- The energy operator -

In classical mechanics the energy of a particle is:

\[ E = K + V \]

\[ E \rightarrow \text{potential energy} \]

\[ K = \frac{1}{2} m \mathbf{v}^2 = \frac{\mathbf{p}^2}{2m} \]

\[ V = V(\mathbf{r}) \]

\[ = \text{position vector of the particle} \]

In Quantum Mechanics:

\[ \mathbf{r} \rightarrow \hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z}) \]

\[ \mathbf{p} \rightarrow \hat{\mathbf{p}} = -i \hbar \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \]

Therefore

\[ K \rightarrow \frac{\hat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2 \]

\[ V \rightarrow V(\hat{\mathbf{r}}) \]

Now we understand the meaning of the Schrödinger equation for a free particle:
\[ i \hbar \frac{\partial \psi(r, t)}{\partial t} = -\frac{\hbar^2}{2m} \Delta \psi(r, t) \]

\[ = \frac{\hat{p}^2}{2m} \psi(r, t) \]

The energy operator

\[ \frac{\hat{p}^2}{2m} + V(r) = \hat{H} \]

is called the Hamiltonian of the system and is denoted with the letter \( \hat{H} \).

For systems more general than a single particle

\[ \psi(r, t) \rightarrow \psi(q, t) \]

but the Schrödinger equation remains the same:

\[ i \hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \]

Where \( \hat{H} \) now is the Hamiltonian for the system.

For a single particle \( \hat{H} \) has ALWAYS the form:

\[ \hat{H} = \frac{\hat{p}^2}{2m} + V(r) \]
For a free-particle

\[ \hat{H}_0 = \frac{\hat{p}^2}{2m} \]

The "0" denotes

free particle

and \[ [\hat{H}_0, \hat{p}] = 0 \Rightarrow \hat{H}_0 \text{ and } \hat{p} \text{ have the same}

eigenfunction. We know that

\[ \hat{p} \phi(x, p) = p' \phi(x, p') \]

where

\[ \phi(x, p) = \frac{1}{(2\pi\hbar)^{3/2}} \exp\left(\frac{i}{\hbar} p \cdot x\right) \]

Therefore

\[ \hat{p}_i^2 \phi(x, p') = \hat{p}_i (p'_i \phi(x, p')) = \hat{p}_i (p'_i \phi(x, p')) = p'_i^2 \phi(x, p') \Rightarrow \]

\[ \Rightarrow \hat{H}_0 \phi(x, p') = \frac{p' \cdot p'}{2m} \phi(x, p') \]

\[ = \frac{p'_x^2 + p'_y^2 + p'_z^2}{2m} \phi(x, p') \]

Homework: Calculate (a) \[ [\hat{A}, \hat{E}] \text{ and } (b) \[ [\hat{A}, \hat{E}] \text{ when} \]

\[ \hat{A} = \frac{\hat{p}^2}{2m} + V(\hat{x}) \text{ for any } V(\hat{x}) \in \mathbb{R} \]
In some cases, when the particle is interacting with another system, it is possible to describe a single part by a **TIME-DEPENDENT** Hamiltonian
\[ \hat{H} = \hat{H}(\mathbf{r}, t) \]

This is the case, e.g., of an atom interacting with an electromagnetic wave.

For the moment, we consider only **TIME-INDEPENDENT** Hamiltonians of the form:
\[ \hat{H} = \hat{H}(\mathbf{r}) \]

In this case:
\[ i \hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \hat{H}(\mathbf{r}) \psi(\mathbf{r}, t) \quad (1.4) \]

can be solved separating the variables:
\[ \psi(\mathbf{r}, t) = U(\mathbf{r}) T(t) \Rightarrow \]
\[ i \hbar \frac{\partial U(\mathbf{r})}{\partial t} = i \hbar \frac{\partial T(t)}{\partial t} \]
\[ \hat{H}(\mathbf{r}) \psi = T(t) (\hat{H} U)(\mathbf{r}) \]

The function \( U(\mathbf{r}) \) is usually denoted as: **STATIONARY STATE**
\( (1.4) \) becomes:

\[
\frac{\text{ith } U(t)}{\text{dt}} = T(t) (\hat{A}U)(t)
\]

We divide both sides by \( T(t) = \hat{U}(t)T(t) \); to obtain:

\[
\text{ith } \frac{1}{T(t)} \frac{\text{d}T(t)}{\text{dt}} = \frac{1}{U(t)} (\hat{A}U)(t)
\]

function of \( t \)

function of \( x \)

So, if

\[
f(t) = \hat{g}(x)
\]

the only possibility is that they are both constant. Let "E" denote this constant:

\[
(1.5a) \quad \text{ith } \frac{\text{d}T(t)}{\text{dt}} = E \ T(t) \quad \text{Two independent equations.}
\]

\[
(1.5b) \quad \hat{A}(t)U(t) = EU(t)
\]

\( = \text{Time-independent Schrödinger equation} \)

It looks like an eigenvalue equation which can be solved (hopefully!) when \( \hat{A}(t) \) is known.
Suppose to know the eigenfunctions $\psi_n(E)$ and the eigenvalues $E_n$ of $\hat{A}(E)$:

$$\hat{A} \psi_n = E_n \psi_n \tag{1.6}$$

(we suppose that they are discrete. For a free-particle this is not true).

Then the time evolution of the state $\psi_n$ is governed by (1.5a) with $E = E_n$:

$$i \hbar \frac{\partial \psi}{\partial t} = E_n \psi$$

whose solution is:

$$\psi(t) = \psi(0) \exp \left( - \frac{i}{\hbar} E_n t \right) \tag{2.6}$$

But if $\psi(0,0) = U(0) \psi(0) = \psi_n(0) \Rightarrow \psi(0) = 1$

and

$$\psi_n(t) = \exp \left( - \frac{i}{\hbar} E_n t \right) \psi_n(0) \tag{2.6}$$

These eigenvalues and eigenfunctions exist if $\hat{A}$ is Hermitian. Now we show that this is the case.
Proof that \( \hat{A} = \hat{A}^+ \)

We start from \( \frac{\partial \hat{\psi}}{\partial t} = \hat{A} \hat{\psi} \)

and \( \int \psi \psi^* \, dq = 1 \implies \)

\( \frac{1}{\partial t} \left( \int \psi \psi^* \, dq \right) = 0 \)

\( \implies \int \left( \frac{\partial \psi}{\partial t} \psi^* + \psi \frac{\partial \psi^*}{\partial t} \right) \, dq = 0 \)

\( \implies \int \left[ \left( \frac{1}{\partial t} \right) (\hat{A} \hat{\psi})^* \psi + \psi^* \left( \frac{\partial}{\partial t} (\hat{\psi}) \right) \right] \, dq = 0 \)

\( \int \psi^* (\hat{A}^+ \hat{\psi}) \, dq = \int \psi^* (\hat{A} \hat{\psi}) \, dq = 0 \)

\( \int \psi^* (\hat{A}^+ \hat{\psi}) \, dq = \int \psi^* (\hat{A} \hat{\psi}) \, dq = 0 \)

\( \int \psi^* (\hat{A}^+ - \hat{A}) \psi \, dq = 0 \) \text{ This must be true for any } \psi \implies \hat{A}^+ = \hat{A} \quad \text{c.v.t.}
Now, since $\hat{H} = \hat{H}^*$ the eigenfunctions are orthogonal (28-8) and complete. This implies that at $t=0$ we can write:

$$\Psi(q_0) = \sum_n a_n \Psi_n(q)$$

where

$$a_n = \int \Psi^*_n(q) \Psi(q_0) dq$$

Since for $t>0$ $\Psi_n(q) \to \Psi_n(q) \exp\left(-\frac{i}{\hbar} E_n t\right) \Rightarrow$

$$\Rightarrow \Psi(q, t) = \sum_n a_n \Psi_n(q) \exp\left(-\frac{i}{\hbar} E_n t\right) \quad (1.8)$$

--- Theorem ---

If a physical quantity $\hat{f}$ is conserved, that is its value does not change with time, the corresponding operator $\hat{f}$ commute with $\hat{H}$.

--- Proof ---

Let $\hat{f}$ such that has mean value $\langle \hat{f} \rangle_\Psi$ when the system is prepared in the state $\Psi$, and let $\frac{d}{dt} \langle \hat{f} \rangle_\Psi = \hat{f}$. The time-derivative of such operator. Then $\hat{f}$ is DEFINED as the quantity such that:

$$\langle \frac{d}{dt} \hat{f} \rangle_\Psi \equiv \frac{d}{dt} \langle \hat{f} \rangle_\Psi$$

$\forall (2.8)$ \quad \text{This is}
By definition
\[ \frac{d}{dt} \langle \hat{f} \rangle_\psi = \frac{i}{\hbar} \int \psi^* (q, t) \hat{f}(t) \psi (q, t) \, dq \]

\[ = \int \frac{\partial \psi^*}{\partial t} (\hat{f} \psi) \, dq + \int \psi^* \left( \frac{\partial \hat{f}}{\partial t} \right) \psi \, dq + \int \psi^* \left( \frac{\partial^2 \psi}{\partial t^2} \right) \, dq \]

but \[ \frac{\partial \psi}{\partial t} = \frac{1}{i \hbar} \hat{H} \psi \Rightarrow \]

\[ \frac{d}{dt} \langle \hat{f} \rangle_\psi = \frac{1}{i \hbar} \int \left( \hat{f}^* \hat{H} \psi \right) \, dq + \int \psi^* \frac{\partial \hat{f}}{\partial t} \psi \, dq \]

\[ + \frac{1}{i \hbar} \int \psi^* \hat{f} \hat{H} \psi \, dq + \int \psi^* \frac{\partial^2 \psi}{\partial t^2} \psi \, dq \]

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

\[ = \int \psi^* \left\{ \frac{1}{i \hbar} [\hat{f}, \hat{H}] + \frac{\partial \hat{f}}{\partial t} \right\} \psi \, dq \quad (1.9) \]

On the other hand, by definition,
\[ \langle \hat{f} \rangle_\psi = \int \psi^* \frac{\partial \hat{f}}{\partial t} \psi \, dq \quad (2.9) \]

Imposing (1.9) = (2.9) we find: \( \frac{\partial \hat{f}}{\partial t} = \frac{1}{i \hbar} [\hat{f}, \hat{H}] + \frac{\partial \hat{f}}{\partial t} \) (3.9)
The last term \( \frac{d\hat{f}}{dt} \) is non-zero only if \( \hat{f} \) has an explicit time-dependence. If this is not the case, as in the conserved observables, we have:

\[
\frac{d\hat{f}}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{f}] = 0 \Rightarrow [\hat{H}, \hat{f}] = 0 \quad \text{c.v.d}
\]

If \( \frac{d\hat{f}}{dt} = 0 \), then its mean value with respect to the energy eigenfunctions \( \psi_n \) is time independent because:

\[
\frac{d}{dt} \int \psi_n^*(q, t) \hat{f} \psi_n(q, t) dq = \frac{d}{dt} \int \psi_n^*(q) e^{\frac{i}{\hbar} \int H(q, t) dq} \frac{i}{\hbar} \int H(q, t) dq \psi_n(q) dq = \int \psi_n^*(q) \frac{d}{dt} \hat{f} \psi_n(q) dq = 0
\]

Their product = 1
The spectrum of $\hat{A}$ is the set of all eigenvalues of $\hat{A}$.

A typical discrete spectrum looks like:

```
\begin{align*}
E & \quad \text{eigenvalue} \\
\downarrow & \quad \downarrow \\
E_0, \psi_0 & \quad \text{eigenfunction}
\end{align*}
```

Simple (or non-degenerate) spectrum

In the case of degenerate eigenvalues we have:

```
\begin{align*}
E & \quad \text{spectrum} \\
\downarrow & \\
E_2, \psi_2^{(1)}, \psi_2^{(2)}, \ldots, \psi_2^{(d_2)} \\
\downarrow & \\
E_1, \psi_1^{(1)}, \psi_1^{(2)}, \ldots, \psi_1^{(d_1)} \\
\downarrow & \\
E_0, \psi_0
\end{align*}
```

Non-simple (or degenerate) spectrum

$\hat{A}\psi_i^{(d)} = E_i \psi_i^{(d)}$

($d = 1, 2, \ldots, d_2$)
When does a degenerate spectrum occur?

When there are two (or more) conserved observables, say \( f \) and \( g \), that are **INCOMPATIBLE** (that is, their associated Hermitian operators \( \hat{f} \) and \( \hat{g} \) do not commute: \( [\hat{f}, \hat{g}] \neq 0 \), e.g., \( [\hat{\mathcal{E}}, \hat{\beta}] = i\hbar \)), but commute with \( \hat{A} \) (because, by hypothesis, they are conserved):

\[ \hat{f}, \hat{g} : [\hat{f}, \hat{g}] \neq 0 \quad \text{and} \quad [\hat{f}, \hat{A}] = 0 = [\hat{g}, \hat{A}] \]

Let \( \hat{\mathcal{G}}_n = \hat{g}_n \phi_n \) and \( \hat{\mathcal{F}}_m = \hat{f}_m \psi_m \) and \( \hat{A} \psi = E \psi \).

Choose \( \psi \) such that \( \hat{\mathcal{F}} \psi = \frac{1}{\lambda} \hat{\mathcal{F}} \psi \), so \( \hat{f} \) has a determined value. I can do because \( [\hat{A}, \hat{f}] = 0 \).

\[ \hat{A}(\hat{\mathcal{F}} \psi) = \hat{\mathcal{F}} \left( \hat{A} \psi \right) = E (\hat{\mathcal{F}} \psi) \]

So \( \hat{\mathcal{F}} \psi \) is an eigenstate of \( \hat{A} \) with eigenvalue \( E \).

However, also \( \hat{A}(\hat{\mathcal{G}} \psi) = \hat{\mathcal{G}}(\hat{A} \psi) = E (\hat{\mathcal{G}} \psi) \) is an eigenstate of \( \hat{A} \) associated with the SAME eigenvalue \( E \).

So, if \( \hat{\mathcal{F}} \psi \neq \kappa \hat{\mathcal{G}} \psi \), then \( \hat{A} \psi \) has at least 2 eigenvalues c-number \( \psi \) and \( \hat{\mathcal{G}} \psi \) (\( \hat{\mathcal{G}} \psi = \hat{\mathcal{F}} \psi \kappa \psi \) by hypothesis) associated with the same eigenvalue \( E \).
However, if it were
\[ \hat{g} = \lambda \hat{g}, \quad \text{and} \quad \hat{f} = \hat{f}, \]
then we would have \[ f = \lambda (\hat{g}) \Rightarrow \]
\[ \Rightarrow \hat{g} = (\frac{f}{\lambda}) \Rightarrow = \hat{g}. \]
So \( \hat{g} \) would also be an eigenstate of \( \hat{g} \). But this cannot be true in general because \( [\hat{f}, \hat{g}] \neq 0 \).

**Note:** There can exist common eigenstates of non-commuting operators. These eigenstates span a subspace where \( [\hat{f}, \hat{g}] = 0 \). In this subspace you can measure simultaneously \( \hat{f} \) and \( \hat{g} \) with a determined value.

**Example:** Let \( F = \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix} \) and \( G = \begin{bmatrix} 0 & x & 0 \\ x & 0 & 0 \\ 0 & 0 & y \end{bmatrix} \)

Then \( [F, G] = \begin{bmatrix} 0 & (a-b)x & 0 \\ -(a-b)x & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \neq 0 \) implies eigenvalues \( (-x, x, y) \).

The eigenvector of \( F \) on \( G \) are, respectively,
\[ \mathbf{v}_1 = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad \mathbf{v}_2 = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad \mathbf{v}_3 = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \]
and \( \mathbf{u}_3 = \mathbf{u}_3 \).
So, if \( f \) and \( g \) have some non-common eigenstates (and it must be so because \( [f, \hat{g}] \neq 0 \)), then \( \hat{A} \) has degenerate eigenvalues.

Let \( \{\psi_{n}^{(i)}, \psi_{n}^{(2)}, \ldots, \psi_{n}^{(dn)}\} \) a set of \( dn \) eigenfunctions associated with the same eigenvalue \( \lambda_n \). Then, any linear combination

\[
\psi = \sum_{i=1}^{dn} c_i \psi_{n}^{(i)}
\]

is associated with \( \lambda_n \) because

\[
\hat{A} \psi = \sum_{i=1}^{dn} c_i \hat{A} \psi_{n}^{(i)} = \lambda_n \sum_{i=1}^{dn} c_i \psi_{n}^{(i)}
\]

So, I can always choose \( dn \) linear combinations

\[
\phi_{ni} = \sum_{j=1}^{dn} c_{ij} \psi_{n}^{(j)} \quad (i = 1, 2, \ldots, dn)
\]

such that

\[
\int \phi_{ni}^* \phi_{nj} \, dq = \delta_{ij}
\]

**Homework** - Prove that there are infinitely many different sets \( \{\phi_{n1}, \phi_{n2}, \ldots, \phi_{ndn}\} \) of orthogonal wavefunctions associated to \( \lambda_n \) by showing that \( C > D \), where

\[
C = \text{number of independent coefficients of the linear transformation generating the set } \{\phi_{n1}, \ldots, \phi_{ndn}\} \text{ from the set } \{\psi_{n1}, \ldots, \psi_{n(dn)}\}
\]

\[
D = \text{number of conditions of normalization and orthogonality satisfied by the set } \{\phi_{n1}, \ldots, \phi_{ndn}\}
\]
Lecture 9

Motives and unitary operators

Let \( \hat{H}_n = E_n \mathbf{y}_n \) and \( \mathbf{y} \) arbitrary.

Then \( \mathbf{y}(t) = \sum \frac{a_n(t)}{\omega_n} \mathbf{y}_n. \) Let \( f \) be an observable.

\[
\langle \hat{f} \rangle_\mathbf{y} = \int \mathbf{y}^*(\hat{f} \mathbf{y}) \, dq
\]

\[
= \int \left( \sum \frac{a_n(t)}{\omega_n} \mathbf{y}_n \right)^* \hat{f} \left( \sum \frac{a_m(q)}{\omega_m} \mathbf{y}_m \right) \, dq
\]

\[
= \sum \frac{a_n(t)}{\omega_n} \frac{a_m(q)}{\omega_m} \int \mathbf{y}_n^* \hat{f} \mathbf{y}_m \, dq
\]

\[
= f_{nm} \Leftarrow \text{matrix element}
\]

\[
= \sum \frac{a_n(t)}{\omega_n} f_{nm} \frac{a_m(q)}{\omega_m} e^{i\omega_{nm} t}
\]

By definition, the operator \( \hat{f} \) is such that:

\[
\langle \hat{f} \rangle_\mathbf{y} = \frac{d}{dt} \langle \hat{f} \rangle_\mathbf{y}
\]

\[
= \frac{d}{dt} \sum_{n,m} \frac{a_n(0)}{\omega_n} f_{nm} \frac{a_m(0)}{\omega_m} e^{i\omega_{nm} t}
\]

\[
= i \sum_{n,m} \omega_{nm} \frac{a_n(0)}{\omega_n} f_{nm} \frac{a_m(0)}{\omega_m} e^{i\omega_{nm} t}
\]
However, by def.:
\[ \langle \hat{f} \rangle \psi = \sum_{\ell} a_n^*(0) f_{nm} a_{\ell}(0) e^{i\omega_{\ell} t} \]
\[ \Rightarrow \]
\[ \hat{f}_{nm} = i \omega_{nm} f_{nm} \]

It is easy to see that for a generic operator \( \hat{f} \):
\[ (\hat{f}^+)_{nm} = (f_{nm})^* \]

be cause
\[ (\hat{f}^+)_{nm} = \int \psi_n^*(\hat{f} \psi_m) \, dq \]
\[ = \int \psi_m(\hat{f}^* \psi_n^*) \, dq = \left( \int \psi_m^*(\hat{f} \psi_n) \, dq \right)^* \]
\[ = (f_{nm})^* \]

The Schrödinger equation
\[ i \hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \quad (1.9) \]

Can also be written in matrix form
Let \( \hat{f} : \hat{f} \phi_n = f_n \phi_n \Rightarrow \psi(q, t) = \sum_n a_n(t) \phi_n(q) \)

Multiply 1.8 by \( \phi_n^* \) and integrate
\[ i \hbar \frac{\partial}{\partial t} \int \phi_n^*(q) \psi \, dq = \int \phi_n^*(q) \hat{H} \psi \, dq \]
\[ = a_n(t) \text{ by def.} \]
\[ = \sum_m a_m(t) H_{nm} \quad ; H_{nm} = \int \phi_n^* \hat{H} \phi_m \, dq \]
Therefore we get:

\[
\frac{\text{i} \hbar dQ_n(t)}{dt} = \sum_m H_{nm} Q_m(t)
\]  \hspace{1cm} (1.3)

If \( \hat{H} \) does not depend on \( t \) (isolated system), this is a first-order differential linear system and solution is trivial for finite dimension \( N \).

Let \( \hat{H} = [H_{nm}] \) a \( N \times N \)

and \( U \) a unitary matrix such that: (\( \Omega \) is time-indep.)

\[
U \hat{H} U^+ = D = \text{diag} (E_1, E_2, \ldots, E_N)
\]

If \( |\Omega\rangle = (\Omega_1, \Omega_2, \ldots, \Omega_N) \) we rewrite (1.3) as:

\[
\text{i} \hbar \frac{\text{d}}{\text{dt}} |\Omega\rangle = \hat{H} |\Omega\rangle \quad \text{multiply from left by } U:
\]

\[
\text{i} \hbar \frac{\text{d}}{\text{dt}} (U |\Omega\rangle) = U \hat{H} |\Omega\rangle \quad \text{identity matrix}
\]

\[
= U H |\Omega\rangle
\]

\[
= (U \hat{H} U^+) |\Omega\rangle
\]

Let \( |\lambda\rangle = U |\Omega\rangle \Rightarrow
\]

\[
\text{i} \hbar \frac{\text{d}}{\text{dt}} |\lambda\rangle = \lambda |\lambda\rangle
\]

\[
\Rightarrow \text{i} \hbar \frac{\text{d}}{\text{dt}} |\lambda\rangle = D |\lambda\rangle
\]

\[
\leftrightarrow \text{i} \hbar \frac{\text{d}}{\text{dt}} b_n = \lambda_n b_n \Rightarrow b_n(t) = b_n(0) e^{\frac{\text{i} \lambda_n t}{\hbar}}
\]
On, equivalently:

\[ |b(t)\rangle = e^{-\frac{iDt}{\hbar}} |b(0)\rangle \]

but \[ |a(t)\rangle = U^\dagger |b(t)\rangle \]

\[ \Rightarrow \]

\[ U^\dagger |b(t)\rangle = (U^\dagger e^{\frac{iDt}{\hbar}} U) U^\dagger |b(0)\rangle \]

\[ \Rightarrow \]

\[ = |a(t)\rangle \]

\[ = \exp\left(-\frac{iHt}{\hbar}\right) |a_0\rangle \]

because \[ U^\dagger e^{-\frac{iDt}{\hbar}} U = U^\dagger \sum_k \frac{(\frac{i\epsilon}{\hbar})^k}{k!} \frac{D^k}{k!} U \]

\[ = \sum_k \frac{(-\frac{i\epsilon}{\hbar})^k (U^\dagger DU)^k}{k!} = e^{-\frac{iHt}{\hbar}} \]

Therefore:

\[ |a(t)\rangle = \exp\left(-\frac{iHt}{\hbar}\right) |a_0\rangle \]

There are some systems for which it is not important to know the spatial dependence of the state,