

## Time dependence of amplitudes: Schroedinger Equation

### *Review*

In previous discussion, we have seen that relative phases matter. If an apparatus is simple in one base set where it has only diagonal amplitudes with different phases, then it can have very complicated, nondiagonal amplitudes in another base set. For states with definite energy, amplitudes take a simple form

$$\langle \varphi, t | E \rangle = e^{-iEt/\hbar}.$$

In a basis where the base states  $|i\rangle$  have definite energy  $E_i$ , the time evolution "apparatus" also has a simple diagonal form

$$\langle j | U(t) | i \rangle = \delta_{ij} e^{-iE_i t / \hbar}.$$

It must be emphasized that this simple diagonal form holds only for a base set with definite-energy base states. In any other basis, the  $U(t)$  amplitudes will be nondiagonal and complicated. Also, although in the definite-energy basis time evolution is a simple multiplication by phase factors, those phase factors are different for different states, so in another basis, the physical consequences of time evolution will be more interesting.

So why don't we just stick to the definite-energy basis? There are a couple answers to that question. First, in most cases, we do not know in the beginning what the definite-energy states are. A lot of effort is devoted to finding them. Second, even if we know them, they are not the states that usually appear as the initial or final states of experiments that we do in the lab. (Since the probabilities associated with definite-energy states do not change in time, experiments with only definite-energy states would be kind of boring.) Thus, we need to be able to talk about time dependence in any basis. That is where the *Schroedinger equation* comes in.

### *Schroedinger equation*

In this section, I will derive the Schroedinger equation. It is a consequence of the assumption that we have already made about the form of the time evolution "apparatus" in a definite-energy basis. (I will start referring to a general apparatus as an *operator*. This is the usual terminology in quantum mechanics. It is called that because it operates on states and somehow changes them into different states.)

I need a little notation. In this section, I will use  $|i\rangle$  to indicate the states of any base set. I will use  $|I\rangle$ , with an uppercase index to indicate the states of the definite-energy basis. Let  $\langle i, t | = \langle i | U(t) | \varphi \rangle$  be the amplitude to find the quanton in state  $i$  at time  $t$ . The Schroedinger equation is a differential equation for  $\langle i, t |$ . The derivation uses two facts. The real input is form of  $U(t)$  in the definite-energy basis. The other fact, which is used repeatedly, is the identity

$$\langle \varphi | \chi \rangle = \sum_i \langle \varphi | i \rangle \langle i | \chi \rangle.$$

To take advantage of what I do know, I put  $U(t)$  into the  $|I\rangle$  basis.

$$\begin{aligned}\psi(i,t) &= \langle i|U(t)|\psi\rangle = \sum_{I,J} \langle i|I\rangle \langle I|U(t)|J\rangle \langle J|\psi\rangle \\ &= \sum_{I,J} \langle i|I\rangle \delta_{IJ} e^{-iE_I t/\hbar} \langle J|\psi\rangle = \sum_I \langle i|I\rangle e^{-iE_I t/\hbar} \langle I|\psi\rangle.\end{aligned}$$

The next step is to simply take the time derivative of this expression. Notice that all the time dependence is displayed explicitly, so this is easy to do.

$$\begin{aligned}i\hbar \frac{\partial \psi(i,t)}{\partial t} &= \sum_I \langle i|I\rangle E_I e^{-iE_I t/\hbar} \langle I|\psi\rangle \\ &= \sum_{I,J} \langle i|I\rangle E_I \langle I|J\rangle e^{-iE_I t/\hbar} \langle J|\psi\rangle = \sum_{I,J} \langle i|I\rangle E_I \langle I|U(t)|J\rangle \langle J|\psi\rangle \\ &= \sum_I \langle i|I\rangle E_I \langle I|U(t)|\psi\rangle = \sum_{j,I} \langle i|I\rangle E_I \langle I|j\rangle \langle j|U(t)|\psi\rangle \\ &= \sum_{j,I} \langle i|I\rangle E_I \langle I|j\rangle \psi(j,t)\end{aligned}$$

The next step is to give a special name to the combination that appears in the last equality above

$$\langle i|H|j\rangle = \sum_I \langle i|I\rangle E_I \langle I|j\rangle$$

These are the amplitudes for the operator  $H$ , which is called the *Hamiltonian*. From this definition, it is easy to show that

$$\langle j|H|i\rangle^* = \langle i|H|j\rangle$$

An operator with this property is said to be *hermitian*. So finally

$$i\hbar \frac{\partial \psi(i,t)}{\partial t} = \sum_j \langle i|H|j\rangle \psi(j,t).$$

This is the Schrodinger equation. It is a differential equation for the time evolution of the wave function. Everything in the equation now refers to an arbitrary base set. There are as many equations as there are base states, *i.e.* one equation for each value of  $i$ . These are not independent equations; they are coupled together by the Hamiltonian. So in the general case, it is a difficult problem.

There are two issues to address. First, you must figure out what Hamiltonian to use for the problem at hand. Second, you need to solve the equation. Neither part is easy. For the solution part, you should think of it as an initial value problem like Newton's Second Law. If we know the initial conditions, *i.e.*  $(j,0)$  for all  $j$ , then we can use the Schrodinger equation to get the wave function  $(i,t)$  at a later time. (Easier said than done.) In some problems, you know what Hamiltonian to use because other people have already figured it out. You are applying it to the problem you want to solve. In other cases, nobody has figured it out yet. Then you make a guess, work out the consequences, and compare with experiment. If you are the first to figure out the

Hamiltonian that works for a big area of physics, you can get a Nobel Prize! We will do problems where the Hamiltonian is known.

In all the cases that will be of interest to us,  $H$  itself does not depend on time. That just says that the quantum system that is being described is interacting according to force laws that are independent of time and with an external environment that is static. All the time dependence comes from changes in the system itself.

### Examples

#### Example 1

The simplest case is if there is only one state the quanton can be in. Then there is only one base state. The Schroedinger becomes

$$i\hbar \frac{\partial \psi(t)}{\partial t} = H\psi(t) .$$

In this case,  $H$  is just a number, and the solution is

$$\psi(t) = e^{-iHt/\hbar} \psi(0) .$$

(You should be able to check that if you put this into the differential equation, the left hand side is equal to the right hand side.) We see that  $H$  should be identified with the energy  $E$  of the state. So it might make more sense to call  $H$  the energy operator, but for historical reasons, it is called the Hamiltonian operator. Also, we could have guessed the solution in this case. Since there is only one state, there is no other state for the quanton to move into, and the probability to be in the one state must be a constant. Thus, it must be a stationary state, and we already know stationary states have this time dependence.

#### Example 2

The next simplest situation has just two base states. The two-state problem is very interesting because it is a good approximation to some nice physics problems and because it can be completely solved relatively easily. It is a bit simpler to change to a matrix notation with  $H_{ij} = \langle i | H | j \rangle$  and  $\psi_i(t) = \langle i | \psi(t) \rangle$ . The most general form of  $H$  is

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{12}^* & H_{22} \end{pmatrix}$$

with the diagonal elements real and  $H_{12} = H_{21}^*$  an arbitrary complex number. The Schroedinger equation is now

$$i\hbar \frac{\partial \psi_1}{\partial t} = H_{11}\psi_1 + H_{12}\psi_2$$

$$i\hbar \frac{\partial \psi_2}{\partial t} = H_{21}\psi_1 + H_{22}\psi_2$$

Let's start with some special cases.

*Example 2a*

Suppose that  $H_{12} = H_{21} = 0$ . Then the two equations uncouple.

$$i\hbar \frac{\partial \psi_1}{\partial t} = H_{11} \psi_1$$

$$i\hbar \frac{\partial \psi_2}{\partial t} = H_{22} \psi_2$$

It is easy to solve these separately because each is just like Example 1. The result is

$$\psi_1(t) = e^{-iH_{11}t/\hbar} \psi_1(0) = e^{-iE_1t/\hbar} \psi_1(0)$$

$$\psi_2(t) = e^{-iH_{22}t/\hbar} \psi_2(0) = e^{-iE_2t/\hbar} \psi_2(0)$$

Again, we could have guessed this. In the basis where  $H$  is diagonal, the base states are stationary states. This describes the spin-1/2 particle in a magnetic field in the  $z$ -direction in the  $z$ -base states with  $E_1 = -\mu B$  and  $E_2 = +\mu B$ .

*Example 2b*

Now suppose that  $H_{11} = H_{22} = E_0$ , and  $H_{12} = H_{21} = -A$  with  $A$  real. This can be used to get a rough approximation to the hydrogen molecular ion. It is two protons (hydrogen nuclei) and one electron. The approximation is to say that the electron can be in its lowest hydrogen state on the first proton; that's base state 1. Or it can be in the lowest state by proton 2 as base state 2. Other possibilities are ignored. Also if it is by proton 1, it will not stay there. It has an amplitude  $H_{21} = -A$  per unit time to jump over to proton 2. When it's at proton 2, it can also jump back to proton 1. In this case the equations are coupled.

$$i\hbar \frac{\partial \psi_1}{\partial t} = E_0 \psi_1 - A \psi_2$$

$$i\hbar \frac{\partial \psi_2}{\partial t} = -A \psi_1 + E_0 \psi_2$$

There are lots of ways to solve these equations. Here is one way that will also be useful later. We assume that there are two stationary states and try to find out what they are. Thus we look for a solution with the time dependence

$$\psi_i(t) = e^{-iEt/\hbar} a_i$$

with  $a_1$  and  $a_2$  constant. Substituting that in and removing a common factor of  $e^{-iEt/\hbar}$  gives the equations

$$\begin{aligned} E a_1 &= E_0 a_1 - A a_2 & \text{or} & & 0 &= (E_0 - E) a_1 - A a_2 \\ E a_2 &= -A a_1 + E_0 a_2 & & & 0 &= (E_0 - E) a_2 - A a_1 \end{aligned}$$

This is great progress. We have reduced the differential equations to a problem in algebra! Find the solution to a pair of coupled, homogeneous linear equations. There is a solution iff the determinant vanishes.

$$0 = (E_0 - E)^2 - A^2$$

This has two solutions

$$E = E_{\pm} = E_0 \pm A .$$

So now we have the energies, but it is also nice to have the stationary states themselves. That means that we want these definite energy states expressed as linear combinations of the original base states  $|1\rangle$  and  $|2\rangle$ , *i.e.* we want the coefficients  $a_1$  and  $a_2$ . However, can we really hope to get both the  $a$ 's completely determined? The pair of equations

$$0 = (E_0 - E)a_1 - Aa_2$$

$$0 = (E_0 - E)a_2 - Aa_1$$

is homogeneous of degree one in the  $a$ 's, *i.e.* each term has exactly one power of an  $a$ . So if some pair  $a_1, a_2$  is a solution, then so is the pair  $za_1, za_2$  with  $z$  any complex number. The  $z$  just appears as a common factor in all the terms. Thus the best I can hope to do is get the ratio of  $a_1$  and  $a_2$ . But that is actually OK. If  $z = |z|e^{i\phi}$ , then the  $z$  is just an overall phase for the state and not a relative phase for the two parts. It does not matter, and I can select it to be anything I want. I will select it so that  $a_1$  is real. The other freedom in  $z$  is  $|z|$ , but that is removed because I must select the  $a$ 's so that the states are normalized  $\langle + | + \rangle = 1$ . Or equivalently the probability to be in state  $|1\rangle$  plus the probability to be in state  $|2\rangle$  must equal one because there are no other possibilities.  $|a_1|^2 + |a_2|^2 = 1$ .

To get the relation between the  $a$ 's for the state with  $E = E_+$ , select either of the two equations above and substitute for  $E$ . I use the first one. That becomes

$$0 = (E_0 - [E_0 + A])a_1 - Aa_2 \quad \text{or} \quad 0 = -a_1 - a_2 .$$

Thus  $a_2 = -a_1$ . Similarly for  $E = E_-$ ,  $a_2 = a_1$ . So for  $E_+$ , we can take  $a_1 = -a_2 = 1/\sqrt{2}$  and for  $E_-$ , we can take  $a_1 = a_2 = 1/\sqrt{2}$ . Putting it all together, the stationary base states are

$$|+\rangle = \frac{1}{\sqrt{2}} (|1\rangle - |2\rangle) \quad \text{with energy } E_+ = E_0 + A$$

$$|-\rangle = \frac{1}{\sqrt{2}} (|1\rangle + |2\rangle) \quad \text{with energy } E_- = E_0 - A$$

So much for the mathematics. What about the physics problem? Remember that? This is supposed to describe  $\text{H}_2^+$ . we see that there are two stationary states. For positive  $A$ ,  $|-\rangle$  has the lower energy, and it gets more lower as  $A$  gets bigger. Remember that  $-A$  is the amplitude for the electron to jump from one proton to the other. We can expect that when the protons are closer it is easier to jump and  $A$  is bigger in magnitude. So as the protons get closer, the energy of the lower states gets lower. This is the behavior of an attractive interaction. Thus when the protons share the electron in the lower energy state, they are attracted to each other. This is the interaction that keeps the molecule from falling apart!

This effect generalizes in many ways. In quantum field theory, all forces are understood as the exchange of particles. For example, the electromagnetic force comes from the exchange of photons.