CHM 305 - Lecture 7 - The Postulates of Quantum Mechanics (Part 2)

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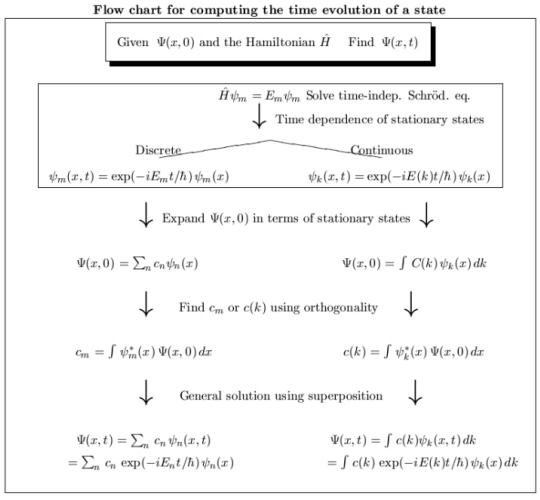
1 Reviewing Postulate 5: Time-dependent Wavefunctions

The evolution in time of a quantum wavefunction is determined by the time-dependent Schrödinger equation. I will write it down the 1D form again here for posterity:

$$\hat{H}\Psi(x,t) = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)\right]\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{1}$$

In general, wavefunctions can have complex temporal dynamics! But recall from Lecture 3 that for stationary states (i.e. quantum standing waves which have wavefunctions that factor neatly into spatial and temporal components, which also happen to be energy eigenstates), it is easy to solve a purely temporal differential equation for the time evolution.

We are often given an arbitrary wavefunction at $t = 0$, $\Psi(x, t = 0)$ and asked to find $\Psi(x,t)$ at all subsequent times. We nearly always want to re-express this wavefunction as a linear combination of energy eigenstates in order to figure out the temporal evolution of the system. The handy flowchart below summarizes this procedure:



Once we have $\Psi(x,t)$, we can use this to calculate everything there is to know about the system at any future point in time, including the time-dependence of spatial probability distributions and the time-dependence of expectation values of interesting observables. Exploring these quantities for both stationary states and superposition states will be the subject of today's lecture!

2 Time-Dependent Probability Distributions

If a system has wavefunction $\Psi(x,t)$, then it has a spatial probability distribution given by $|\Psi(x,t)|^2$. Let's examine what this looks like for both stationary states of the system and superposition states.

2.1 Stationary States

If $\psi_n(x)$ is an energy eigenstate (e.g. a stationary state) with energy E_n and index n, then we can write down its simple time-dependence as:

$$\Psi_n(x,t) = \psi_n(x)\, e^{-iE_n t/\hbar} \equiv \psi_n(x)\, e^{-i\omega_n t} \tag{2}$$

where $\omega_n \equiv E_n/\hbar$.

What makes $\Psi_n(x,t)$ a stationary state? It turns out that energy eigenstates have probability distributions that are not time dependent:

$$\begin{aligned}
\Big|\Psi_n(x,t)\Big|^2 &= \Psi_n^*(x,t)\cdot\Psi_n(x,t) && (3)\\
&= \Big[\psi_n(x)e^{-i\omega_n t}\Big]^*\cdot\Big[\psi_n(x)e^{-i\omega_n t}\Big] && (4)\\
&= \Big[\psi_n^*(x)e^{+i\omega_n t}\Big]\cdot\Big[\psi_n(x)e^{-i\omega_n t}\Big] && (5)\\
&= \Big|\psi_n(x)\Big|^2 \quad \neq \quad f(t) && (6)
\end{aligned}$$

This is indeed not a function of time, since the complex conjugate of the temporal component cancels itself out.

2.2 Superposition states

What if we are not in a stationary energy eigenstate? The probability distribution will have a more interesting time-dependence in this case. Consider the following superposition of energy eigenstates:

$$\Psi(x,t) = c_1\psi_1(x)e^{-i\omega_1 t} + c_2\psi_2(x)e^{-i\omega_2 t} \tag{7}$$

where $\psi_1(x)$ and $\psi_2(x)$ are energy eigenfunctions (or stationary states).

The probability distribution will now be given by:

$$\begin{aligned}
|\Psi(x,t)|^2 &= \Big|c_1\psi_1(x)e^{-i\omega_1 t} + c_2\psi_2(x)e^{-i\omega_2 t}\Big|^2 && (8)\\
&= \Big[c_1^*\psi_1^*(x)e^{+i\omega_1 t} + c_2^*\psi_2^*(x)e^{+i\omega_2 t}\Big]\Big[c_1\psi_1(x)e^{-i\omega_1 t} + c_2\psi_2(x)e^{-i\omega_2 t}\Big] && (9)\\
&= |c_1|^2|\psi_1(x)|^2 \quad + \quad |c_2|^2|\psi_2(x)|^2 \quad + \quad c_1^*c_2\psi_1^*(x)\psi_2(x)e^{+i(\omega_1-\omega_2)t}\\
&\qquad\qquad + \quad c_2^*c_1\psi_2^*(x)\psi_1(x)e^{+i(\omega_2-\omega_1)t} && (10)
\end{aligned}$$

Here the time-dependence *does not* cancel out neatly! The likelihood that we find the particle in a given region of space changes with time. In fact, the probability distribution sloshes back and forth with a frequency of $|\omega_1 - \omega_2| = |E_1 - E_2|/\hbar$.

Here's the most general form of the time-dependent probability distribution for an arbitrary superposition of energy eigenstates:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iw_n t} \tag{11}$$

$$\rightarrow \quad |\Psi(x,t)|^2 = \sum_{n=1}^{\infty} |c_n|^2 |\psi_n(x)|^2 \quad + \quad \sum_{n=1}^{\infty} \sum_{\substack{m=1 \\ m\neq n}}^{\infty} c_n^* c_m \psi_n^*(x) \psi_m(x) e^{+i(\omega_n - \omega_m)t} \tag{12}$$

It's a general phenomenon that superposition states have temporal dynamics that oscillate at frequencies related to the energy differences between each pair of energy eigenstates present in the superposition. These oscillations typically correspond to a "sloshing" of where the particle is most likely to be found. See example animations here and on the course Canvas page.

Practice Problem 1: Consider a particle in a box of length a with wavefunction given by

$$\Psi(x,t) = \frac{1}{\sqrt{2}} \left[\psi_1(x) e^{-i\omega_1 t} + \psi_2(x) e^{-i\omega_2 t} \right]$$

Consider the time-dependent probability that we find the particle in the left half of the box, $x = [0, a/2]$, by evaluating

$$P\left[0, \frac{a}{2}\right] = \int_0^{a/2} dx |\Psi(x,t)|^2$$

Show that this quantity takes the form, where c is a constant:

$$P\left[0, \frac{a}{2}\right] = \frac{1}{2} + c \cdot \cos\left[(\omega_1 - \omega_2)t\right]$$

3 Time-Dependent Expectation Values of Energy

Let's now examine how expectation values of various operators evolve in time.

3.1 Expected Energy for a Stationary States

Consider again that $\psi_n(x)$ is an energy eigenstate (e.g. a stationary state) with energy E_n and time-dependence given by

$$\Psi_n(x,t) = \psi_n(x)\, e^{-i\omega_n t} \tag{13}$$

Let's calculate the expectation value of energy for this system:

$$\langle E(t) \rangle = \int_{-\infty}^{\infty} dx \ \left[\psi_n(x)\, e^{-i\omega_n t}\right]^* \hat{H} \left[\psi_n(x) e^{-i\omega_n t}\right] \tag{14}$$

$$= \int_{-\infty}^{\infty} dx \ \left[\psi_n^*(x)\, e^{+i\omega_n t}\right] \left[\hat{H} \psi_n(x) e^{-i\omega_n t}\right] \tag{15}$$

$$= \int_{-\infty}^{\infty} dx \ \left[\psi_n^*(x)\, e^{+i\omega_n t}\right] \left[E_n \psi_n(x) e^{-i\omega_n t}\right] \tag{16}$$

$$= E_n \int_{-\infty}^{\infty} dx \ \cancel{\psi_n^*(x)\psi_n(x)}^{\,1} \cancel{e^{+i\omega_n t} e^{-i\omega_n t}}^{\,1} = \quad E_n \quad \neq \quad f(t) \tag{17}$$

This seems reasonable enough! An energy eigenfunction $\psi_n(x)$ has well-defined energy E_n, and this energy is conserved even as the stationary state evolves in time.

3.2 Expected Energy for a Superposition State

Let's now return to our arbitrary superposition of energy eigenstates, $\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iw_n t}$, and evaluate how the expected energy will evolve in time:

$$\begin{aligned}
\langle E(t) \rangle &= \int_{-\infty}^{\infty} dx \left[\sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i\omega_n t} \right]^* \hat{H} \left[\sum_{m=1}^{\infty} c_m \psi_m(x) e^{-i\omega_m t} \right] \\
&= \int_{-\infty}^{\infty} dx \left[\sum_{n=1}^{\infty} c_n^* \psi_n^*(x) e^{+i\omega_n t} \right] \left[\sum_{m=1}^{\infty} c_m E_m \psi_m(x) e^{-i\omega_m t} \right] \\
&= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n^* c_m E_m \underbrace{\int_{-\infty}^{\infty} dx \; \psi_n^*(x) \psi_m(x)}_{\delta_{nm}} \; e^{+i(\omega_n - \omega_m)t} \\
&= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n^* c_m E_m \delta_{nm} e^{+i(\omega_n - \omega_m)t} \\
&= \sum_{n=1}^{\infty} |c_n|^2 E_m \quad = \quad \langle E(0) \rangle \quad \neq \quad f(t)
\end{aligned}$$

where in the last step, the δ_{nm} term kills one of the two sums, and sends the complex exponential to 1 when $n = m$.

This result should perhaps surprise you! $\langle E \rangle$ is never a function of time, even in an arbitrary superposition state of energy eigenfunctions. The expectation value of energy is always conserved; if we know it at time $t = 0$, it will remain unchanged for all subsequent times (as long as we don't mess around with the system). Energy eigenfunctions have very particular time dependence that again cancels out neatly in this case. This is one more reason why energy is a very special quantity in quantum mechanics!

Practice Problem 2: What is the expected value of the energy of the particle-in-a-box superposition state below?

$$\Phi(x,t) = \frac{1}{\sqrt{2}} \Psi_1(x,t) + \frac{1}{\sqrt{2}} \Psi_2(x,t) \tag{18}$$

$$= \frac{1}{\sqrt{2}} \left(\frac{2}{a} \right)^{1/2} \sin\left(\frac{\pi x}{a} \right) e^{-iE_1 t/\hbar} + \frac{1}{\sqrt{2}} \left(\frac{2}{a} \right)^{1/2} \sin\left(\frac{2\pi x}{a} \right) e^{-iE_2 t/\hbar} \tag{19}$$

4 Expectation Values of Observables Other than Energy

Let's now examine the time-dependent expectation value of some observable other than energy, given by the general $\hat{A}$ operator. For this approach, we will define the following eigenfunctions and

eigenvalues of both the $\hat{A}$ operator, as well as the Hamiltonian of the system, $\hat{H}$:

$$\hat{H}\psi_n(x) = E_n\psi_n(x) \tag{20}$$

$$\hat{A}\phi_n(x) = a_n\phi_n(x) \tag{21}$$

4.1 Expectation Values for Stationary States

We will start by preparing the system in the lowest energy eigenstate, $\psi_1(x)$, at $t = 0$:

$$\Psi_1(x,t) = \psi_1(x)e^{-i\omega_1 t} \tag{22}$$

We will now attempt to calculate the expected value for the $\hat{A}$ operator over time:

$$\langle A(t)\rangle = \int_{-\infty}^{\infty} dx \left[\psi_1^*(x)e^{+i\omega_1 t}\right] \hat{A} \left[\psi_1(x)e^{-i\omega_1 t}\right] \tag{23}$$

We run into a bit of a problem right away; it's not so obvious how $\hat{A}$ will act on the $\psi_n(x)$, which are eigenfunctions of $\hat{H}$ rather than $\hat{A}$. To evaluate this, we will need to restate our wavefunction in terms of the $\phi_n(x)$ eigenfunctions of $\hat{A}$. The $\phi_n(x)$ form a perfectly good basis set, so we can write:

$$\psi_1(x) \equiv \sum_{n=1}^{\infty} c_n\phi_n(x), \qquad \text{where} \quad c_n \equiv \int_{-\infty}^{\infty} \phi_n^*(x)\psi_1(x)dx \tag{24}$$

We can now write Eqn. 23 as:

$$\langle A(t)\rangle = \int_{-\infty}^{\infty} dx \left[\sum_{n=1}^{\infty} c_n^*\phi_n^*(x)e^{+i\omega_1 t}\right] \hat{A} \left[\sum_{m=1}^{\infty} c_m\phi_m(x)e^{-i\omega_1 t}\right] \tag{25}$$

$$= \int_{-\infty}^{\infty} dx \left[\sum_{n=1}^{\infty} c_n^*\phi_n^*(x)e^{+i\omega_1 t}\right] \left[\sum_{m=1}^{\infty} c_m a_m\phi_m(x)e^{-i\omega_1 t}\right] \tag{26}$$

$$= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} c_n^* c_m a_m \int_{-\infty}^{\infty} dx\ \phi_n^*(x)\phi_m(x)\cancel{e^{+i\omega_1 t}}\cancel{e^{-i\omega_1 t}} \tag{27}$$

$$= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} c_n^* c_m a_m \delta_{nm} = \sum_{m=1}^{\infty} |c_m|^2 a_m = \langle A(t=0)\rangle \neq f(t) \tag{28}$$

What we've found here is somewhat profound. When we initialize a system in an eigenstate of the Hamiltonian, the expectation value of *any* physical observable is unchanging in time! This makes some sense; we know that the spatial probability distribution of a stationary state is time-independent, so it follows that physical observables of the system will be fixed along with the probability distribution. That said, we do still have to evaluate the sum in Eqn. 28 to calculate this fixed value of $\langle A\rangle$, since we did not initialize the system in one of the eigenstates of $\hat{A}$.

4.2 Expectation Values for Non-Stationary States

This leaves us with one more interesting situation to explore: what happens in time if we initialize our system in an eigenstate of $\hat{A}$ that is not an energy eigenstate? Using the same eigenfunctions defined in Eqns. 20-21 above, let's prepare the following state:

$$\Psi(x,0) = \phi_1(x) \quad \text{at} \quad t = 0 \tag{29}$$

We first need to write down the time-dependence of this wavefunction; to do that we need to recast it in terms of energy eigenstates. Just as we could express our $\psi_n(x)$ energy eigenstates in the $\phi_n(x)$ basis of $\hat{A}$ eigenstates, we can express our $\phi_n(x)$ eigenstates in the basis of $\psi_n(x)$ eigenstates. So:

$$\phi_1(x) \equiv \sum_{n=1}^{\infty} b_n \psi_n(x), \qquad \text{where} \quad b_n \equiv \int_{-\infty}^{\infty} \psi_n^*(x)\phi_1(x)dx \tag{30}$$

$$\rightarrow \quad \Psi(x,t) = \sum_{n=1}^{\infty} b_n \psi_n(x) e^{-i\omega_n t} \tag{31}$$

So now we have a nice expression for the time-dependence of our wavefunction, and we can write down the time-dependent expectation value for $\langle A(t)\rangle$:

$$\langle A(t)\rangle = \int_{-\infty}^{\infty} dx \left[\sum_{n=1}^{\infty} b_n \psi_n(x) e^{-i\omega_n t}\right]^* \hat{A} \left[\sum_{m=1}^{\infty} b_m \psi_m(x) e^{-i\omega_m t}\right]^* \tag{32}$$

And we run into the same problem we faced in the previous section: the $\psi_n(x)$ basis is useful to write down time-dependence, but makes it mathematically difficult to apply $\hat{A}$ to our wavefunction. To proceed, would need to express each $\psi_n(x)$ in terms of the $\phi_n(x)$ basis again:

$$\psi_n(x) \equiv \sum_{q=1}^{\infty} c_{nq} \phi_q(x) \tag{33}$$

where the c_{nq} coefficients now have two labels, to represent the contribution of the q^{th} $\phi_q(x)$ eigenstate to the n^{th} $\psi_n(x)$ eigenstate.

Our $\langle A(t)\rangle$ calculation therefore becomes a bit of a nightmare to evaluate:

$$\langle A(t)\rangle = \int_{-\infty}^{\infty} dx \left[\sum_{n=1}^{\infty} b_n e^{-i\omega_n t} \sum_{q=1}^{\infty} c_{nq}\phi_q(x)\right]^* \hat{A} \left[\sum_{m=1}^{\infty} b_m e^{-i\omega_m t} \sum_{p=1}^{\infty} c_{mp}\phi_p(x)\right] \tag{34}$$

We'll stop here, since it should be clear already that this expression will include complicated sums as well as non-negligible time-dependent oscillations.

The big takeaway here is that if our system is not initially prepared in a stationary state of the Hamiltonian, the expectation values of any observable $\hat{A}$ other than energy will have complicated time dependence! It doesn't even matter if the system is prepared in an eigenfunction of the $\hat{A}$ operator at $t = 0$ – in this case you may have a simple expression for $\langle A\rangle$ at $t = 0$, but there will still be complicated time-dependence at all subsequent times.

The only caveat here is that $\langle A\rangle$ will be time-independent if $\hat{A}$ is special and commutes with (e.g. shares the same eigenfunctions as) the Hamiltonian! More on this next lecture!

5 Some Final Takeaways

A quick summary of what we've just learned:

1. The probability distribution $|\Psi(x,t)|^2$ will be *time-independent* if $\Psi(x,t)$ is an energy eigenstate (e.g. a stationary state).

2. The probability distribution $|\Psi(x,t)|^2$ will be *time-dependent* if $\Psi(x,t)$ is a superposition of energy eigenstates, with oscillations at the difference in frequencies between components present in the superposition.

3. The expected value of energy $\langle E \rangle = \int dx\, \Psi^*(x,t)\hat{H}\Psi^*(x,t)$ is *always time-independent*, whether the system is prepared in an energy eigenstate or in a superposition of energy eigenstates. Energy is special!

4. The expected value of an arbitrary operator $\langle A(t) \rangle$ will be *time-independent* if $\Psi(x,t)$ is an energy eigenstate and will in general be *time-dependent* if $\Psi(x,t)$ is a superposition of energy eigenstates.