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 \( H(\mathbf{p}, \mathbf{r}) \):

\[
\frac{d\mathbf{r}}{dt} = \nabla_{\mathbf{p}} H(\mathbf{p}, \mathbf{r}) \quad (1)
\]

\[
\frac{d\mathbf{p}}{dt} = -\nabla_{\mathbf{r}} H(\mathbf{p}, \mathbf{r}) \quad (2)
\]

The classical Hamiltonian is:

\[
H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) = \text{KE} + \text{PE} = E \quad (3)
\]

Substituting above, we get:

\[
\frac{d\mathbf{r}}{dt} = \nabla_{\mathbf{p}} H(\mathbf{p}, \mathbf{r}) = \frac{\mathbf{p}}{m} = \mathbf{v} \quad (4)
\]

and

\[
\frac{d\mathbf{p}}{dt} = -\nabla_{\mathbf{r}} H(\mathbf{p}, \mathbf{r}) = -\nabla_{\mathbf{r}} V(\mathbf{r}) = \mathbf{F}, \quad (5)
\]

which are just the definition of momentum and Newton’s second law \( \mathbf{F} = m\mathbf{a} \).
We can transfer these same ideas to quantum mechanics. Consider a simple plane wave:

\[ \Psi = A \cdot \exp[i(k \cdot r - \omega t)] \]  

(6)

Based on work of Planck, Eistein and de Broglie, for particle as wave (e.g., photon, free electron), \( E = \hbar \omega, \ p = \hbar k \). 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:

\[-\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r)\psi(r, t) = i\hbar \frac{\partial \psi(r, t)}{\partial t}.\]  

(7)

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

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

\[ \hbar = \frac{\hbar}{2\pi} \]

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

\[ i\hbar \frac{\partial \phi(t)}{\partial t} = E\phi(t) \]  

(8)

\[-\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r)\psi(r, t) = E\psi(r) \]  

(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 \( V = V_0, \ E > V_0(= 0 \text{ for free electron}) \) 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, \( k = (k_x, k_y, k_z) \)).

\[
k = \frac{2\pi}{\lambda} \tag{12}
\]

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

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