General Properties of Stationary States

Let us recall the integration by parts formula from integral calculus

\[ \int_a^b u \, dv = uv \bigg|_a^b - \int_a^b v \, du \quad (1) \]

or, in more detail,

\[ \int_a^b u(x) \frac{\partial v(x)}{\partial x} \, dx = u(x)v(x) \bigg|_a^b - \int_a^b v(x) \frac{\partial u(x)}{\partial x} \, dx \quad (2) \]

In quantum mechanics, generally the boundary term \( uv \bigg|_a^b \) is zero, either because both boundaries evaluate to zero or to the same value. Therefore we can safely assume it is zero, \( uv \bigg|_a^b = 0 \).

Hence in quantum mechanics the integration by parts equation is

\[ \int_a^b u \, dv = - \int_a^b v \, du \quad (3) \]

Two applications of integration by parts gives

\[ \int_a^b u \frac{\partial^2 v}{\partial x^2} \, dx = \int_a^b v \frac{\partial^2 u}{\partial x^2} \, dx \quad (4) \]

or, in 3d,

\[ \int_a^b u \nabla^2 v = \int_a^b v \nabla^2 u \quad (5) \]

Property 1

The energies \( E_n \) in the TISE

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi_n + V \psi_n = E_n \psi_n \quad (6) \]

are real, even though \( \psi_n \) may be complex.

Proof: Multiply through by \( \psi_n^* \) and integrate to get

\[ -\frac{\hbar^2}{2m} \int \psi_n^* \nabla^2 \psi_n + \int \psi_n^* V \psi_n = E_n \int \psi_n^* \psi_n \quad (7) \]

But \( \int \psi_n^* \nabla^2 \psi_n \) and \( \int \psi_n \nabla^2 \psi_n^* \) are complex conjugates and since they are also equal, they must be real. Therefore \( E_n \) is real.

Orthogonality
Different stationary states (of the same TISE) are orthogonal to each other, namely
\[ \int \psi_n \psi_m^* = 0 \quad \text{if} \quad m \neq n \]  
(8)

**Proof**: Write down the TISE for \( \psi_n \) and the complex conjugate of this equation for \( \psi_m \).

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi_n + V \psi_n = E_n \psi_n \]  
(9)

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi_m^* + V \psi_m^* = \underbrace{E_m}_{\text{always real}} \psi_m^* \]  
(10)

Multiply Eq. (9) by \( \psi_m^* \) and integrate, and multiply Eq. (10) by \( \psi_n \) and integrate:

\[ -\frac{\hbar^2}{2m} \int \psi_m^* \nabla^2 \psi_n + \int \psi_m^* V \psi_n = E_n \int \psi_m^* \psi_n \]  
(11)

\[ -\frac{\hbar^2}{2m} \int \psi_n \nabla^2 \psi_m^* + \int \psi_n V \psi_m^* = E_m \int \psi_n \psi_m^* \]  
(12)

Subtracting, we get \((E_n - E_m) \int \psi_n \psi_m^* = 0\). If \( n \neq m \), there are two cases. Case 1: non-degenerate. \( E_n \neq E_m \) \( \Rightarrow \int \psi_n \psi_m^* = 0 \). If all these states are also normalized, they are said to be “orthonormal”. Case 2: degenerate. \( E_n \) can equal \( E_m \) even if \( n \neq m \). The proof is more complicated than the non-degenerate case. We need to use the Gram-Schmitt orthogonalization procedure to construct orthogonal states by taking appropriate linear combinations of the two wavefunctions. (proof omitted)

**Expectation Value**

Suppose we have a quantity \( Q(x, y, z) \) depending only on the particle coordinates (and not on the momenta). Since \(|\psi|^2\) is a probability density,

\[ \langle Q \rangle = \iiint Q(x, y, z) |\psi|^2 dx \, dy \, dz \]  
(13)

is its average or mean value in the usual probability sense. In other words, it is a weighted average with \(|\psi|^2\) being the weight. In quantum mechanics this is generally called the expectation value and is denoted by angular brackets \( \langle \cdot \rangle \). Usually we break \(|\psi|^2\) up, since multiplication is commutative, and write:

\[ \langle Q \rangle = \iiint \psi^* Q \, \psi \, dx \, dy \, dz \]  
(14)
Since $|\psi|^2$ is a probability density in space, how do we get information about quantities that depend on the particle momentum? We can get an expression for its expectation value by appealing to the Correspondence Principle, which says “Quantum mechanics must reduce to classical mechanics in some way”! To be able to turn this into a mathematical statement, we shall require that quantum mechanics reproduce classical mechanics “on average”, namely at the level of expectation value.

In particular, we have in classical mechanics that

$$p_x = mv = m \frac{x}{t} \quad (15)$$

Taking the average (expectation value) of both sides gives the quantum analog

$$\langle p_x \rangle = m \frac{d}{dt} \langle x \rangle \quad (16)$$

Let us work out the $d\langle x \rangle/dt$ term in detail

$$\frac{d}{dt} \langle x \rangle = \frac{d}{dt} \int \psi^* x \psi = \int \frac{\partial \psi^*}{\partial t} x \psi + \int \psi^* \frac{\partial \psi}{\partial t} \quad (17)$$

Now, we need to use the TDSE as follows

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V \psi \quad (18)$$

$$\Rightarrow \frac{\partial \psi}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} - \frac{i\hbar}{\hbar} V \psi \quad \text{and} \quad \frac{\partial \psi^*}{\partial t} = -\frac{i\hbar}{2m} \frac{\partial^2 \psi^*}{\partial x^2} + \frac{i\hbar}{\hbar} V \psi^* \quad (19)$$

Substituting these expressions into Eq. (17) gives

$$-\frac{i\hbar}{2m} \int \frac{\partial^2 \psi^*}{\partial x^2} x \psi + \frac{i\hbar}{2m} \int \psi^* \frac{\partial^2 \psi}{\partial x^2} \quad (20)$$

Now we will apply integration by parts twice to the first term as follows

$$\int \frac{\partial^2 \psi^*}{\partial x^2} x \psi = \int \psi^* \frac{\partial^2}{\partial x^2} (x \psi) = \int \psi^* \left( 2 \frac{\partial \psi}{\partial x} + x \frac{\partial^2 \psi}{\partial x^2} \right) \quad (21)$$

This yields

$$\frac{d}{dt} \langle x \rangle = -\frac{i\hbar}{m} \int \psi^* \frac{\partial \psi}{\partial x} \quad (23)$$
Multiplying by \( m \), we finally obtain

\[
\langle p_x \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} \quad (24)
\]

What about \( \langle p_x^2 \rangle \)? An important classical formula involving \( p_x^2 \) is

\[
\frac{p_x^2}{2m} + V(x) = \text{constant} \quad (25)
\]

(conservation of energy for a 1d system)

In order to use the correspondence principle, we will take the TISE

\[
-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V \psi = E \psi \quad (26)
\]

and multiply both sides by \( \psi^* \) and integrate

\[
-\frac{\hbar^2}{2m} \int \psi^* \frac{\partial^2 \psi}{\partial x^2} + \int \psi^* V \psi = E \int \psi^* \psi \quad (27)
\]

The 2\textsuperscript{nd} term is just \( \langle V \rangle \), and the RHS is clearly a constant since \( \int \psi^* \psi = 1 \). Therefore, by analogy, the first term can be identified with the first term of Eq. (25).

\[
\frac{p_x^2}{2m} = -\frac{\hbar^2}{2m} \int \psi^* \frac{\partial^2 \psi}{\partial x^2} \quad (28)
\]

Thus we can identify

\[
\langle p_x^2 \rangle = -\hbar^2 \int \psi^* \frac{\partial^2 \psi}{\partial x^2} \quad (29)
\]

### Quantum Operators

We have just deduced that, in 1d,

\[
\langle p_x \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} \quad \text{and} \quad \langle p_x^2 \rangle = -\hbar^2 \int \psi^* \frac{\partial^2 \psi}{\partial x^2} \quad (30)
\]

If we now define a momentum operator by

\[
\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad (31)
\]

where the “hat” denotes an operator, we can write

\[
\langle p_x \rangle = \int \psi^* \hat{p}_x \psi \quad (32)
\]
\begin{align}
\langle p_x^2 \rangle &= \int \psi^* \hat{p}_x^2 \psi \\
\text{where } \hat{p}_x^2 \text{ means } \hat{p}_x \hat{p}_x, \text{ namely apply the operator twice}
\end{align}

Note that if \( \hat{A} \) and \( \hat{B} \) are operators, and we define \( \hat{C} = \hat{A} \hat{B} \), then \( \hat{C} \psi \) means \( \hat{A}(\hat{B}\psi) \), \textit{i.e.} from right to left like composition of functions, \((f \circ g)(x) = f(g(x))\).

An obvious generalization suggests

\begin{align}
\langle p_x^n \rangle &= \int \psi^* \hat{p}_x^n \psi \\
\text{Recall, also, that for powers of } x,
\end{align}

\begin{align}
\langle x^n \rangle &= \int \psi^* x^n \psi
\end{align}

All of this can be united by postulating the following general principle:

The expectation value of any property \( Q(x, y, z, p_x, p_y, p_z) \) depending on the coordinates and/or the momenta of the particle is given by

\begin{align}
\langle Q \rangle &= \int \int \int \psi^* \hat{Q} \psi dx dy dz
\end{align}

where \( \hat{Q} \) is an operator obtained by making the replacement

\begin{align}
\hat{x} \to x, \quad \hat{y} \to y, \quad \hat{z} \to z, \quad \hat{p}_x \to -i\hbar \frac{\partial}{\partial x}, \quad \hat{p}_y \to -i\hbar \frac{\partial}{\partial y}, \quad \hat{p}_z \to -i\hbar \frac{\partial}{\partial z}
\end{align}

in the classical mechanics expression for \( Q \).

Example: the classical mechanics expression for the energy is

\begin{align}
E = \frac{p^2}{2m} + V
\end{align}

To turn this into an operator, we must realize that \( p^2 = p \cdot p = p_x^2 + p_y^2 + p_z^2 \to -\hbar^2 \nabla^2 \) so that the energy operator is

\begin{align}
-\frac{\hbar^2}{2m} \nabla^2 + V = \hat{H}
\end{align}

This operator dominates quantum theory so it is given a special symbol \( H \), called the “Hamiltonian” operator. Schroedinger’s Equations can thus be written succinctly as

\begin{align}
\hat{H} \psi = i\hbar \frac{\partial \psi}{\partial t} \quad \text{time dependent}
\end{align}

\begin{align}
\hat{H} \psi_n = E_n \psi_n \quad \text{time independent}
\end{align}
“Sharpness” of the \( Q \) distribution

Now that we can calculate expectation values, we can also calculate standard deviations. For any property \( Q \), the deviation from the mean value is just \( Q - \langle Q \rangle \). The squared deviation is \((Q - \langle Q \rangle)^2 = Q^2 - 2Q\langle Q \rangle + \langle Q \rangle^2\) and the mean value of this is \( \langle Q^2 \rangle - 2\langle Q \rangle^2 + \langle Q \rangle^2 = \langle Q^2 \rangle - \langle Q \rangle^2 \). The root mean square (RMS) deviation = standard deviation =

\[
\Delta Q = \sqrt{\langle Q^2 \rangle - \langle Q \rangle^2}
\] (42)

\( \Delta Q \) is a measure of the “sharpness” of the distribution of \( Q \) values in a given \( \psi \). Generally \( \Delta Q \neq 0 \). \( \Rightarrow \) \( Q \) is spread over a range of values. However, there are special situations in which \( Q \) is not spread out, \textit{i.e.} \( \Delta Q = 0 \).

\textbf{Eigenfunctions & Eigenvalues}

Consider functions \( \psi \) satisfying

\[ \hat{Q}\psi = q\psi, \quad q \in \mathbb{C} \] (43)

\textit{i.e.} \( \hat{Q} \) operating on \( \psi \) produces a number \( q \) multiplied by \( \psi \). These \( \psi \)'s are called the eigenfunctions of \( Q \) and the corresponding numbers \( q \) the eigenvalues.

For an eigenfunction of \( Q \),

\[
\langle Q \rangle = \int \psi^*\hat{Q}\psi = \int \psi^*q\psi = q \int \psi^*\psi = q
\] (44)

since we will assume that \( \psi \) is normalized. Also,

\[
\langle Q^2 \rangle = \int \psi^*\hat{Q}^2\psi = \int \psi^*\hat{Q}(\hat{Q}\psi) = \int \psi^*\hat{Q}(q\psi) = q \int \psi^*\hat{Q}\psi = q^2
\] (45)

where we assume that the operator \( \hat{Q} \) is linear which let us perform the manipulation \( \hat{Q}(q\psi) = q\hat{Q}\psi \). Hence \( \Delta Q = \sqrt{\langle Q^2 \rangle - \langle Q \rangle^2} = \sqrt{q^2 - q^2} = 0 \). Thus, if \( \psi \) is an eigenfunction of the operator \( \hat{Q} \), the property \( Q \) has an absolutely precise value, the eigenvalue. \underline{Only} under these conditions can we have precise, well-defined values of physical properties in quantum theory.

For example, the stationary states satisfy \( \hat{H}\psi_n = E_n\psi_n \), namely the stationary states are eigenfunctions of the energy operator (the Hamiltonian operator)