Physics 342 Lecture 11

More into quantum mechanics! Last lecture we had, finally, constructed (derived?) the fundamental equation of quantum mechanics that governs time evolution of the wavefunction $\psi(x,t)$:

$$\hat{H}|\psi\rangle = i\hbar \frac{\partial}{\partial t}|\psi\rangle.$$ This is called the Schrödinger equation.

For the case in which the Hamiltonian $\hat{H}$ is time-independent, this can be simplified. First, we identified the eigenfunctions of the time derivative operator:

$$i\hbar \frac{\partial}{\partial t}\alpha(t) = E\,\alpha(t),$$ where E is the energy, and so

$\alpha(t) = e^{-\frac{iEt}{\hbar}}$. As an energy, E is the eigenvalue of the Hamiltonian.

Now, we can expand the wavefunction in a basis of eigenstates $|\psi_i\rangle$ of the Hamiltonian that are time-independent. That is,

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle,$$ where $|\psi_i\rangle = |\psi_i(x)\rangle$ and

$\frac{d}{dt}E_i = 0$. Then, the wavefunction can be written as:

$$|\psi\rangle = \sum_i \alpha_i(t)|\psi_i\rangle = \sum_i e^{-\frac{iE_it}{\hbar}}\beta_i|\psi_i\rangle,$$

for some complex constant β_i. Thus, the problem of solving the Schrödinger equation is reduced to diagonalization of the time-independent Hamiltonian:

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle,$$

where $|\psi_i\rangle$ is now an eigenstate, and E_i is an eigenvalue of $\hat{H}$, both of which are time-independent. The coefficient β_i can be found by orthonormality of the basis $\{|\psi_i\rangle\}_i$:

$$\beta_i = \langle\psi_i|\psi\rangle = \sum_j \langle\psi_i|\,\beta_j\,|\psi_j\rangle = \sum_j \beta_j \langle\psi_i|\psi_j\rangle = \beta_i.$$

Here, we have set $t=0$ to eliminate the exponential temporal factors.

With this formalism, it is easy to show that the normalization of the wavefunction is maintained for all time t. If the wave function is normalized at $t=0$, then:

$$\langle\psi(t=0)|\psi(t=0)\rangle = \sum_{i,j} \langle\psi_i|\,\beta_i^*\beta_j\,|\psi_j\rangle = \sum_i |\beta_i|^2 = 1.$$

Now, the inner product of the wave function at a later time t is:

$$\langle\psi(t)|\psi(t)\rangle = \sum_{i,j} \langle\psi_i|\,\beta_i^* e^{\frac{iE_i t}{\hbar}} e^{-\frac{iE_j t}{\hbar}}\beta_j|\psi_j\rangle$$

$$= \sum_{i,j} \beta_i^*\beta_j\, e^{\frac{-i(E_j-E_i)t}{\hbar}} \underbrace{\langle\psi_i|\psi_j\rangle}_{\delta_{ij}}$$

$$= \sum_i |\beta_i|^2 = 1 \quad \checkmark$$

This "conservation of probability" follows from the fact that the Hamiltonian is Hermitian.

A couple of lectures ago, we had introduced the notion of an expectation value of a Hermitian operator $T = T^\dagger$, given a quantum state defined by a wavefunction, $\Psi(x,t)$. The expectation value is nothing more than a matrix element of T:

$$E_T = \langle \Psi | T | \Psi \rangle = \int dx\, \Psi^*(x,t)\, T\, \Psi(x,t).$$

Unlike the normalization, $\langle \Psi | \Psi \rangle$, for a general Hermition operator, this expectation value is not constant in time. Can we determine how it changes in time?

To do this, we will write the expectation value as a function of time:

$$E_T(t) = \langle \Psi | T | \Psi \rangle (t).$$

If the time is evolved forward by a small amount Δt, we can Taylor expand:

$$E_T(t+\Delta t) = E_T(t) + \Delta t \frac{d}{dt} E_T(t) + \ldots$$

Equivalently, we can evolve the wavefunctions in the integral forward in time. By the schrödinger equation, this is accomplished by the Hamiltonian; that is,

$$\Psi(x,t+\Delta t) = e^{-\frac{i\Delta t \hat{H}}{\hbar}} \Psi(x,t) = \Psi(x,t) - \frac{i\Delta t \hat{H}}{\hbar} \Psi(x,t) + \ldots,$$

where, again, we Taylor expand the exponential. The time evolution of the complex conjugate of Ψ is therefore:

$$\Psi^*(x, t+\Delta t) = \Psi^*(x,t) + \Psi^*(x,t)\,\frac{i\Delta t\,\hat{H}}{\hbar} + \cdots$$

Note we keep Ψ^* to the left of $\hat{H}$ as we think of it as a "row vector". Therefore, to linear order in Δt, the integral becomes:

$$\int dx\, \Psi^*(x,t+\Delta t)\, T\, \Psi(x,t+\Delta t)$$

$$\cong \int dx \left(\Psi^*(x,t) + \Psi^*(x,t)\frac{i\Delta t\,\hat{H}}{\hbar}\right) T \left(\Psi(x,t) - \frac{i\Delta t\,\hat{H}}{\hbar}\Psi(x,t)\right)$$

$$\cong \int dx\, \Psi^*(x,t)\, T\, \Psi(x,t)$$

$$+ \frac{i\Delta t}{\hbar}\int dx\, \Psi^*(x,t)\left(\hat{H}T - T\hat{H}\right)\Psi(x,t) + \mathcal{O}(\Delta t^2)$$

The first term is nothing more than the expectation value at time t, and so, setting the expansion of the left and right sides equal, we find:

$$\frac{d\langle\Psi|T|\Psi\rangle}{dt} = \frac{i}{\hbar}\langle\Psi|\hat{H}T - T\hat{H}|\Psi\rangle$$

In this derivation, we have assumed that the operator T itself has no explicit time dependence, so it's partial time derivative is 0:

$$\frac{\partial T}{\partial t} = 0.$$

If this isn't true, we need to include it on the right:

$$\frac{d\langle\Psi|T|\Psi\rangle}{dt} = \frac{i}{\hbar}\langle\Psi|\hat{H}T - T\hat{H}|\Psi\rangle + \langle\Psi|\frac{\partial T}{\partial t}|\Psi\rangle.$$

(This Partial derivative comes from explicit time Taylor expansion in the integral expression for the expectation value.)

The most intriguing part of this time-dependence of expectation value is the difference of the product of $\hat{H}$ and T. We call this the <u>commutator</u> of $\hat{H}$ and T denoted as:

$$\hat{H}T - T\hat{H} \equiv [\hat{H}, T].$$

Thus, we say that the time dependence of the expectation value is 0 if $\hat{H}$ and T <u>commute</u>.

The existence of commutators should be very unfamiliar to your experience in classical mechanics. There, everything is just a regular function of real numbers, and real numbers commute: $ab = ba$, for $a, b \in \mathbb{R}$. However, as we had long motivated this topic, operators are like <u>matrices</u> and for two matrices $\mathbb{A}$, $\mathbb{B}$, it need not be true that

$$\mathbb{A}\mathbb{B} = \mathbb{B}\mathbb{A}.$$

For a simple counter example, consider the 2x2 matrices

$$\mathbb{A} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad B = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Additionally, both $\mathbb{A}$ and $\mathbb{B}$ are Hermitian matrices.
The product $\mathbb{A}\mathbb{B}$ is:

$$\mathbb{A}\mathbb{B} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

while the product $\mathbb{B}\mathbb{A}$ is:

$$\mathbb{B}\mathbb{A} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

and so their commutator is

$$[\mathbb{A}, \mathbb{B}] = \mathbb{A}\mathbb{B} - \mathbb{B}\mathbb{A} = \begin{pmatrix} 0 & 2 \\ -2 & 0 \end{pmatrix} \neq 0 \, !$$

So, it is natural, then, to expect that two Hermitian operators $\hat{H}$ and T on phase space do not commute, just like matrix multiplication isn't necessarily commutative.

To make some sense out of this, let's end today with a calculation of the time dependence of expectation values of the momentum operator, $\hat{p}$. We will assume that $\hat{p}$ itself has no explicit time dependence: $\partial\hat{p}/\partial t = 0$, so our evolution equation is:

$$\frac{d\langle\hat{p}\rangle}{dt} = \frac{i}{\hbar}\langle[\hat{H}, \hat{p}]\rangle,$$ where we have compactly denoted the integration over the wavefunctions with the brackets:

$$\langle\hat{p}\rangle \equiv \langle\psi|\hat{p}|\psi\rangle, \text{ and } \langle[\hat{H}, \hat{p}]\rangle = \langle\psi|[\hat{H}, \hat{p}]|\psi\rangle.$$

So, what is the commutator of $\hat{H}$ and $\hat{p}$? First, recall the expansion of the Hamiltonian into kinetic and potential energies:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x).$$

Just focusing on the kinetic energy, $\frac{\hat{p}^2}{2m}$, this commutes with momentum $\hat{p}$:

$$\hat{K}\hat{p} = \frac{\hat{p}^2}{2m}\hat{p} = \hat{p}\frac{\hat{p}^2}{2m} \rightarrow \hat{p}\hat{K},$$ as "2m" is just a scalar, constant number.

So, the commutator of the Hamiltonian and momentum is just the commutator of the potential and $\hat{p}$:

$$[\hat{H},\hat{p}] = [V(x),\hat{p}].$$

We might think that this remaining commutator is just 0 too, but remember $\hat{p}$ is a derivative:

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}.$$

As a derivative, it must act on some function $f(x)$ on its right. Another way to say this is that the purpose in life of operators like $\hat{H}$, $\hat{p}$, etc., are to act on states/functions. So, our trick for evaluating the commutator that remains is to put a function $f(x)$ on its right, perform the commutator, and then remove $f(x)$. Such a function is called a "test function", and is just there to keep us honest with manipulations of linear operators.

So, we want to compute:

$$[V(x),\hat{p}]f(x) = V(x)\left(-i\hbar\frac{\partial}{\partial x}\right)f(x) - \left(-i\hbar\frac{\partial}{\partial x}\right)V(x)f(x)$$

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

$$= V(x)\left(-i\hbar\frac{\partial}{\partial x}\right)f(x),$$

where we used the product rule on the second and third lines. Note now that the first and third terms cancel, ~~...~~ while the second term remains, Eliminating $f(x)$, we therefore find:

$$[V(x), \hat{p}] = i\hbar \frac{\partial V}{\partial x}.$$

Plugging this into our differential equation for the time dependence of $\langle \hat{p} \rangle$, we find:

$$\frac{d\langle \hat{p} \rangle}{dt} = \left\langle \frac{i}{\hbar}\left(i\hbar \frac{\partial V}{\partial x}\right)\right\rangle = -\left\langle \frac{\partial V}{\partial x}\right\rangle.$$

Does this look familiar? For a conservative force in classical mechanics, we can express that force as a derivative of a potential energy:

$$F_{cons} = -\frac{\partial U}{\partial x}.$$

Thus, this is just like Newton's second law! However, it is a statement of time dependence of expectation values of the momentum operator $\hat{p}$. This whole structure is a manifestation of the Ehrenfest Theorem, which is often colloquially stated as expectation values satisfying the classical equations of motion (which is slightly misleading, but correct in spirit).

This whole procedure required properties of the commutation relation of momentum $\hat{p}$ with the position operator $\hat{x}$. ~~...~~ Eigenvalues of $\hat{x}$ are nothing more than a position x:

$\hat{x}|v\rangle = x|v\rangle$, where $|v\rangle$ is an eigenstate of position. Position x is always real, so $\hat{x}$ is a Hermitian operator, just like momentum.

The commutation relation of $\hat{x}$ and $\hat{p}$ can be evaluated in the same way as $V(x)$ and $\hat{p}$:

$$[\hat{x},\hat{p}]f(x) = x\left(-i\hbar\frac{\partial}{\partial x}\right)f(x) - \left(-i\hbar\frac{\partial}{\partial x}\right)x f(x)$$

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

$$= i\hbar f(x).$$

Thus, their commutator is: $\boxed{[\hat{x},\hat{p}] = i\hbar}$

This is a profoundly important relation in quantum mechanics, so central it is called the <u>canonical commutation relation</u>. We will see more consequences of commutators next lecture.