Orthonormality of Stationary States:

Provided that $\Psi_n(x)$ is properly normalized,

$$\int dx \, \Psi_n^*(x) \Psi_n(x) = 1.\$$

Can also show that for $m \neq n$, $\Psi_m$ and $\Psi_n$ are orthogonal:

$$\int dx \, \Psi_m^*(x) \Psi_n(x) = 0 \quad \text{for} \quad m \neq n.$$

We combine this into the single statement that the set $\{ \Psi_n(x) \}$ is orthonormal

$$\int dx \, \Psi_m^*(x) \Psi_n(x) = \delta_{mn} = \sum \delta \quad \text{if} \quad m = n.$$

This is true not only for the particle in a box, but in general:

Energy eigenfunctions form a complete orthonormal basis.

(Here, "energy eigenfunction" means "state of definite energy," another word for a stationary state.)

"Complete" means that the functions $\Psi_n(x)$ span the full space of functions $\Psi(x)$ satisfying the boundary conditions. Therefore, they form a basis in which an arbitrary $\Psi(x)$ can be expanded (like the basis of unit vectors $\hat{x}, \hat{y}, \hat{z}$ for vectors in 3D).

We will prove orthogonality after we have introduced the Hamiltonian operator. Completeness is harder (involves proof of convergence to the desired function $\Psi(x)$ and is best left to the mathematicians.)
Expansion of $\psi(x)$ in energy eigenfunctions

Suppose that a function $\psi(x) = \Psi(x,0)$ (compatible with B.C.'s) has the expansion

$$\psi(x) = \sum_n C_n \psi_n(x),$$

(like $\vec{v} = \sum V_n \vec{e}_n$ for vectors)

Then

$$\int dx \, \psi_n^*(x) \psi(x) = \int dx \, \psi_n^*(x) \sum_m C_m \psi_m(x)$$

$$= \sum_m C_m \int dx \, \psi_n(x) \psi_m(x)$$

$$= \sum_m C_m \delta_{nm}$$

$$= C_n.$$  

So,

$$C_n = \frac{1}{\int dx \, \psi_n^*(x) \psi(x)}.$$  

(like $V_n = \vec{e}_n^* \cdot \vec{V}$ for vectors in a complex vector space)

At time $t$,

$$\Psi(x,t) = \sum_n C_n \psi_n(x,t).$$

Probability of observing energy $E_n$

Normalization:

$$1 = \int dx \, \Psi^*(x,t) \Psi(x,t) = \int dx \, \left( \sum_m C_m^* \psi_m(x) e^{i E_m t / \hbar} \right) \left( \sum_n C_n \psi_n(x) e^{-i E_n t / \hbar} \right)$$

$$= \sum_n \sum_m C_m^* C_n e^{i (E_m - E_n) t / \hbar} \left( \int dx \, \psi_m^*(x) \psi_n(x) \right)$$

$$= \sum_n C_n^* C_n e^{0}$$

$$\delta_{mn} = \delta \frac{m = n}{0} \text{ otherwise}.$$ 

$$1 = \sum_n |C_n|^2.$$  

Can interpret $|C_n|^2$ as probability of observing $E_n$, since
$|c_n|^2$ is the only quantity that is:

(i) non-negative
(ii) sums to 1
(iii) determined by $\Psi_n(x,t)$ and the basis $\psi_n(x)^2$ alone.

Thus, we write

$$P_n = |c_n|^2 \quad \text{(prob. of measuring } E = E_n)$$

and define the expectation value

$$\langle E \rangle = \sum_n P_n E_n = \sum_n |c_n|^2 E_n.$$  

Note that as an "average" value, the expectation value of the energy need not agree with any of the allowed energies $E_n$.

Since "$\hat{E}$" $\Psi_n(x,t) = E_n \Psi_n(x,t)$ ($\hat{E}$ = $i\hbar \frac{\partial}{\partial t}$ "energy operator")

we can also write

$$\langle E \rangle = \sum_n |c_n|^2 E_n = \int dx \, \Psi^* \hat{E} \Psi(x,t). \quad \text{(*)}$$

(Only difference compared to last computation $\sum_n |c_n|^2 = \int dx \, \Psi^* \Psi$ is that there is an $E_n$ in the sum.)

But,

$$\hat{E} \Psi(x,t) = \left( \frac{\hat{p}^2}{2m} + V(x) \right) \Psi(x,t) \quad \text{(Schrödinger equation),}$$

so can replace "$\hat{E}$" by $\left( \frac{\hat{p}^2}{2m} + V(x) \right)$ in Eq. (\text{(*)}).

We define the Hamiltonian operator $\hat{H}$ to be

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x).$$
Then, the expression for \( \langle E \rangle \) can be written
\[
\langle E \rangle = \int d\mathbf{x} \, \Psi^* \hat{H} \Psi,
\hat{H} = \frac{\hat{p}^2}{2m} + V(x).
\]

Compare to
\[
\langle p \rangle = \int d\mathbf{x} \, \Psi^* \hat{p} \Psi,
\hat{p} = -i\hbar \frac{\partial}{\partial x} \quad \text{(momentum operator)},
\]
and
\[
\langle x \rangle = \int d\mathbf{x} \, \Psi^* \hat{x} \Psi,
\hat{x} = x \quad \text{(position operator)}.
\]

In terms of \( \hat{H} \), we can write
\[
\hbar \frac{\partial}{\partial t} \Psi(x,t) = \hat{H} \Psi(x,t) \quad \text{(Schrödinger eq.)},
\]
and, for stationary states \( \tilde{\Psi}(x,t) = \psi(x) e^{-iEt/\hbar} \)
\[
\hat{H} \psi(x) = E \psi(x) \quad \text{(time-dependent Schrödinger eq.)}.
\]

Finally, we define the uncertainty in the energy in the same way as for \( x \) and \( p \):
\[
\langle \Delta E \rangle^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2.
\]
then \( \psi(x) \) is an eigenfunction of the operator \( \hat{A} \) with eigenvalue \( a \). (I.e., \( \psi(x) \) is a wavefunction of definite \( A \), with value \( A = a \).)

Note: Townsend uses the notation \( \text{Aop} \) instead of \( \hat{A} \).

Examples

1. \( \hat{p} = -i\hbar \frac{\partial}{\partial x} \). Want to solve \( \hat{p} \psi_p(x) = p \psi_p(x) \).

\[ \psi_p(x) = Ne^{ikx} = Ne^{i\frac{px}{\hbar}}, \quad p = \hbar k \quad \text{(eigenfunction of } \hat{p}) \]
   (Check: \(-i\hbar \frac{\partial}{\partial x} (e^{i\frac{px}{\hbar}}) = (-i\hbar)(\frac{ip}{\hbar}) e^{i\frac{px}{\hbar}} = pe^{i\frac{px}{\hbar}} \).

2. \( \hat{x} = x \)

   We will talk about eigenfunctions of \( \hat{x} \) (Dirac \( \delta \)-functions) soon.

3. \( \hat{H} = \frac{\hat{p}^2}{2m} + V(x) \)

   Suppose that \( \psi_E(x) \) is a solution to the time-independent Schrödinger equation with energy \( E \). Then,

\[ \hat{H} \psi_E(x) = E \psi_E(x), \quad (*) \]

So that \( \psi_E(x) \) is an eigenfunction of the Hamiltonian operator \( \hat{H} \) with eigenvalue \( E \). This equation, together with boundary conditions, determines the possible energy eigenvalues \( E \). Note: From \( \Phi_E(x,t) = \psi(x) e^{-iEt/\hbar} \), it's also true that \( "\hat{E}" \Phi_E(x,t) = E \Phi_E(x,t) \), for \( "\hat{E}" = \hbar \frac{\partial}{\partial t} \), but this equation does determine the set of allowed \( E \).

Since \( i\hbar \frac{\partial}{\partial t} e^{-iEt/\hbar} = E e^{-iEt/\hbar} \) for any \( E \).
For this reason, we will think of the Hamiltonian as the energy operator from now on, and will not refer to "E" again.)