2.4: Energy Eigenvalue Problem

The energy operator is called **Hamiltonian**. The first postulate stated that the time dependence of the wavefunction is dictated by the Schrödinger equation:

$$i\hbar\frac{\partial\psi(\vec{x},t)}{\partial t}=\mathcal{H}\psi(\vec{x},t)$$

If we assume that $\psi(\vec{x},t)$ is the product of a time-dependent part T(t) and a time-independent one $\varphi(\vec{x})$, we can attempt to solve the equation by separation of variables. From $\psi(\vec{x},t)=T(t)\varphi(\vec{x})$, we can rewrite the Schrödinger equation (using the fact that $\mathcal{H}$ does not change T(t)):

$$i\hbar\frac{\partial T(t)\varphi(\vec{x})}{\partial t}=\mathcal{H}[T(t)\varphi(\vec{x},t)] \quad \rightarrow \quad \varphi(\vec{x})\cdot i\hbar\frac{\partial T(t)}{\partial t}=T(t)\cdot\mathcal{H}[\varphi(\vec{x},t)]$$

and we rearrange terms based on their dependence on t or $\vec{x}$

$$\frac{1}{T(t)}i\hbar\frac{\partial T(t)}{\partial t}=\frac{1}{\varphi(\vec{x})}\mathcal{H}[\varphi(\vec{x},t)]$$

Each side has to be equal to a constant, in order for the equality to hold. Then the time-independent wavefunction obeys the time-independent Schrödinger equation:

$$\boxed{\mathcal{H}\varphi(\vec{x})=E\varphi(\vec{x})}$$

where E is identified as the energy of the system. If the wavefunction is given by just its time-independent part, $\psi(\vec{x},t)=\varphi(\vec{x})$, the state is *stationary*. Thus, the time-independent Schrödinger equation allows us to find stationary states of the system, given a certain Hamiltonian.

Notice that the time-independent Schrödinger equation is nothing else than the eigenvalue equation for the Hamiltonian operator. It is thus particularly interesting to study eigenvalues and eigenfunctions of this operator (which, as said, correspond to the energies and stationary states of the system)[5].

In general, the wavefunction describing the state of a quantum system is not.

The energy of a particle has contributions from the kinetic energy as well as the potential energy:

$$E=\frac{1}{2m}\left(p_x^2+p_y^2+p_z^2\right)+V(x,y,z)$$

In quantum mechanics we can find the equivalent operator by substituting the quantum operators for the position and momentum in the above expression:

$$\mathcal{H}=\frac{1}{2m}\left(\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2\right)+V(\hat{x},\hat{y},\hat{z})$$

or more explicitly:

$$\mathcal{H}=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(x,y,z)$$

and in a compact form

$$\boxed{\mathcal{H}=-\frac{\hbar^2}{2m}\nabla^2+V(x,y,z)}$$

(Notice that V (x, y, z) is just a multiplicative operator, in the same way as the position is).

Note

5 I want to clarify the distinction between eigenfunctions and wavefunctions. In this class we are interested in both. The eigenfunctions are related to a given operator, and they are the solutions to the eigenvalue equation for that operator. They are

important since they form a basis and they allow us to calculate the probability of obtaining a given measurement outcome. The wavefunction describes the state of the quantum system. In general, it is not an eigenfunction. However, *if* we are considering a *stationary* state, the wavefunction that represents it must be an eigenfunction of the Hamiltonian (energy) operator. Thus in that particular case only (which is a quite common case!) the wavefunction is also an eigenfunction.

Free particle

In 1D, for a free particle there is no potential energy, but only kinetic energy that we can rewrite as:

$$\mathcal{H} = \frac{1}{2m}p^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

The eigenvalue problem $\mathcal{H}w_n(x) = E_n w_n(x)$ is then the differential equation

$$\mathcal{H}w_n(x) = E_n w_n(x) \rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2 w_n(x)}{\partial x^2} = E_n w_n(x)$$

we rewrite it as:

$$\frac{\partial^2 w_n(x)}{\partial x^2} + \frac{2mE_n}{\hbar^2}w_n = 0 \rightarrow \frac{\partial^2 w_n(x)}{\partial x^2} + k_n^2 w_n = 0$$

where we used the identity

$$\boxed{\frac{\hbar^2 k_n^2}{2m} = E_n}$$

between the kinetic energy eigenvalue E_n and the wavenumber k_n (and the momentum $p_n = \hbar k_n$).

For a free particle there is no restriction on the possible energies, E_n can be any positive number. The solution to the eigenvalue problem is then the eigenfunction:

$$w_n(x) = A\sin(k_n x) + B\cos(k_n x) = A' e^{ik_n x} + B' e^{-ik_n x}$$

We see that there are two independent functions for each eigenvalue E_n. Also there are two distinct momentum eigenvalues $\pm k_n$ for each energy eigenvalue, which correspond to two different directions of propagation of the wave function $e^{\pm ik_n x}$.