hbar k = \text{crystal momentum} \tag{14}$$