Chapter 4 – Postulates of Quantum Mechanics

Math Chapter C

A brief reminder on vectors:

In 3 dimensions define orthonormal basic vectors

\( \hat{i}, \hat{j}, \hat{k} \)  \hspace{1cm} \text{Or} \hspace{1cm} \hat{e}_1, \hat{e}_2, \hat{e}_3

\[ \vec{u} = x\hat{i} + y\hat{j} + z\hat{k} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \]  \hspace{1cm} \text{Or} \hspace{1cm} \vec{u} = \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix}

\[ \vec{v} = \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix} = v_x\hat{i} + v_y\hat{j} + v_z\hat{k} \]

Vector has both direction and a length

Vector Addition \( \vec{u} + \vec{v} \)

\[ \vec{u} + \vec{v} = \begin{pmatrix} u_x + v_x \\ u_y + v_y \\ u_z + v_z \end{pmatrix} \]

Multiplication by a scalar
Winter 2013
Chem 350: Introductory Quantum Mechanics

Chapter 4 – Postulates of Quantum Mechanics

Multiply length by $\alpha$

Inner Product

$$\vec{u} \cdot \vec{v} = u_x v_x + u_y v_y + u_z v_z$$

$$\vec{e}_i \cdot \vec{e}_j = \delta_{ij}$$

$$\sum_i u_i \vec{e}_i \cdot \sum_j v_j \vec{e}_j = \sum_i u_i v_i \delta_{ij} = \sum_i u_i v_i$$

Length

$$|\vec{u}| = \sqrt{\vec{u} \cdot \vec{v}}$$

Angle

$$\vec{u} \cdot \vec{v} = |\vec{u}| |\vec{v}| \cos \theta$$

$$\vec{u} = \begin{pmatrix} 2 \\ -1 \\ 3 \end{pmatrix}$$

$$\vec{v} = \begin{pmatrix} 1 \\ 1 \\ -2 \end{pmatrix}$$

$$|\vec{u}| = \sqrt{2^2 + 1^2 + 3^2} = \sqrt{14}$$

$$|\vec{v}| = \sqrt{1^2 + 1^2 + 2^2} = \sqrt{6}$$

$$(\vec{u} \cdot \vec{v}) = 2 \cdot 1 + (-1) \cdot 1 + 3 \cdot (-2) = -5$$

$$\cos \theta = \frac{-5}{\sqrt{14} \cdot \sqrt{6}} \quad \Rightarrow \quad \theta = \ldots$$

Examples of use of inner product in physics

Work

$$\vec{F} \cdot \vec{l} = |F||l| \cos \theta$$

$$|F||l| \cos \theta = mgh$$

$$h = l \cos \theta$$

Or: Dipole moment

$$\vec{u} = \sum_i q_i \vec{r}_i$$

Charges $q_i$ at position $r$

$$\mu_x = q \frac{r}{2} + (-q) \left( -\frac{r}{2} \right)$$

$qr$ points in the positive direction from $-$ to $+$

If we apply an electric field $\vec{E}$
\[ V = -\vec{\mu} \cdot \vec{E} \quad \text{(more later)} \]

Another important product is the vector or cross product
\[ \vec{u} \times \vec{v} : \text{perpendicular to the plane spanned by} \ \vec{u} \ \text{and} \ \vec{v} \]
Length: \[ |\vec{u}| |\vec{v}| \sin \theta : \text{sign from right hand rule} \]

Mathematical formula
\[
\begin{vmatrix}
\vec{e}_1 & \vec{e}_2 & \vec{e}_3 \\
u_x & u_y & u_z \\
v_x & v_y & v_z
\end{vmatrix}
\]

\[ \vec{u} \times \vec{v} = \vec{e}_1(u_y v_z - u_z v_y) - \vec{e}_2(u_z v_x - u_x v_z) + \vec{e}_3(u_x v_y - u_y v_x) \]

Check: Orthogonal to \( \vec{u} \), \( \vec{v} \)

Famous Physics example:
Lorentz Magnetic Force: \[ \vec{F} = q(\vec{V} \times \vec{B}) \]

Apply magnetic field \( \vec{B} \) → force → acceleration to \( \vec{V} \), \( \vec{B} \)
→ charged particle precesses around \( \vec{B} \)

Change direction of velocity, not speed

Also: Angular Momentum
\[ \vec{L} = \vec{r} \times \vec{p} = -\vec{p} \times \vec{r} \]
\[ (yP_x - xP_y)\vec{e}_1 + (zP_x - xP_z)\vec{e}_2 + (xP_y - yP_x)\vec{e}_3 \]
\[
\begin{align*}
L_z &= xP_y - yP_x \\
L_y &= zP_x - xP_z \\
L_x &= yP_z - zP_y
\end{align*}
\]

Remember
Cyclic Permutation

The Postulates of Quantum Mechanics

A) Observables

To any observable, or measurable quantity \( A \), in Quantum Mechanics corresponds a linear Hermitian operator \( \hat{A} \)

If one performs a measurement of \( A \), only eigenvalues \( a_i \) of the operator \( \hat{A} \) can be obtained

Operators in quantum mechanics are obtained by replacing
\[
\begin{align*}
P_x &= -i\hbar \frac{\partial}{\partial x} \\
P_y &= -i\hbar \frac{\partial}{\partial y} \\
P_z &= -i\hbar \frac{\partial}{\partial z}
\end{align*}
\]
A function of position, e.g. \( V(x) \) is interpreted as multiplication by \( V(x) \rightarrow \hat{V}(x) \)

\[ \rightarrow \text{To know possible outcome from experiment:} \]

\[ \text{Solve } \hat{A}\phi_n(x) = a\phi_n(x) \]

\[ \xrightarrow{\text{Eigenvalue}} \]

With operator \( \hat{A} \) we often need to impose boundary conditions

<table>
<thead>
<tr>
<th>Observable</th>
<th>( x, y, z )</th>
<th>( \hat{x}, \hat{y}, \hat{z} )</th>
<th>multiply</th>
</tr>
</thead>
<tbody>
<tr>
<td>Momentum</td>
<td>( P_x, P_y, P_z )</td>
<td>(-ih\frac{\partial}{\partial x}, -ih\frac{\partial}{\partial y}, -ih\frac{\partial}{\partial z})</td>
<td></td>
</tr>
<tr>
<td>Kinetic energy</td>
<td>( T = \frac{P^2}{2m} )</td>
<td>( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} )</td>
<td></td>
</tr>
<tr>
<td>Potential Energy</td>
<td>( V(x) )</td>
<td>( \hat{V}(x) )</td>
<td></td>
</tr>
<tr>
<td>Total Energy</td>
<td>( E )</td>
<td>( \hat{H} = \hat{T} + \hat{V} )</td>
<td></td>
</tr>
<tr>
<td>Angular momentum</td>
<td>( l_x = yP_z - zP_y )</td>
<td>( \hat{L}_x = -ih \left( y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( l_y = zP_x - xP_z )</td>
<td>( \hat{L}_y = -ih \left( z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( l_z = xP_y - yP_x )</td>
<td>( \hat{L}_z = -ih \left( x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) )</td>
<td></td>
</tr>
<tr>
<td>Spin</td>
<td>( \hat{S}_x, \hat{S}_y, \hat{S}_z )</td>
<td>( \hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 )</td>
<td></td>
</tr>
</tbody>
</table>

We have discussed linear operators and eigenvalue equations. What does Hermitian mean?

An operator \( \hat{A} \) is Hermitian if for any pair of functions \( f(x) \) and \( g(x) \) in the domain of the operator (ie. Satisfying the boundary conditions)
it is true that
\[ \int_{a}^{b} f^*(x) \left( \hat{A} g(x) \right) dx = \int_{a}^{b} g(x) \left( \hat{A} f(x) \right)^* dx \]

In higher dimensions
\[ \int_{\text{domain}} f^*(\tau) \left( \hat{A} g(\tau) \right) d\tau = \int_{\text{domain}} g(\tau) \left( \hat{A} f(\tau) \right)^* d\tau \]

The domain of integration is part of the definition of Hermitian operator (Boundary conditions)

In words: act with $\hat{A}$ on $g$ and integrate with $f^*$ should be equal to act with $\hat{A}$ of $f$, take complex conjugate, and integrate against $g(\tau)$.

We can write the latter expression also as
\[ \int g(\tau) \left( \hat{A} f \right)^* d\tau = \left[ \int g(\tau) \left( \hat{A} f \right) d\tau \right]^* \]

Example of Hermitian operators
\[ V(x) \quad : \quad V(x) \text{ is a real function} \]
\[ \int f^*(x) V(x) g(x) dx = \int g(x) V(x) f^*(x) dx = \int g(x) V(x) f(x)^* dx \quad (V \text{ real!}) \]

\[ \hat{P}_x = -i\hbar \frac{\partial}{\partial x} : \]
\[ \int_{-\infty}^{\infty} f^*(x) \left( -i\hbar \frac{\partial g}{\partial x} \right) dx = \left[ -i\hbar f^*(x) g(x) \right]_p - \int -i\hbar \frac{\partial f^*}{\partial x} g(x) dx \quad \text{(partial integration)} \]
\[ = \int \hbar \frac{\partial f^*}{\partial x} g(x) dx \]
\[ = \int g(x) \left[ -i\hbar \frac{\partial f}{\partial x} \right]^* dx \]
\[ = \int g(x) \left( \hat{P}_x f(x) \right)^* dx \]

Likewise $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ and other listed operators are Hermitian

Operators in Quantum Mechanics are required to be Hermitian because these operators have very nice mathematical properties:
Properties of Hermitian Operators

a) The eigenvalues are all real
b) The eigenfunctions can be chosen to be orthonormal
c) Any function $\psi(x)$ can be expressed as linear combination $\psi(x) = \sum_n C_n \phi_n(x)$

\[
C_n = \int_{\text{domain}} \phi_n^* (x) \psi(x) dx
\]

Let us denote eigenvalues of $\hat{A}$ to be $a_n$ with eigenfunctions $\phi_n(x)$

Then: Eigenvalues are real

\[
\int \phi_n^* (\hat{A} \phi_n) dx = \int \phi_n^* (\hat{A} \phi_n) dx
\]

\[
a_n \int \phi_n^* (x) \phi_n(x) dx = a_n \int \phi_n^* (x) \phi_n(x) dx
\]

\[
a_n = a_n^*, \quad a_n \text{ is real}
\]

2) Eigenfunctions corresponding to different eigenvalues are orthonormal

\[
\int \phi_k^* (x) \hat{A} \phi_l (x) dx = \int \phi_k^* (\hat{A} \phi_l (x)) dx
\]

\[
(a_i - a_k) \int \phi_k^* (x) \phi_l (x) dx = 0
\]

\[
a_k^* = a_k, \quad a_i \neq a_k
\]

\[
\Rightarrow \int_{\text{domain}} \phi_k^* (x) \phi_l (x) dx = 0
\]

\[
\Rightarrow \phi_k, \phi_l \text{ are orthogonal if } a_k \neq a_l
\]

3) If $\phi_k (x)$ and $\phi_l (x)$ have the same eigenvalue (degenerate) then any linear combination is also eigenfunction with the same eigenvalue

\[
\hat{A} \psi(x) = \hat{A} (C_k \phi_k (x) + C_l \phi_l (x))
\]

\[
= C_k \hat{A} \phi_k (x) + C_l \hat{A} \phi_l (x) \quad \text{[Linear]}
\]

\[
= C_k a_k \phi_k (x) + C_l a_l \phi_l (x) \quad \text{[Same Eigenvalue]}
\]

\[
= a_k (C_k \phi_k (x) + C_l \phi_l (x))
\]

\[
= a \psi(x)
\]

4) If $\phi_k (x)$ and $\phi_l (x)$ are degenerate (same $a$), but are not orthogonal, we can make them orthonormal

Eg. \[
\int \phi_k^* (x) \phi_l (x) dx = c
\]

\[
\phi_l^{\text{new}} \rightarrow \phi_l (x) - c \phi_k (x) \quad \phi_k \text{ normalized}
\]
\[ \int \phi_k^*(x)(\phi_l(x) - c\phi_k(x))dx = c - c \cdot 1 = 0 \rightarrow \text{normalize } \phi_{\text{new}} \]

This is true in general.

With any Hermitian operator we can associate a set of orthonormal functions \( \phi_k(x) \)

\[ \hat{A}\phi_k(x) = a_k\phi_k(x) \]

Earlier \[ \int_{\text{domain}} \phi_k^*(x)\phi_l(x)dx = \delta_{kl} \]

\[ = \begin{cases} 1 & k = l \\ 0 & k \neq l \end{cases} \]

5) Any (suitable) wave function can expressed as a linear combination of the \( \phi_k(x) \)

\[ \psi(x) = \sum_k C_k \phi_k(x) \]

**Completeness Property**

This statement is hard to prove and we assume it to be true

\[ \rightarrow \text{Further consequences} \]

5a) Normalization

\[ \int \psi^*(x)\psi(x)dx \]

\[ = \int \left( \sum_l c_l^* \phi_l^*(x) \cdot \sum_k c_k \phi_k(x) \right)dx \]

\[ = \sum_l c_l^* \sum_k c_k \int \phi_l^*(x)\phi_k(x)dx \]

\[ = \sum_l c_l^* \sum_k c_k \delta_{lk} \]

\[ = \sum_l c_l^* (0 + 0 + ... c_l + 0 + ...) \]

\[ = \sum_l c_l^* c_l = \sum_l |c_l|^2 \]

Normalized Wavefunction: \( \sum_l |c_l|^2 = 1 \)

5b) Expectation Values

\[ \int \psi^*(x)\hat{A}\psi(x)dx \]

\[ = \int \left( \sum_k c_k^* \phi_k^*(x)\hat{A} \sum_l c_l \phi_l(x) \right)dx \]

\[ = \sum_k c_k^* \sum_l c_l a_l \int \phi_k^*(x)\phi_l(x)dx \]
\[ \psi(x) = \sum_k c_k \phi_k(x) \]

This assumes we know the coefficient. We can calculate it!

\[ c_k = \int \phi_k^*(x) \psi(x) dx = \int \phi_k^*(x) \sum_i c_i \phi_i(x) dx \]

\[ = \sum_i c_i \int \phi_k^*(x) \phi_i(x) dx = \sum_i c_i \delta_{ki} \]

\[ = 0 + 0 + ... + c_k + 0 + ... \]

\[ = c_k \quad \text{Indeed!} \]

We can now discuss the predictions of Quantum Mechanics regarding measurements.

**Discussion of Measurement**

If we decide to measure a quantity \( A \), we associate with it a Quantum Mechanical operator \( \hat{A} \)

Solve for eigenfunctions and eigenvalues

\[ \hat{A} \phi_k(x) = a_k \phi_k(x) \]

\[ \rightarrow \text{Type of Measurement } \rightarrow \hat{A}, \{ a_k \phi_k(x) \} \]

If we measure \( A \) for individual quantum system, we get always an eigenvalue (rolling the dice)

Possible Outcomes \( a_1, a_2, a_3, \ldots \)
Probability: \[
\frac{N_1}{N_{tot}} = P_1(a_1), \quad \frac{N_2}{N_{tot}} = P_2(a_2)
\]

What determines the probabilities? The wavefunction (normalized) \( \psi(x) \)!!

If we do a large number of measurements on identical microscopic systems, collectively described by the wavefunction we find the value \( a_k \) with probability \( P_k \)

\[
P_k = c_k^* c_k = \left| c_k \right|^2
\]

\[
c_k = \int \phi_k^* (x) \psi(x) dx
\]

How do we prepare an ensemble described by wavefunction \( \psi(x) \)?

Could be the ground state of a molecule (low \( T \))

\[
\psi(x) = \psi_0 \quad \hat{H} \psi_0(x) = E_0 \psi_0(x)
\]

This is like ‘measuring’ the energy first, then measure \( \hat{A} \)

We could alternatively measure \( \hat{B} \) and collect all Microsystems with eigenvalue \( b_k \)

Take those systems that yield eigenvalue \( b_k \). They are described by \( \psi_{b_k}(x) \)

\[
\hat{B} \psi_{b_k}(x) = b_k \psi_{b_k}(x)
\]

Why? If I measure \( B \) again I would measure \( b_k \) with certainty (if it does not change over time)

\[
C_{b_k} = \int \psi_{b_k}^* (x) \psi(x) dx = 1
\]

\[
\rightarrow \psi(x) = \psi_{b_k}(x) \cdot (e^{i\theta})
\]

→ A measurement is the standard procedure to prepare an ensemble of microscopic systems in a well-defined wavefunction (takes some effort!)
Discussion of Uncertainty Relations

If I measure \( \hat{A} \) for an ensemble, can I get a sharp value for \( \hat{A} \)?

\[ \rightarrow \text{Yes: use } \psi(x) = \phi_a(x) \]

\[ \rightarrow \langle \hat{A} \rangle = a, \quad \langle \hat{A}^2 \rangle = a^2, \quad \sigma_A = 0 \]

Next question, if I would measure \( \hat{A} \) and \( \hat{B} \) for an ensemble, can I create a sharp value for both \( \hat{A} \) and \( \hat{B} \)?

If \( \psi(x) \) is eigenstate of \( \hat{A} \) and eigenstate of \( \hat{B} \)

\[ \hat{A}\psi(x) = a\psi(x) \]
\[ \hat{B}\psi(x) = b\psi(x) \]
\[ \psi(x) = \phi_{a,b}(x) \]

When can I create a sharp value for measuring \( \hat{A} \) and \( \hat{B} \), for each compatible value of \( a \) and \( b \)?

If \( \hat{A} \) and \( \hat{B} \) have a complete set of common eigenstates

\[ \hat{A}\phi_{a,b}(x) = a\phi_{a,b}(x) \]
\[ \hat{B}\phi_{a,b}(x) = b\phi_{a,b}(x) \]

Completeness Property:

Any \( \psi(x) \) :

\[ \psi(x) = \sum_{(ab)} c_{ab}\phi_{ab}(x) \]

\[ \hat{A}\hat{B}\psi(x) = \hat{A}\sum_{(ab)} c_{ab}b\phi_{ab}(x) = \sum_{(ab)} c_{ab}ab\phi_{ab}(x) \]

\[ \hat{B}\hat{A}\psi(x) = \hat{B}\sum_{(ab)} c_{ab}a\phi_{ab}(x) = \sum_{(ab)} c_{ab}ba\phi_{ab}(x) \]

\[ \rightarrow (\hat{A}\hat{B} - \hat{B}\hat{A})\psi(x) = 0 \quad \forall \psi \]

Hence, If and only if: \( [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \) then

\( \hat{A} \) and \( \hat{B} \) have complete set of common eigenfunctions

And: We can create samples to measure sharp values of both \( \hat{A} \) and \( \hat{B} \)
If $\hat{A}$ and $\hat{B}$ commute measuring $\hat{B}$ does not destroy the value measured for $\hat{A}$ (compare to my example of measuring lunchboxes for schoolkids)

After sample preparation: we can obtain completely sharp values $\sigma_A = \sigma_B = 0$

What if $\hat{A}$ and $\hat{B}$ do not commute?

→ Mathematical uncertainty Principle

$$\Delta A \Delta B \geq \frac{1}{2} |\langle \psi | [\hat{A}, \hat{B}] | \psi \rangle|$$

→ Depends on the state ($\psi$) in general

If $\hat{A}$ and $\hat{B}$ have no common eigenstate then:

One cannot generate an ensemble in which one obtains sharp values for both $\hat{A}$ and $\hat{B}$

Most famous example: Measure position and momentum

$$[\hat{x}, \hat{P}_x] = x \left( -i\hbar \frac{\partial}{\partial x} \right) \psi(x) - \left( -i\hbar \frac{\partial}{\partial x} x \psi(x) \right)$$

$$= -i\hbar x \frac{\partial \psi}{\partial x} - \left( -i\hbar \psi(x) - i\hbar x \frac{\partial \psi}{\partial x} \right)$$

$$= +i\hbar \psi(x)$$

$$[\hat{x}, \hat{P}_x] = i\hbar$$

$$\Delta x \Delta p \geq \frac{1}{2} |\langle \psi | i\hbar | \psi \rangle| = \frac{\hbar}{2}$$
Heisenberg Uncertainty Relation

\[ \Delta x \Delta p > \frac{1}{2} \hbar \]

Not simultaneously measure \( x \), \( p \) !! This was discussed originally by Heisenberg, for his famous microscope, but we can only verify for ensembles as discussed above.

Special Topic: Continuous eigenvalues

Consider

\[ \hat{P}_x = -i\hbar \frac{\partial}{\partial x} \quad (1d) \]

Eigenfunctions

\[ e^{ikx} \hat{P}_x e^{ikx} = \hbar k e^{ikx} \]

\( k \) can have any value

but \( \psi(x) = e^{ikx} \) cannot be normalized:

\[ \int_{-\infty}^{\infty} (e^{ikx})^* e^{ikx} dx \]

\[ \int_{-\infty}^{\infty} e^{-ikx} e^{ikx} dx = \int_{-\infty}^{\infty} 1 dx \to \infty ! \]

And orthonormality is ill-defined

\[ \int_{-\infty}^{\infty} e^{-ik_1 x} e^{ik_2 x} dx = \int_{-\infty}^{\infty} e^{-i(k_1 - k_2)x} dx = \frac{1}{-i(k_1 - k_2)} e^{-i(k_1 - k_2)x} \bigg|_{-\infty}^{\infty} \]

Function keeps oscillating, does not vanish at infinity...

Continuous ‘spectra’ require special care

\[ c_k = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ikx} \psi(x) dx \]

Converges if \( \psi(x) \) is normalized

Other example position \( \hat{x} \)

\[ \hat{x} \phi_a(x) = x \phi_a(x) = a \phi_a(x) \]

\( (x-a) \phi_a(x) = 0 \quad \rightarrow \phi_a(x) = 0 \) if \( x \neq a \)

\[ \phi_a(x) = ? \] if \( x = a \)

\[ \phi_a(x-a) = \delta(x-a) \]

\[ \int \delta(x-a) = 1 \]
\[ \delta(x - a) \quad \text{Dirac delta function} \]
\[ \text{a.k.a. normalization } \int_{a}^{b} \delta(x - a) \psi(x) \, dx = \psi(a) \]

\[ P(a) : \text{ the probability to find particle at } a \]
\[ P(a) = |\psi(x)|^2 \, dx \]
\[ P(x) \, dx = |\psi(x)|^2 \, dx \]
This definition is consistent with the postulates (follows from the postulates).
Continuous eigenvalues require more sophisticated mathematics (distributions).

**The Time-Dependent Schrödinger Equation**

Time dependence of \( \psi(x, t) \):

\[ i\hbar \frac{\partial \psi}{\partial t}(x, t) = \hat{H}\psi(x, t) \]
\[ \psi(x, t_0) = \text{to be specified: initial conditions} \]

Assume \( \hat{H} \) is time-independent

\[ \rightarrow \quad \text{As in chapter 2 we consider separation of variables} \]

**Try** \[ \psi(x, t) = \phi(x)\gamma(t) \]
\[ \forall x, t \]
\[ \phi(x) i\hbar \frac{\partial \gamma}{\partial t} = \gamma(t) \hat{H}\phi(x) \]
\[ i\hbar \frac{\partial \gamma}{\partial t} / \gamma(t) = \frac{\hat{H}\phi(x)}{\phi(x)} = E \quad : \text{both are constant} \]

\[ \rightarrow \quad \hat{H}\phi_n(x) = E_n\phi_n(x) \]
\[ i\hbar \frac{\partial \gamma}{\partial t} = E_n\gamma(t) \quad \rightarrow \quad \gamma(t) = e^{-\frac{iE_n t}{\hbar}} \]

\[ \rightarrow \quad \text{Special solutions: Stationary states} \]
\[ \psi(x, t) = \phi_n(x) e^{-\frac{iE_n (t-t_0)}{\hbar}} \]
These states are called stationary states because
\[ |\psi(x,t)|^2 = \phi_n(x)^* e^{-iE_n t/\hbar} \phi_n(x) e^{iE_n t/\hbar} = |\phi_n(x)|^2 \text{ independent of } t \]

Also \( \langle A \rangle_t = \langle \hat{A} \rangle \) and even probability to find eigenvalue \( a \) are independent of time:

\[
\hat{A}X_a(x) = aX_a(x) \\
C_a(t) = \int X_a(x)^* \phi_a(x) dx \cdot e^{-iE_a t} \\
P_a(t) = |C_a|^2 = c_a^* c_a = c_a^* (0)c_a(0) = P_a(0) \text{ independent of time!!}
\]

\( \rightarrow \) But: stationary states are very special

The general solution is linear combination:

\[
\psi(x,t) = \sum_n c_n \phi_n(x) e^{-iE_n (t-t_0)/\hbar} \\
\frac{i\hbar}{\hbar} \frac{\partial \psi}{\partial t} = \sum_n c_n \phi_n(x)E_n e^{-iE_n (t-t_0)/\hbar} \\
= \sum_n c_n (\hat{H} \phi_n(x)) e^{-iE_n (t-t_0)/\hbar} \\
= \hat{H} \sum_n c_n \phi_n(x) e^{-iE_n (t-t_0)/\hbar}
\]

(reminder \( \hat{H} \) independent of \( t \), no electromagnetic fields)

\[
\psi(t = t_0) = \sum_n c_n \phi_n(x) \\
\rightarrow \text{ specify } \psi(t = t_0) \\
\rightarrow c_n = \int \phi_n^* (x) \psi(x,t = t_0) dx \\
\rightarrow \psi(x,t) \text{ is determined for all time, very simple!!}
\]

Probability to find \( E_n \)?

\[
c_n(t) = \int \phi_n^* (x) \sum_m c_m^* \phi_m(x) e^{-iE_m (t-t_0)/\hbar} \\
= c_n e^{-iE_n (t-t_0)/\hbar} \\
|c_n|^2 = |c_n(0)|^2
\]
→ independent of time $E$ is conserved $= \sum_n P_n E_n$

Other properties, eg. $\langle \hat{\dot{x}} \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{\dot{\psi}}(x) dx \rightarrow$ oscillation in time

Further remarks:
All depends on initial wave function, which is arbitrary in principle [compare to classical mechanics $\rightarrow$ specify $X_a(0), P_a(0)$ for all particles $\rightarrow X(t), P(t)$ follows from equation of motion]

Stationary States: $\phi(t = 0) = \phi_n(x)$ energy eigenstates
S.E. Predicts: excited states live forever
Q.M: does not predict thermal equilibrium over time

$\rightarrow$ need to combine quantum mechanics with
a) Statistical mechanics
b) Electromagnetic field (even in a vacuum)

Excited states decay: From quantum electrodynamics (Dirac 1927, Feynman, Schrodinger, Tomonaga 1949...)

**Time-dependence of expectation values**

$$\langle A(t) \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) \hat{A} \psi(x,t) dx$$

$$\frac{d}{dt} \langle A(t) \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) \frac{d\hat{A}}{dt} \psi(x,t) + \int_{-\infty}^{\infty} \psi^*(x) \frac{\partial \hat{A}}{\partial t} \psi(x) + \int_{-\infty}^{\infty} \psi^*(x) \hat{A} \frac{d\psi(x,t)}{dt}$$

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \quad \frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} \hat{H} \psi$$

$$\left( i\hbar \frac{\partial \psi}{\partial t} \right)^* = (\hat{H} \psi)^*$$

$$-i\hbar \frac{\partial \psi^*}{\partial t} = \hat{H} \psi^*$$

Assume: $\frac{\partial \hat{A}}{\partial t} = 0$ $\quad \hat{A}$ : Hermitian

$$\frac{d}{dt} \langle A \rangle = \int_{-\infty}^{\infty} \psi(x,t) \left( \hat{A} \frac{\partial \psi}{\partial t} \right)^* dx + \int_{-\infty}^{\infty} \psi^*(x,t) A \frac{\partial \psi}{\partial t}$$

$$= \int \psi^*(x,t) \hat{A} \frac{-i}{\hbar} \hat{H} \psi dx + \int \psi^*(x) \hat{A} \frac{-i}{\hbar} \hat{H} \psi(x) dx$$
\[
\begin{align*}
&= + \frac{i}{\hbar} \int \psi(x,t) \left( \hat{A}\hat{H}\psi(x,t) \right) dx - \frac{i}{\hbar} \int \psi(x,t) \hat{H}\psi(x,t) dx \\
&= \frac{i}{\hbar} \int \psi(x,t) \hat{A}\hat{H}\psi(x,t) dx - \frac{i}{\hbar} \int \psi(x,t) \hat{H}\psi(x,t) dx \\
&= \frac{i}{\hbar} \int \psi(x,t) (\hat{A} - \hat{H})\psi(x,t) dx
\end{align*}
\]

Or

\[
i\hbar \frac{d\langle A \rangle}{dt} = \langle [\hat{A}\hat{H}] \rangle,
\]

**Difficult Step:** General product of 2 Hermitian operators

\[
\int f^* \hat{A}\hat{B}g(x) dx = \int \hat{B}g(x) (\hat{A}f)^* dx = \int g(x) (\hat{B}\hat{A}f)^* dx
\]

Reverse Operators!

**Examples:**

\[
i\hbar \int \frac{\partial P}{\partial t} = \int \left[ P, H \right]
\]

\[
= \left[ -i\hbar \frac{\partial}{\partial x}, -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right]
\]

\[
i\hbar \int \frac{\partial P}{\partial t} = -i\hbar \int \frac{\partial V}{\partial x}
\]

\[
= - \int \left( \frac{\partial V}{\partial x} \right)
\]

Same as from Classical Mechanics

\[
ma = m \frac{d^2 v}{dt^2} = F = - \frac{\partial V}{\partial x}
\]

\[
= \frac{dP}{dt} = - \frac{\partial V}{\partial x}
\]

Also

\[
i\hbar \int \frac{\partial x}{\partial t} = \int \left[ x, -\frac{\hbar}{2m} \frac{d^2}{dx^2} + V(x) \right]
\]

\[
= \int \left[ + \frac{\hbar^2}{m} \frac{\partial}{\partial x} \right]
\]

\[
= i\hbar \int \left[ -i\hbar \frac{\partial}{\partial x} \right]
\]
\[ i \hbar \frac{\partial}{\partial t} \langle P \rangle = \frac{i}{m} \langle P \rangle \]

Or

\[ \frac{\partial}{\partial t} \langle \hat{X} \rangle = \frac{1}{m} \langle P \rangle \]

Again: Same as in Classical Mechanics

Ehrenfest theorem:

Expectation values in Quantum Mechanics obey relations from classical mechanics