Lecture 5: The Schrödinger Equation: Time Dependence, Stationary States, and the "Prime Directive"

A few comments on the uncertainty principle: Lecture #4 concluded with an outline of the deriva-tion of the uncertainty principle,

$$\Delta x \Delta p \geq \hbar/2$$

Before we move on to other topics, there are a couple of points to be made

1. $(\Delta x)^2$ was defined in that derivation as $\langle (\hat{x} - \langle \hat{x} \rangle)^2 \rangle$, which we recognize as the variance. Thus Δx is the standard deviation. Similarly for Δp. This a more precise statement of the uncertainty principle is $\sigma_x \sigma_p \geq \frac{\hbar}{2}$.

2. Our initial focus will be on 1D problems. The uncertainty principle in 3D reads

$$\sigma_x \sigma_{p_x} \geq \frac{\hbar}{2} \qquad \sigma_y \sigma_{p_y} \geq \frac{\hbar}{2} \qquad \sigma_z \sigma_{p_z} \geq \frac{\hbar}{2}$$

   That is, it applies to all three dimensions.

3. An extreme (not possible to realize experimentally!) but informative case is given by the delta function representation

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ipx/\hbar} d(\frac{p}{\hbar})$$

   So if x is perfectly known, the sum over momenta include all values, equally weighted.

4. The uncertainty relationship has an analog in energy and time. We consider the kinetic energy for our wave packet

$$\Delta E = \Delta \frac{p^2}{2m} = \frac{p}{m} \Delta p$$

So an uncertainty in momentum implies an uncertainty in energy. Now consider a measure-ment of the time it takes for the wave packet to pass a monitor that we set up to measure its passage. But as the width of the packet is uncertain by Δx, there must be a corresponding uncertainty in the time measurement,

$$\Delta t = \frac{\Delta x}{v} = \frac{m}{p} \Delta x \geq \frac{m}{p} \frac{\hbar}{2\Delta p} = \frac{\hbar}{2} \frac{1}{\Delta E} \quad \text{so} \quad \Delta E \, \Delta t \geq \frac{\hbar}{2}$$

Later in this lecture we will discuss QM states of definite energy – solutions of the time-independent Schrödinger equation. Because these states have a definite energy, they last forever – consistent with the uncertainty principle.

One particular stationary-state problem we will treat is the hydrogen atom. In our treatment we will neglect the coupling of these states to the emission of photons – then all of the states are stationary, and live forever. This is an idealization. In the real world, the $n = 2$ p state decays to the $1s$ ground state by emitting a photon, and the lifetime Δt of this state is known – this should be understood as the typical time one waits until a decay occurs (everything is uncertain in QM – there is a probability to decay in a given interval, but you cannot predict a priori when a given hydrogen atom will decay). Because the $2p$ does not live forever, its energy is uncertain, and the "fuzziness" of its energy is given by by $\sim \hbar/\Delta t$. The energies of the photons one would measured by repeatedly preparing hydrogen in the $2p$ state, then monitoring the decay, would reflect this uncertain energy of the $2p$ state.
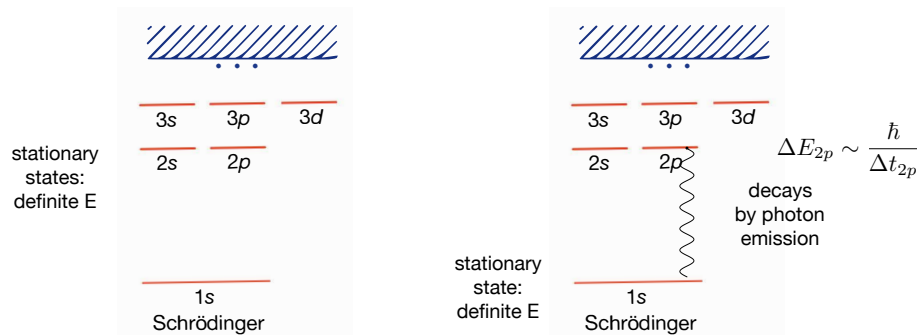

Figure 1: On the left, an idealized hydrogen atom neglecting the possibility of electromagnetic decay. All states – the QM orbits around the proton that the electron could occupy – would have definite energies and be stationary, persisting forever. On the right, a more complete QM treatment, where the possibility of electromagnetic transition from the $2p$ state to the $1s$ is included. Because the $2p$ state can decay, it lives for a finite time and consequently its energy is uncertain by a small amount, which would be reflected in the decay photon energies. In contrast, the $1s$ ground state cannot decay, and thus is a stationary state with definite energy. Note the $2s$ state – it is a very interesting because its electromagnetic decay is highly suppressed, so it lives a very long time. So its energy spread (called the width) is much smaller than that of the $2p$ state.

Whether a state is truly stationary or merely very long lived in a QM calculation thus can depend on the completeness of our quantum mechanics. It is very useful to adopt the stationary state description of hydrogen shown on the left of Fig. 1, then treat the additional physics on the right in a form of perturbation theory, as the spread in the state energies is very small. We will now discuss stationary states and their central role in solving quantum mechanics.

Another consequence of the energy-time uncertainty principle is tunneling – energy conservation can be violated if done so for a sufficiently short time. Historically Kelvin had argued that the Sun's energy was produced by its gradual gravitational contraction. But Darwin and others argued that the geologic record indicated an age of the earth that was too long for this theory to be viable. Eddington then postulated, prior to QM, that stars generate their energy through nuclear fusion, the combination of four protons into ^{4}He. The nuclear binding energy is the sun's energy – about 26 MeV per ^{4}He produced. But when this process is described classically, it requires too high a temperature: challenged on this point, Eddington famously told his critics "go and find a hotter place."

The issue was resolved in 1928 by George Gamow, who described quantum tunneling. The Sun's core is a 1.5 $\times 10^7$ K hot plasma consisting primarily of free protons and electrons – it is too hot for atoms to form. The burning of protons to form ^{4}He begins with the weak interaction step $p + p \rightarrow D + e^+ + \nu_e$. This reaction can occur only if two protons can approach each other within the range of the nuclear force, $\sim$ few $\times 10^{-15}$ m. But the protons are very low in energy, typically 10 keV, and they are held apart by their replusive Coulomb interaction, which reaches about 500 keV. As the figure shows, classically the protons would be prevented from approaching each other, stopping and turning around at the aptly named classical turning point – where the proton'ss initial kinetic energy is match by the repulsive Coulomb barrier.

But quantum mechanics allows barrier penetration – what this means is that when we solve quantum mechanics the wave function penetrates into the classically forbidden region. This penetration dies off exponentially, but if the barrier is significantly narrow, the probability of reaching the other side of the barrier, where a nucleus can form because of the attractive nuclear potential, is nonzero. In fact, we owe our existence to the details of this barrier – it is low enough to allow nuclear fusion, but slow enough to regulate nuclear burning in the Sun so that the fuel can last 10 By. And 5 By is apparently required for life to involve the intelligence it needs to figure this out,

through QM. One consequence of the tunneling: the Sun is a huge but very very slow reactor. Its energy production per cubic meter is comparable to that of a high-quality bicycle light.

This tunneling is consistent with the uncertainty principle: One can pass through the classically forbidden region as long as the time spent there is not more than $\sim \hbar/\Delta E$ where ΔE is the height of the barrier above the classical turning point energy.
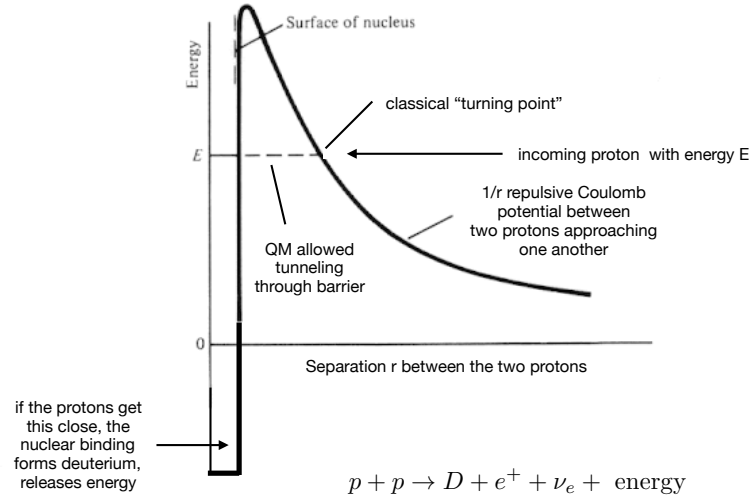

Figure 2: An illustration (not to scale) of barrier penetration by two approaching protons. Classically, proton energies in the solar core are too low to allow them to get close enough to feel the short-range attractive nuclear force, to fuse and form deuterium, while producing energy along with a positron e^+ and a solar neutrino ν_e. The classical turning point is where the protons come to rest, then are rejected (accelerating away from each other). In quantum mechanics, however, the protons can enter the classically forbidden region, if they do so for only a short time. While a detailed calculation requires one to compute the penetration of the wave function into the forbidden region (where it dies off exponentially), the ability to do so is encoded in the uncertaintry principle, $\Delta E \Delta t \geq \frac{\hbar}{2}$.

Stationary states and the time-independent Schrödinger equation: We begin with the the time dependent Schroedinger equation

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

The V here could in principle be a function of both x and t: $V(x,t)$. For example, the electron

might be in a cycling uniform magnetic field whose strength is being adjusted by an experimentalist. Here we assume this is not the case: V is assumed time independent, so $V = V(x)$ not $V = V(x,t)$. We then look for a solution of the form

$$\psi(x,t) = \phi(x)e^{-iEt/\hbar}$$

yielding the time-independent Schrödinger equation

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\phi(x) \equiv \hat{H}(x)\phi(x) = E\phi(x)$$

Note that we now have regular derivatives – $\phi(x)$ just depends on x. That is, we have reduced the problem to solving a differential equation only in x. In general when we solve this equation, including boundary conditions having to do with how a particle might be confined, etc., there will exist solutions only for specific energy eigenvalues E_i. That is, our solutions are $\{\psi_i(x)\}$ with energy eigenvalues $\{E_i\}$. These solutions are called the *stationary states*. The name comes from the fact that

$$|\psi_i(x,t)|^2 = |\phi_i(x)|^2$$

as the simple energy-phase cancels out. Thus for such states the probability for finding the particle is a region δx is stationary - it does not evolve in time. They are also states of definite energy – we have just seen that these two statements are consistent with the uncertainty principle. A system in a stationary state stays in that state forever, and only such states can have a precise energy.

> The probability density $|\Psi(x,t)|^2$ is independent of time for a stationary state.

Stationary states and their definite energies: We have stated above that stationary states have a definite energy and thus persist for all time, but can we prove that? Yes: that's easy

$$\langle\hat{H}\rangle = \int_{-\infty}^{\infty}\phi^*(x)\hat{H}\phi(x)dx = E\int_{-\infty}^{\infty}\phi^*(x)\phi(x)dx = E \quad \text{and} \quad \langle\hat{H}^2\rangle = \int_{-\infty}^{\infty}\phi^*(x)\hat{H}\hat{H}\phi(x)dx = E^2$$

Therefore

$$\sigma_H \equiv \sqrt{\langle\hat{H}^2\rangle - \langle\hat{H}\rangle^2} = 0$$

The energy has zero standard deviation - no width. These indeed are states of definite energy.

This means that if you measure the energy of a stationary state, you will always get the same answer.

Stationary states as an orthonormal basis: We will do several calculations where we find all of the states of the time-independent Schrödinger equation – the first being the infinite square will. Most examples will be problems where a particle occupies some region of space and where the "outcome" of a measurement could be a specific particle location x_i (to within the tolerance allowed by our measuring instrument). As there are an infinite number of outcomes, it should not be surprising that the number of stationary states is also infinite. These (properly normalized) states $\{\phi_i\}$ with energies $\{E_i\}$ are solutions of the time-independent Schrödinger equation for a given potential $V(x)$. We argue below that they form an orthonormal basis. We first show that any two stationary-state wave functions belonging to different energies are orthogonal – which requires us to define "orthogonality" for wave functions.

By assumption we have

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\phi_1(x) \equiv \hat{H}(x)\phi_1(x) = E_1\phi_1(x) \quad \left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\phi_2(x) \equiv \hat{H}(x)\phi_2(x) = E_2\phi_2(x)$$

Multiplying on the left, we can then write

$$\phi_2^*(x)\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\phi_1(x) = E_1\phi_2^*(x)\phi_1(x) \quad \text{and}$$

$$\phi_1^*(x)\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\phi_2(x) = E_2\phi_1^*(x)\phi_2(x) \Rightarrow \phi_1(x)\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\phi_2^*(x) = E_2\phi_1(x)\phi_2^*(x)$$

where we conjugated to get the RHS of the second line. Now subtract and integrate over all x

$$\int_{-\infty}^{\infty}\left[\phi_2^*(x)\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\phi_1(x) - \phi_1(x)\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\phi_2^*(x)\right]dx = (E_1-E_2)\int_{-\infty}^{\infty}\phi_1(x)\phi_2^*(x)dx$$

Notice that the second term on the right can be partially integrated twice to get

$$\phi_1(x)\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\phi_2^*(x)\right]dx = \phi_2^*(x)\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\phi_1(x)dx$$

which is identical to the first term. So we find

$$0 = (E_1 - E_2)\int_{-\infty}^{\infty}\phi_1(x)\phi_2^*(x)dx \Rightarrow \int_{-\infty}^{\infty}\phi_1(x)\phi_2^*(x)dx = 0 \text{ if } E_1 \neq E_2$$

The vanishing integral above is what we mean by the orthogonality of two functions. You should be able to see that by breaking up discretizing the integral – approximating it as a finite sum over

the region L in x where our wave packet is found – that this integral is just a generalization of the standard dot product of two finite-dimensional complex vectors.

Specifically, consider two orthonomal vectors in the plane,. We all know

$$\hat{x} \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \hat{y} \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad \text{then} \qquad \hat{x} \cdot \hat{x} = \hat{y} \cdot \hat{y} = 1 \quad \text{and} \quad \hat{x} \cdot \hat{y} = 0$$

We can generate similar but complex vectors by rotating the basis by 45 degrees – some of you may recognize these as the spherical unit vectors that carry good angular momentum

$$\hat{e}_1 \equiv -\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \qquad \hat{e}_{-1} \equiv \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \qquad \hat{e}_1^* \cdot \hat{e}_1 = \hat{e}_{-1}^* \cdot \hat{e}_{-1} = 1 \quad \text{and} \quad \hat{e}_1^* \cdot \hat{e}_{-1} = \hat{e}_{-1}^* \cdot \hat{e}_1 = 0$$

Our orthonormal stationary-state function basis is exactly the generalization of this, but to vectors of infinite length – which requires us to integrate rather than do a finite sum over components

> Normalized stationary-state solutions form an orthonormal basis:
> $$\int_{-\infty}^{\infty} \phi_i^*(x)\phi_i(x)dx = 1 \qquad \int_{-\infty}^{\infty} \phi_j^*(x)\phi_i(x)dx = 0, \ i \neq j$$

But there was an exception noted above – our conclusion of orthogonality depended on the absence of degeneracy, that $E_1 \neq E_2$. What if that is not the case? Again, we know the solution from our experience with ordinary vectors: The Gram-Schmidt process. If we have two normalized vectors $\vec{u}$ and $\vec{v}$ that are linearly independent but not orthogonal, then we can form the new orthonormal basis by defining

$$\vec{u}_1 \equiv \vec{u} \qquad \vec{u}_2 = \vec{v} - \vec{u} \cdot \vec{v} \, \vec{u} \quad \text{so that} \quad \vec{u}_1 \cdot \vec{u}_2 = \vec{u} \cdot \vec{v} - \vec{u} \cdot \vec{v} = 0$$

then normalizing $\vec{u}_2$. We can do the same if we have two normalized functions $\phi_1(x)$ and $\phi_2(x)$ that are not orthogonal, with the same energy eigenvalue E

$$\phi_1(x) \rightarrow \phi_1(x) \qquad \phi_2(x) \rightarrow \phi_2(x) - \phi_1(x) \int_{-\infty}^{\infty} \phi_1^*(y)\phi_2(y)dy \equiv \phi_2'(x)$$

Then

$$\int_{-\infty}^{\infty} \phi_1^*(x)\phi_2'(x)dx = \int_{-\infty}^{\infty} \phi_1^*(x)\phi_2(x)dx - \int_{-\infty}^{\infty} \phi_1^*(x)\phi_1(x)dx \int_{-\infty}^{\infty} \phi_1^*(y)\phi_2(y)dy = 0$$

So if we normalize $\phi_2'(x)$ we then have two orthogonal basis functions $\phi_1(x)$, $\phi_2'(x)$, and by the principle of superposition, $\phi_2'(x)$ is also a solution of the time-independent Schrödinger equation with eigenvalue E. As the Gram-Schmidt procedure can be carried out for an arbitrary number of vectors within a degenerate subspace, we are done.

In practice the tedious Gram-Schmidt process is almost never needed: degeneracies usually arise for a reason known to the quantum mechanic, and she chooses wave function labels that reflect the physics. As we will discuss later, this amounts to finding operators other than $\hat{H}$ that commute with $\hat{H}$. If we find such an operator, we can label our eigenstates by the quantum numbers of both $\hat{H}$ (energy) and this other operator. These other labels distinguish the degenerate state, and guarantee their orthogonality. For example, the $n = 2$ levels of the hydrogen atom are four-fold degenerate (ignoring electron spin). But we use the commuting operators $(\hat{H}, \hat{L}, \hat{L}_z)$ to label the states $2s$ and $2p$, the latter with three possible $\hat{L}_z$ (magnetic) quantum numbers 1,0, and -1. So labeled, all four states will be orthogonal. This should sound important to you, and indeed it is – so we will be talking a lot about finding a maximal set of mutually commuting operators that can provided goods quantum labels for wave functions.

Stationary states form a complete basis: The basis just formed above, $\{E_i, \phi_i(x), I = 1, \cdots, \infty\}$, is a *complete orthonormal basis* for the time independent Schrödinger equation. We will not provide a general proof here, but we will encounter bases that soon that you will recognize as complete, such as the Fourier series. Consequently any general function in the space can be expanded int term of the basis of stationary states, with coefficients that follow from the orthogonality condition,

> Expansion of an arbitrary wave function $\Phi(x)$ in terms of the stationary states, a complete orthonormal basis:
>
> $$\Phi(x) = \sum_{i=1}^{\infty} c_i \phi_i x) \qquad c_i = \int_{-\infty}^{\infty} \phi_i^*(x) \Phi(x) dx$$

The "Prime Directive": Finally we come a result so important that we can dub it, in homage to Star Trek, the *prime directive.*

Suppose some experimentalist has started up some experiment at time t_0 that is governed by QM

– perhaps some interesting wave packet $\Psi(x, t_0)$ that is arbitrary, not corresponding to any one of the stationary states. This wave packet might describe the possible position outcomes for a particle, should we interrogate it at time t_0. The wave function would be normalized – $\int_{-\infty}^{\infty} |\Psi(x, t_0)|^2 dx = 1$. Because the stationary states form a complete set, we know

$$\Psi(x, t_0) = \sum_i c_i \phi_i(x)$$

But the wave packet is normalized and the stationary states are an orthonormal set. So

$$1 = \int_{-\infty}^{\infty} |\Psi(x, t_0)|^2 dx = \sum_{j=1}^{\infty} \sum_{i=1}^{\infty} c_j^* c_i \int_{-\infty}^{\infty} \phi_j^*(x) \phi_i(x) dx = \sum_{j=1}^{\infty} \sum_{i=1}^{\infty} c_j^* c_i \delta_{ji} = \sum_{i=1}^{\infty} |c_i|^2$$

So $|c_i|^2$ is the initial probability of being in the ith stationary state. To simplify notation let's set our clock to start at t_0, so $t_0 = 0$. Then consider the wave function

$$\Psi(x, t) = \sum_i c_i \phi_i(x) e^{-iE_i t/\hbar}, \quad t > 0$$

Plugging this into the time-dependent Schroedinger equation (superposition principle) yields

$$\sum_i E_i c_i \phi_i(x) e^{-iE_i t/\hbar} = \sum_i E_i c_i \phi_i(x) e^{-iE_i t/\hbar}$$

So we have a solution. Consequently we have what you might call the *prime directive* in quantum mechanics:

> The prime directive: Let $\{\phi_i(x)\}$ and $\{E_i\}$ denote the complete set of stationary-state solutions and eigenvalues, that is
>
> $$\left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \phi_i(x) = E_i \phi_i(x)$$
>
> Given an wave packet at $t = 0$, $\Psi(x, t = 0) = \sum_i c_i \phi_i(x)$, then the solution of the time dependent Schroedinger equation is
>
> $$\Psi(x, t) = \sum_i c_i \phi_i(x) e^{-iE_i t/\hbar}$$

This is powerful result. It implies that apart from the special case of a pure stationary state, the stationary components of wave functions propagate with different phases, interfering in a time-dependent way. Thus the probability at some point x, $|\Psi(x,t)|^2$, is not fixed – not stationary – but instead varies in time. But it also states the probabilities $|c_i|^2$ do not evolve in time - all of the physics comes from time-varying interference.

According to the primary directive we should

1. Find the stationary states and their eigenvalues;

2. Exploit their simplicity to express the time evolution of an arbitrary wave packet

So we now roll up our sleeves and start this program.