Lecture 5

Last time

Galilean relativity

expect that the laws of physics are independent of location, orientation (rotations), time, and constant velocity shifts

Quantum mechanics

experiments measure probabilities

\[ P_{\psi_1} = \langle \psi_1 | \psi \rangle^2 = 1 \int |\psi^*(\vec{r})\psi(\vec{r})|^2 d^3r \]

transformations that preserve \( \langle \psi_1 | \psi \rangle \) are unitary \( U^*U = I \)

these preserve quantum probabilities

\[ |\phi\rangle \rightarrow |\phi'\rangle = U|\phi\rangle \]
\[ |\psi\rangle \rightarrow |\psi'\rangle = U|\psi\rangle \]

\[ \langle \phi' | \psi' \rangle = \langle U|\phi | U|\psi \rangle = \langle \phi | U^* U | \psi \rangle = \langle \phi | \psi \rangle \]

If \( U \) depends on a parameter \( a \) and statistical
\[ U(a) U(b) = U(a+b) \]
\[ U(0) = I \quad U^+(a) = U^-(a) = U(-a) \]

The we showed
\[ \frac{dU}{da} = -iG U(a) \quad ; \quad G = i \frac{dU}{da} U^+(a) \]

where \( G = G^+ \) and \( G \) is independent of \( a \)
\[ U(a) = \sum_{n=0}^{\infty} \left( -ia \right)^n \frac{G^n}{n!} = e^{-iGa} \]
\[ \frac{dU}{da} = \sum_{n=0}^{\infty} \left( -in (-ia)^{n-1} \frac{G^n}{n(n-1)!} = -iG \sum_{n=1}^{\infty} \left( -ia \right)^{n-1} \frac{G^{n-1}}{(n-1)!} \right) \]

let \( m = n-1 \) \quad m = 0 \rightarrow \infty
\[ = -iG \sum_{m=0}^{\infty} \frac{(-ia)^m}{m!} G^m = -iG U(a) \]

This shows that the conditions on the top of the page imply that \( U(a) \) has this general form.

Space translations
\[ T(a) \psi(x) = \psi(x-a) \]
This defines a coordinate translational moves the wave function to the right by a -ie a space translation.

If $\psi(x)$ is a nice function with a convergent Taylor series then

$$T(a)\psi(x) = \psi(x-a) =$$

$$\sum_{n=0}^{\infty} \frac{(-a)^n}{n!} \frac{d^n}{dx^n} \psi(x) =$$

$$\sum_{n=0}^{\infty} \frac{a^n}{n!} (\frac{-i}{\hbar})^n (\frac{\hbar}{i} \frac{d}{dx})^n \psi(x)$$

We recognize $\frac{\hbar}{i} \frac{d}{dx}$ as the linear momentum operator. It satisfies

$$P = \frac{\hbar}{i} \frac{d}{dx} = P^\dagger$$

$$T(a)\psi(x) = \sum_{n=0}^{\infty} \frac{(-ia)^n}{n!} P^n \psi(x)$$

$$= e^{-\frac{1}{\hbar} P \cdot a} \psi(x)$$

This has the form $e^{-i\hbar a}$ where

$\gamma = \frac{1}{\hbar} P$
In this case $p$ is called the infinitesimal generator of translations.

Problem 6.2 (HW) - You will be asked to show that $T(a)$ is unitary.

If we want to calculate the expectation value of $x$ in the state $T(a)|\psi\rangle$

$$\langle x \mid T(a) \psi \rangle = \psi(x-a)$$

$$\langle T(a) \psi \times T(a) \psi \rangle =$$

$$\int \psi^\ast(x-a) \times \psi(x-a) \, dx = \int \psi^\ast(y)(y+a) \psi(y) \, dy$$

If we can express this as

$$\langle x+a \rangle$$

we can express this as

$$\langle \psi \mid T(a)x T(a) \mid \psi \rangle$$

With

$$T^\dagger(a) \times T(a) = x+a$$
rather than changing the coordinates in the wave function, we can transform the operator $x$ and use the original wave function

$$\langle \psi' | x' | \psi' \rangle = \langle \psi | x | \psi \rangle$$

$$| \psi' \rangle = T(a) | \psi \rangle$$

$$x' = T(a)^{\dagger} x T(a)$$

more generally - for any operator $O$ the translated operator $O'$ is defined by

$$O' = T(a)^{\dagger} O T(a)$$

So far we have not discussed how these transformations relate to the laws of physics.

Consider

$$\frac{d}{dt} \langle \psi(t) | T(a) | \psi(t) \rangle =$$

using the Schrödinger equation
\[ i \hbar \frac{d}{dt} \langle \psi(t) | = H | \psi(t) \rangle \]

\[ \frac{d}{dt} \langle \psi(t) | = - \frac{i}{\hbar} H | \psi(t) \rangle \]

\[ \frac{d}{dt} \langle \psi(t) | T(a) | \psi(t) \rangle = \]

\[ \frac{i}{\hbar} \langle \psi | H T(a) | \psi \rangle - \frac{i}{\hbar} \langle \psi | T(a) H | \psi \rangle = \]

\[ \frac{i}{\hbar} \langle \psi | (H T(a) - T(a) H) | \psi \rangle \]

This will vanish for all time if

\[ \langle \psi(t) | (H T(a) - T(a) H) | \psi(t) \rangle = 0 \]

If this holds for all a then if we differentiate this expression with respect to a and set a = 0

\[ \frac{d}{da} e^{-i \frac{P_a}{\hbar}} = -i \frac{P_a}{\hbar} e^{-i \frac{P_a}{\hbar}} = -i \frac{P_a}{\hbar} \quad \text{(at a = 0)} \]

The the above becomes

\[ \langle \psi(t) | \left( -\frac{i}{\hbar} \right) (H P - P H) | \psi(t) \rangle = 0 \]
This shows that a sufficient condition for \( \langle \Psi | T(t) | \Psi \rangle \) to be independent of time is that

\[
H \rho - \rho H = 0
\]

To understand this consider the Coulomb Hamiltonian

\[
H = -\frac{k^2}{2m_1} \nabla_1^2 - \frac{k^2}{2m_2} \nabla_2^2 + \frac{e^2}{4\pi \varepsilon_0 |r_1 - r_2|}
\]

If we replace

\[
\begin{align*}
\bar{r}_1 &\to \bar{r}_1 + \bar{a} \\
\bar{r}_2 &\to \bar{r}_2 + \bar{a}
\end{align*}
\]

\[
\nabla_1' = \nabla_1, \quad \nabla_2' = \nabla_2 - \frac{1}{|\bar{r}_1 + \bar{a} - \bar{r}_2 - \bar{a}|} = \frac{1}{|\bar{r}_1 - \bar{r}_2|}
\]

For this Hamiltonian

\[ T(\alpha) H T(\alpha) = H \]

which means that it is invariant with respect to translations.

If we differentiate this equation by \( \bar{a} \) and set \( \bar{a} = 0 \)

\[
(\bar{\rho} H - H \bar{\rho}) = 0
\]
which means that $H$ commutes with the momentum operator.

Consider
\[
\frac{d}{dt} \langle \Psi(t) | P | \Psi(t) \rangle = \frac{i}{\hbar} \langle \Psi(t) | [H, P] | \Psi(t) \rangle = 0
\]

which means that the expectation value of the momentum is conserved.

Note
\[ i \hbar \frac{d}{dt} \langle \Psi \rangle = H \langle \Psi \rangle \]

\[ (i \hbar)^2 \frac{d^2}{dt^2} = H^2 \langle \Psi \rangle \]

provided $H$ is independent of time

\[ \frac{d}{dt} \langle \Psi \rangle = \langle \Psi | \frac{i}{\hbar} H \rangle \]

as in the case of translations, we get a formal solution using the Taylor series:

\[ |\Psi(t)\rangle = U(t) |\Psi(0)\rangle \]

\[ U(t) = e^{\frac{i}{\hbar} (-\frac{i}{\hbar})^n H^n t^n} \]

\[ = e^{\frac{i}{\hbar} H t} \]
If we consider
\[ \langle \psi(t) | P | \psi(t) \rangle = \]
\[ \langle U(t) \psi(t) | P U(t) \psi(t) \rangle = \]
\[ \langle \psi(0) U^+(t) P U(t) \psi(t) \rangle \]

In this case the time dependence is put in the operator
\[ P(t) = U^+(t) P(0) U(t) \]
\[ = \mathbb{E} + \frac{i \hbar}{\hbar} \vec{p} \]

\[ \frac{d\mathbb{E}}{dt} = \frac{i}{\hbar} \mathbb{E} \left[ H, P \right] \]
\[ = 0 \quad \text{if} \quad \left[ H, P \right] = 0 \]

This shows that \( P \) is conserved.

In general if \( H \) is independent of time and \( \left[ O, H \right] = 0 \) then

\[ \frac{dO}{dt} = \frac{i}{\hbar} \left[ H, O \right] = 0 \]

is conserved.
Summary

If the Hamiltonian is invariant with respect to translations then momentum is conserved where the momentum operator is the infinitesimal generator of translations.

The condition $[H, \hat{p}] = 0$ means $p$ is independent of $t$ and the expectation value of $p$ is independent of $t$.

We also have

$$ T(a) = e^{-i pa/\hbar} \quad \quad \hat{U}(t) = e^{-i Ht/\hbar} $$

$$ p = p^+ \quad \quad H = H^+ $$

$$ T^+(a) = T(a) \quad \quad \hat{U}^+(t) = \hat{U}(t) $$

We also note because $[H, H^+] = 0$ that (for $H$ independent of $t$)

$$ \frac{dH}{dt} = \frac{i}{\hbar} [H, H^+] = 0 $$

which implies energy is conserved.
The Coulomb hamiltonian has some other symmetries:

\[ v_i^2 = \tilde{v}_i \cdot \tilde{v}_i \]
\[ |\tilde{r}_1 - \tilde{r}_2| = \sqrt{\tilde{r}_1 \cdot \tilde{r}_1 + \tilde{r}_2 \cdot \tilde{r}_2 - 2 \tilde{r}_1 \cdot \tilde{r}_2} \]

Both of these quantities involve products which are invariant under rotations and reflection:

\[ \tilde{r} \rightarrow \tilde{r}' = -\tilde{r} \]

Space reflection symmetry is a little different than translational or rotational symmetry.

We define the parity operator \( \hat{\Pi} \):

\[ \hat{\Pi} \psi(x) = \psi(-x) \]

In this case we have

\[ \hat{\Pi}^2 \psi(x) = \hat{\Pi} \psi(-x) = \psi(-(-x)) = \psi(x) \]

so \( \hat{\Pi}^2 = I \)
we also have

\[ \langle \Pi \phi \mid \Pi \psi \rangle = \]

\[ \int_{-\infty}^{\infty} \phi^*(x) \psi(-x) \, dx \quad \text{let } y = -x \]

\[ \int_{-\infty}^{\infty} \phi(y) \psi(y) \, dy \]

\[ \int_{-\infty}^{\infty} \phi'(y) \psi(y) \, dy = \langle \phi \mid \psi \rangle \]

which shows that \( \Pi \) is unitary.

Since \( \Pi^2 = I \), \( \Pi \) is its own inverse so

\[ \Pi = \Pi^{-1} = \Pi^+ \]

so it is both Hermitian and unitary.

**Homework**

\[ \Pi \times \Pi = -\mathbf{I} \]

\[ \Pi \phi \Pi = -\phi \]

If \( [H, \Pi] = 0 \)
then \( i \) \( \Psi \) 

\[ H \Psi = E \Psi \]

\[ H \Pi \Psi = \Pi H \Psi = \Pi E \Psi = E \Pi \Psi \]

then \( \Psi \) and \( \Pi \Psi \) are eigenstates with the same energy

\[ \phi_+ = N (\Psi \pm \Pi \Psi) \]

\[ \Pi \phi_+ = N (\Pi \Psi \pm \Psi) \]

\[ = \pm N (\Psi \pm \Pi \Psi) \]

\[ = \phi_+ \]

This means that if \( [H, \Pi] = 0 \) then it is possible to simultaneously diagonalize \( H \) and \( \Pi \)

\[ \frac{d \Pi}{dt} = \frac{d}{dt} \left( U^\dagger(t) \Pi U(t) \right) \]

\[ = U^\dagger(t) \left( \frac{\hbar}{i} H \Pi - \frac{\hbar}{i} \Pi H \right) U(t) \]

\[ = \frac{\hbar}{i} U^\dagger(t) [H, \Pi] U(t) = 0 \]

so if \( [H, \Pi] = 0 \) then the parity eigenvalue is conserved.
Pseudo vectors and pseudo scalars

\[ \Pi \cdot \Pi = \Pi (\vec{F} \times \vec{p}) \cdot \Pi \]

\[ = \Pi \vec{\tau} \cdot \Pi \times \Pi \vec{p} \cdot \Pi \]

\[ = (\vec{F} \cdot \Pi \vec{p}) \times (\Pi \vec{p}) = \vec{F} \times \vec{p} = \vec{L} \]

Unlike \( \vec{x} \) and \( \vec{p} \) which change sign under space reflection, the angular momentum vector does not change sign.

If we consider

\[ \Pi \cdot \vec{\tau} \cdot \Pi \cdot \Pi = \Pi \vec{\tau} \cdot \Pi \vec{p} \cdot \Pi \cdot \Pi \]

\[ = \vec{L} \cdot \vec{p} = -\vec{L} \cdot \vec{p} \]

\( \vec{L} \cdot \vec{p} \) behaves differently than \( \vec{p} \cdot \vec{p} \)

\( \vec{x} \times \vec{x} \) or \( \vec{x} \cdot \vec{x} \), under space reflection.

It is called a pseudo scalar.

Spin behaves the same way

\[ \hat{\Pi} \cdot \hat{S} \cdot \hat{P} = \hat{S} \]
Selection rules

Spherical Harmonics

\[ \hat{n} \mathbf{Y}^m_\ell (\hat{\mathbf{r}}) = \mathbf{Y}^m_\ell (\mathbf{-r}) = (-)^\ell \mathbf{Y}^m_\ell (\mathbf{r}) \]

This follows because the \( \mathbf{Y}^m_\ell \) are proportional to \( p^\ell \cos \theta \).

Consider

\[ \langle \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} | Q | \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} \rangle = \]

\[ \langle \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} | \hat{n}^2 \hat{\mathbf{r}}^2 | \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} \rangle = \]

\[ \langle \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} | \hat{n} \hat{\mathbf{r}} \hat{n} | \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} \rangle = \]

\[ (-)^{\ell+\ell'} \langle \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} | \hat{n} \hat{\mathbf{r}} \hat{n} | \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} \rangle \]

Assume \( \hat{n} \hat{\mathbf{r}} \hat{n} = (-)^\ell \hat{\mathbf{r}} \hat{n} \).

\[ (-)^{\ell+\ell'+p} \langle \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} | Q | \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} \rangle \]

This will vanish unless

\[ \ell + \ell' + p \text{ is even} \]
If \( \mathbf{q} = q \hat{e} \) is an electric dipole operator, \( \hat{n} \mathbf{q} \hat{n} = - \mathbf{q} \).

Then \( \mathbf{q} \cdot \mathbf{q} \) must be odd to get a non-zero result.

In particular,

\[
\langle \text{nem} | q \hat{e} | \text{nem} \rangle = 0
\]

**Rotational Symmetry**

\[
x' = x \cos \theta - y \sin \theta
\]

\[
y' = y \cos \theta + x \sin \theta
\]

\[
R(\theta)\psi(xyz) = \psi(x' \cos \theta - y' \sin \theta, y' \cos \theta + x' \sin \theta, z)
\]

This rotates the wave function in the counterclockwise direction.

This has the property

\[
R_z(\phi_1) R_z(\phi_2) = R_z(\phi_1 + \phi_2)
\]

\[
R_z(0) = I
\]
It is also unitary because
\[ \frac{d\Psi}{d\Pi} = \det \begin{vmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{vmatrix} = \cos^2 \theta + \sin^2 \theta = 1 \]

Thus,
\[
\Psi \begin{pmatrix} x \cos \theta - y \sin \theta \\ y \cos \theta + x \sin \theta \end{pmatrix} 
\]
\[
= \Psi (x, y, z) + \Theta \left( \frac{\partial \Psi}{\partial x} (-y \sin \theta - x \cos \theta) \right) 
\]
\[
= \Psi (x, y, z) + \Theta \left( x \frac{\partial \Psi}{\partial y} - y \frac{\partial \Psi}{\partial x} \right) 
\]
\[
= \Psi (x, y, z) - \frac{i}{\hbar} \left( x \frac{\hbar^2}{2m} i \frac{\partial}{\partial x} - y \frac{\hbar^2}{2m} i \frac{\partial}{\partial y} \right) \Psi 
\]
\[
= \Psi (x, y, z) - \frac{i}{\hbar} (\vec{x} \times \vec{p}) \Psi 
\]

In this case

\[
L_z = \vec{x} \times \vec{p} 
\]

\[
R_\theta (\theta) = e^{-i \theta \cdot L_z} 
\]

Here we see \( L_z \) is the \( z \) component of the angular momentum operator. It is the generator of rotations about the \( z \) axis.
For the Coulomb Hamiltonian
\[ R(\theta) H R(\theta) = H \]
differentiating with respect to \( \theta \) gives
\[ [H, L_z] = 0 \]
and
\[ L_z(t) = U^+(t)L_zU(t) = L_z \]

\[ \frac{dL_z}{dt} = i\hbar U^+(t)[H, L_z]U(t) = 0 \]

which means that the angular momentum about the \( z \) axis is conserved.

What was true for the \( z \) axis works for any axis
\[ R(\theta) = e^{-i\hbar \hat{n} \cdot \vec{L}\theta} \]

where \( \hat{n} \cdot \vec{L} \) is the generator of rotation about the \( \hat{n} \) axis,
where \( \vec{L} = \vec{r} \times \vec{p} \) is the angular momentum operator.