MathChapter C

A brief reminder on vectors:

In 3 dimensions define orthonormal basic vectors

\[ \vec{i}, \vec{j}, \vec{k} \quad \text{Or} \quad \vec{e}_1, \vec{e}_2, \vec{e}_3 \]

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

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

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
\[ \alpha \vec{u} = \begin{pmatrix} \alpha u_x \\ \alpha u_y \\ \alpha u_z \end{pmatrix} \quad \text{Multiply length by } \alpha \]

Inner Product
\[ \vec{u} \cdot \vec{v} = u_x v_x + u_y v_y + u_z v_z \]
\[ \vec{e}_i \cdot \vec{e}_j = \delta_{ij}, \quad \vec{e}_1 = \vec{i}, \quad \vec{e}_2 = \vec{j}, \quad \vec{e}_3 = \vec{k} \]
\[ (\sum_i u_i \vec{e}_i \cdot \sum_j v_j \vec{e}_j) = \sum_{i,j} u_i v_j \delta_{ij} = \sum_i u_i v_i \]

Length \[ |\vec{u}| = \sqrt{\vec{u} \cdot \vec{v}} \]

Angle \[ \vec{u} \cdot \vec{v} = |\vec{u}| |\vec{v}| \cos \theta \]

Example:
\[ \vec{u} = \begin{pmatrix} 2 \\ -1 \\ 3 \end{pmatrix}, \quad \vec{v} = \begin{pmatrix} 1 \\ 1 \\ -2 \end{pmatrix} \]
\[ |\vec{u}| = \sqrt{2^2 + (-1)^2 + 3^2} = \sqrt{14} \quad |\vec{v}| = \sqrt{1^2 + 1^2 + (-2)^2} = \sqrt{6} \]
\[ (\vec{u} \cdot \vec{v}) = 2 \cdot 1 + (-1) \cdot 1 + 3 \cdot (-2) = -5 \]
\[ \cos \theta = \frac{-5}{\sqrt{14} \cdot \sqrt{6}} \quad \Rightarrow \quad \theta = \ldots \]

Examples of use of inner product in physics

\[ \text{Work} = \vec{F} \cdot \vec{l} = |\vec{F}| |\vec{l}| \cos \theta \]
\[ |\vec{F}| |\vec{l}| \cos \theta = mgh \]
\[ h = l \cos \theta \]

Or:
Dipole moment
\[ \vec{u} = \sum_i q_i \vec{r}_i \quad \text{Charges } q_i \text{ at position } \vec{r}_i \]
\[ \mu_x = q \frac{r}{2} + (-q) \left( \frac{-r}{2} \right) \]

QR points in the positive direction from \(-\) to \(+\)

If we apply an electric field \( \vec{E} \)

\[ V = -\vec{\mu} \cdot \vec{E} \]

(more later)

Another important product is the vector or cross product

\( \vec{u} \times \vec{v} \): perpendicular to the plane spanned by \( \vec{u} \) and \( \vec{v} \)

Length: \(|\vec{u}||\vec{v}| \sin \theta\): sign from right hand rule

Mathematical formula

\[
\begin{vmatrix}
\hat{e}_1 & \hat{e}_2 & \hat{e}_3 \\
\vec{u}_x & \vec{u}_y & \vec{u}_z \\
\vec{v}_x & \vec{v}_y & \vec{v}_z
\end{vmatrix}
\] (determinant)

\[ \vec{u} \times \vec{v} = \hat{e}_1(u_yv_z - u_zv_y) - \hat{e}_2(u_zv_x - u_xv_z) + \hat{e}_3(u_xv_y - u_yv_x) \]

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

Famous Physics example:

Lorentz Magnetic Force: \( \vec{F} = q(\vec{v} \times \vec{B}) \)

Apply magnetic field \( \vec{B} \rightarrow \) force \( \rightarrow \) acceleration to \( \vec{v}, \vec{B} \)

\( \rightarrow \) charged particle precesses around \( \vec{B} \)

Change direction of velocity, not speed

Also: Angular Momentum

\[ \vec{L} = \vec{r} \times \vec{p} = -\vec{p} \times \vec{r} \]

\[(yP_z - zP_y)\hat{e}_1 + (zP_x - xP_z)\hat{e}_2 + (xP_y - yP_x)\hat{e}_3\]

\[
\begin{align*}
L_z &= xP_y - yP_x \\
L_y &= zP_x - xP_z \\
L_x &= yP_z - zP_y
\end{align*}
\]

Remember

Cyclic Permutation \( x \rightarrow y \rightarrow z \)

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, eg. \( V(x) \) is interpreted as multiplication by \( V(x) \rightarrow \hat{V}(x) \)

\( \rightarrow \) To know possible outcomes from experiment:

Solve \( \hat{A}\phi(x) = \alpha \phi(x) \)

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

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<table>
<thead>
<tr>
<th>Observable</th>
<th>Operator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>( x, y, z )</td>
</tr>
</tbody>
</table>

**Momentum**

\[
\begin{align*}
T_x &= \frac{P_x^2}{2m} \\
T &= \frac{P^2}{2m}
\end{align*}
\]

\[
\begin{align*}
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \\
-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \\
-\frac{\hbar^2}{2m} \nabla^2
\end{align*}
\]

**Potential Energy**

\( V(x) \)

\( \hat{V}(x) \):

\( \hat{H} = \hat{T} + \hat{V} \)

\( = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(\vec{r}) \)

**Total Energy**

\( \hat{E} \)

\( \hat{L}_x = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) \)

\( \hat{L}_y = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} \right) \)

\( \hat{L}_z = -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) \)

\( \hat{S}_x, \hat{S}_y, \hat{S}_z \)

\( \hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \)

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 (i.e. satisfying the boundary conditions):

It is true that

$$\int_{a}^{b} f^*(x) \left( \hat{A} g(x) \right) dx = \left[ \int_{a}^{b} g(x) \left( \hat{A} f(x) \right)^* dx \right]$$

In higher dimensions

$$\int_{\text{domain}} f^*(\tau) \left( \hat{A} g(\tau) \right) d\tau = \int_{\text{domain}} g(\tau) \left( \hat{A} f(\tau) \right)^* d\tau$$

$\implies$ 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 $\hat{A}$ on $f$, 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

$V(x)$: $V(x)$ is a real function

$$\int f^*(x) V(x) g(x) dx = \int g(x) V(x) f^*(x) dx = \int g(x) (V(x)f(x))^* dx \ (V \ real!)$$

$P_x = -i\hbar \frac{\partial}{\partial x}$:

$$\int_{-\infty}^{\infty} f^*(x) \left( -i\hbar \frac{\partial g}{\partial x} \right) dx = \left[ -i\hbar f^*(x) g(x) \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} -i\hbar \frac{\partial f^*}{\partial x} g(x) dx \ \ (\text{partial integration})$$

$$= \int_{-\infty}^{\infty} i\hbar \frac{\partial f^*}{\partial x} g(x) dx$$

$$= \int_{-\infty}^{\infty} g(x) \left[ -i\hbar \frac{\partial f}{\partial x} \right]^* dx$$

$$= \int_{-\infty}^{\infty} g(x) (\hat{P}_x f(x))^* dx$$

$$= \left[ \int_{-\infty}^{\infty} g(x) (\hat{P}_x f(x)) dx \right]^*$$
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 $\psi(x) = \sum_n C_n \phi_n(x)$

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

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 orthogonal

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

$$(a_l - a_k^*) \int \phi_k^*(x)\phi_l(x) dx = 0$$

$$a_k^* = a_k^* \quad \text{by assumption } a_l \neq a_k$$

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

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

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

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

$$= C_k \hat{A}\phi_k(x) + C_l \hat{A}\phi_l(x)$$ [Linear]
\[ C_k a \phi_k(x) + C_l a \phi_l(x) \] [Same Eigenvalue]
\[ a(C_k \phi_k(x) + C_l \phi_l(x)) \]
\[ a \psi(x) \]

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

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

This is true in general.

It follows that with any Hermitian operator we can associate a set of orthonormal functions \( \phi_k(x) \)

\[ \hat{A} \phi_k(x) = a_k \phi_k(x) \]
\[ \int_{\text{domain}} \phi_k^* (x) \phi_l(x) dx = \delta_{kl} \]
\[ = \begin{cases} 1 & k = l \\ 0 & k \neq l \end{cases} \]

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

→ Further consequences

5a) Normalization

\[ \int \psi^* (x) \psi(x) dx \]
\[ = \int \left( \sum_l c_l^* \phi_l^* (x) \cdot \sum_k c_k \phi_k(x) \right) dx \]
\[ = \sum_l c_l^* \sum_k c_k \int \phi_l^* (x) \phi_k(x) dx \]
\[ = \sum_l c_l^* \sum_k c_k \delta_{lk} \]
\[ = \sum_l c_l^* (0 + 0 + \ldots c_l + 0 + \ldots) \]
5b) Expectation Values

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

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

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

\[ = \sum_k c_k \sum_l c_l a_i \delta_{kl} \]

\[ = 0 + 0 + \ldots c_k a_k + \ldots \]

\[ = \sum_k (c_k^* c_k) a_k = \langle A \rangle = \sum_k P_k a_k \]

5c)

\[ \langle A^2 \rangle = \ldots = \sum_l |c_l|^2 a_l^2 = \langle A \rangle = \sum_l P_l a_l^2 \]

From this we deduce that \( P_k \) the probability to find \( a_k \) is given by \( c_k^* c_k \) if

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

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

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

\[ = \sum_l c_l \int \phi_k^* (x) \phi_l (x) dx = \sum_l c_l \delta_{kl} \]

\[ = 0 + 0 + \ldots c_k + 0 + 0 + \ldots \]

\[ = c_k \]

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: $\frac{N_1}{N_{tot}} = P_1(a_1), \frac{N_2}{N_{tot}} = P_2(a_2)$

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 $P_k$

$$P_k = c_k^* c_k = |c_k|^2$$
$$c_k = \int \phi_k^* (x) \psi(x) dx$$

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

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

→ 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 \( \hat{A} \) ?

→ Yes: use \( \psi(x) = \phi_{a}(x) \)

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

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 \( \psi(x) \):

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

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

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

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 school kids in notes posted on the web.)

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

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

\[ \rightarrow \text{Mathematical uncertainty Principle} \]
\[ \Delta A\Delta B \geq \frac{1}{2} \left| \langle \psi | [\hat{A}, \hat{B}] | \psi \rangle \right| \]

\[ \rightarrow \text{Depends on the state (} \psi \text{) in general} \]

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

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

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

Chapter 4 – Postulates of Quantum Mechanics
\[
= -i\hbar \frac{\partial \psi}{\partial x} - \left( -i\hbar \psi(x) - i\hbar x \frac{\partial \psi}{\partial x} \right) \\
= +i\hbar \psi(x)
\]

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

\[
\Delta x \Delta p \geq \frac{1}{2} \left| \langle \psi | i\hbar | \psi \rangle \right| = \frac{1}{2} \hbar
\]

Famous Heisenberg Uncertainty Relation

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:

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

And orthonormality is ill-defined

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

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 (this is called a Fourier transform in mathematics)
Other example: eigenfunctions of position operator $\hat{x}$
\[ \hat{x}\phi_a(x) = x\phi_a(x) = a\phi_a(x) \]
\[ (x-a)\phi_a(x) = 0 \quad \rightarrow \phi_a(x) = 0 \text{ if } x \neq a \]
\[ \phi_a(x) = ? \text{ if } x = a \]
\[ \phi_a(x-a) = \delta(x-a) \]
\[ \int \delta(x-a) = 1 \]
\[ \delta(x-a) \quad \text{Dirac delta function} \]
a.k.a. normalization \[ \int_{-\infty}^{\infty} \delta(x-a)\psi(x)dx = \psi(a) \]

$P(a)$: 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 (i.e. follows from the postulates).

Continuous eigenvalues require more sophisticated mathematics (They are distributions (Schwartz)).

**The Time-Dependent Schrödinger Equation**

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

Assume $\hat{H}$ is time-independent
\[ \rightarrow \text{ As in chapter 2 we consider separation of variables} \]

Try \[ \psi(x,t) = \phi(x)\gamma(t) \]
\[ \forall x,t \quad \phi(x)i\hbar \frac{\partial \gamma}{\partial t} = \gamma(t)\hat{H}\phi(x) \]
\[ i\hbar \frac{\partial \gamma}{\partial t} / \gamma(t) = \frac{\hat{H}\phi(x)}{\phi(x)} = E \quad \text{: both are constant} \]
\[ \hat{H}\phi_n(x) = E_n\phi_n(x) \]
\[ i\hbar \frac{\partial \gamma}{\partial t} = E_n\gamma(t) \quad \rightarrow \quad \gamma(t) = e^{\frac{-iE_n t}{\hbar}} \]

\[ \text{Special solutions: Stationary states} \]
\[ \psi(x,t) = \phi_n(x)e^{\frac{-iE_n (t-t_0)}{\hbar}} \]

These states are called stationary states because
\[ |\psi(x,t)|^2 = \phi_n(x)^* e^{\frac{ih}{\hbar}} \phi_n(x) e^{\frac{ih}{\hbar}} \]
\[ = |\phi_n(x)|^2 \quad \text{independent of } t \]

Also \( \langle A \rangle_t = \langle A \rangle_{t_0} \) and even probability to find eigenvalue \( a \) are independent of time:
\[ \hat{A}X_a(x) = aX_a(x) \]
\[ C_a(t) = \int X_a(x)\phi_n(x)dx \cdot e^{-iE_n/t \hbar} \]
\[ P_a(t) = |C_a|^2 = c_a^* c_a = c_a^* (0)c_a(0) = P_a(0) \quad \text{independent of time!!} \]

\[ \text{But: stationary states are very special} \]

The general solution is linear combination:
\[ \psi(x,t) = \sum_n c_n \phi_n(x) e^{\frac{-iE_n (t-t_0)}{\hbar}} \]
\[ i\hbar \frac{\partial \psi}{\partial t} = \sum_n c_n \phi_n(x) E_n e^{\frac{-iE_n (t-t_0)}{\hbar}} \]
\[ = \sum_n c_n (\hat{H}\phi_n(x)) e^{\frac{-iE_n (t-t_0)}{\hbar}} \]
\[ = \hat{H}\sum_n c_n \phi_n(x) e^{\frac{-iE_n (t-t_0)}{\hbar}} \]

(reminder \( \hat{H} \) independent of \( t \), e.g. no electromagnetic fields!)
\[ \psi(t = t_0) = \sum_n c_n \phi_n(x) \]
\[ \rightarrow \text{specify } \psi(t = t_0) \]
\[ c_n = \int \phi_n^*(x)\psi(x,t = t_0)dx \]
\[ \rightarrow \psi(x,t) \text{ is determined for all time, very simple!!} \]
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. $\langle \hat{x} \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{x} \psi(x) dx \rightarrow$ oscillation in time

Further remarks:

All depends on initial wave function, which is arbitrary in principle [compare to classical mechanics $\rightarrow$ specify $X_\alpha(0), P_\alpha(0)$ 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, Schwinger, Tomonaga 1949…). In practice we often describe isolated molecule by quantum mechanics. Molecules collide, and this is another mechanism for decay and the reaching of thermal equilibrium (complicated issue).

**Time-dependence of expectation values**

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

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

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}(\psi) \quad \frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} \hat{H}(\psi)$$
\[
\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = (\hat{H}\psi)^* \\
-\hbar \frac{\partial \psi^*}{\partial t} = \hat{H}\psi^*
\]

Assume: \( \frac{\partial A}{\partial t} = 0 \) \( \hat{A} \): Hermitian

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

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

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

Or

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

Difficult Step: General product of 2 Hermitian operators

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

Examples:

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

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

\[ \left\langle \frac{\partial P}{\partial t} \right\rangle = \left\langle \frac{\partial V}{\partial x} \right\rangle \quad \text{Same as from Classical Mechanics!} \]

(Ehrenfest theorem)

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

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

Also

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

\[ = \left\langle x, \frac{\hbar^2}{m} \frac{\partial}{\partial x} \right\rangle \]

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

\[ = \frac{i\hbar}{m} \left\langle P \right\rangle \]

Or

\[ \left\langle \frac{\partial x}{\partial t} \right\rangle = \frac{1}{m} \left\langle P \right\rangle \quad \text{Again: Same as in Classical Mechanics} \]

Ehrenfest theorem:

Expectation values in Quantum Mechanics obey relations from classical mechanics.