

You remember that $C_i(t)$ is the amplitude $\langle i | \psi \rangle$ to find the state ψ in one of the base states i (at the time t). So Eq. (8.39) tells us how each of the coefficients $\langle i | \psi \rangle$ varies with time. But that is the same as saying that Eq. (8.39) tells us how the state ψ varies with time, since we are describing ψ in terms of the amplitudes $\langle i | \psi \rangle$. The variation of ψ in time is described in terms of the matrix H_{ij} , which has to include, of course, the things we are doing to the system to cause it to change. If we know the H_{ij} —which contains the physics of the situation and can, in general, depend on the time—we have a complete description of the behavior in time of the system. Equation (8.39) is then the quantum mechanical law for the dynamics of the world.

(We should say that we will always take a set of base states which are fixed and do not vary with time. There are people who use base states that also vary. However, that's like using a rotating coordinate system in mechanics, and we don't want to get involved in such complications.)

8-5 The Hamiltonian matrix

The idea, then, is that to describe the quantum mechanical world we need to pick a set of base states i and to write the physical laws by giving the matrix of coefficients H_{ij} . Then we have everything—we can answer any question about what will happen. So we have to learn what the rules are for finding the H 's to go with any physical situation—what corresponds to a magnetic field, or an electric field, and so on. And that's the hardest part. For instance, for the new strange particles, we have no idea what H_{ij} 's to use. In other words, no one knows the *complete* H_{ij} for the whole world. (Part of the difficulty is that one can hardly hope to discover the H_{ij} when no one even knows what the base states are!) We do have excellent approximations for nonrelativistic phenomena and for some other special cases. In particular, we have the forms that are needed for the motions of electrons in atoms—to describe chemistry. But we don't know the full true H for the whole universe.

The coefficients H_{ij} are called *the Hamiltonian matrix* or, for short, just *the Hamiltonian*. (How Hamilton, who worked in the 1830's, got his name on a quantum mechanical matrix is a tale of history.) It would be much better called *the energy matrix*, for reasons that will become apparent as we work with it. So the problem is: Know your Hamiltonian!

The Hamiltonian has one property that can be deduced right away, namely, that

$$H_{ij}^* = H_{ji}. \quad (8.40)$$

This follows from the condition that the total probability that the system is in *some* state does not change. If you start with a particle—an object or the world—then you've still got it as time goes on. The total probability of finding it somewhere is

$$\sum_i |C_i(t)|^2,$$

which must not vary with time. If this is to be true for any starting condition ϕ , then Eq. (8.40) must also be true.

As our first example, we take a situation in which the physical circumstances are not changing with time; we mean the *external* physical conditions, so that H is independent of time. Nobody is turning magnets on and off. We also pick a system for which only one base state is required for the description; it is an approximation we could make for a hydrogen atom at rest, or something similar. Equation (8.39) then says

$$i\hbar \frac{dC_1}{dt} = H_{11}C_1. \quad (8.41)$$

Only one equation—that's all! And if H_{11} is constant, this differential equation is easily solved to give

$$C_1 = (\text{const})e^{-(i/\hbar)H_{11}t}. \quad (8.42)$$

This is the time dependence of a state with a definite energy $E = H_{11}$. You see why H_{ij} ought to be called the energy matrix. It is the generalization of the energy for more complex situations.

Next, to understand a little more about what the equations mean, we look at a system which has two base states. Then Eq. (8.39) reads

$$i\hbar \frac{dC_1}{dt} = H_{11}C_1 + H_{12}C_2, \quad (8.43)$$

$$i\hbar \frac{dC_2}{dt} = H_{21}C_1 + H_{22}C_2.$$

If the H 's are again independent of time, you can easily solve these equations. We leave you to try for fun, and we'll come back and do them later. Yes, you can solve the quantum mechanics without knowing the H 's, so long as they are independent of time.

8-6 The ammonia molecule

We want now to show you how the dynamical equation of quantum mechanics can be used to describe a particular physical circumstance. We have picked an interesting but simple example in which, by making some reasonable guesses about the Hamiltonian, we can work out some important—and even practical—results. We are going to take a situation describable by two states: the ammonia molecule.

The ammonia molecule has one nitrogen atom and three hydrogen atoms located in a plane below the nitrogen so that the molecule has the form of a pyramid, as drawn in Fig. 8-1(a). Now this molecule, like any other, has an infinite number of states. It can spin around any possible axis; it can be moving in any direction; it can be vibrating inside, and so on, and so on. It is, therefore, not a two-state system at all. But we want to make an approximation that all other states remain fixed, because they don't enter into what we are concerned with at the moment. We will consider only that the molecule is spinning around its axis of symmetry (as shown in the figure), that it has zero translational momentum, and that it is vibrating as little as possible. That specifies all conditions except one: *there are still the two possible positions for the nitrogen atom*—the nitrogen may be on one side of the plane of hydrogen atoms or on the other, as shown in Fig. 8-1(a) and (b). So we will discuss the molecule as though it were a two-state system. We mean that there are only two states we are going to really worry about, all other things being assumed to stay put. You see, even if we know that it is spinning with a certain angular momentum around the axis and that it is moving with a certain momentum and vibrating in a definite way, there are still two possible states. We will say that the molecule is in the state $|1\rangle$ when the nitrogen is "up," as in Fig. 8-1(a), and is in the state $|2\rangle$ when the nitrogen is "down," as in (b). The states $|1\rangle$ and $|2\rangle$ will be taken as the set of base states for our analysis of the behavior of the ammonia molecule. At any moment, the actual state $|\psi\rangle$ of the molecule can be represented by giving $C_1 = \langle 1 | \psi \rangle$, the amplitude to be in state $|1\rangle$, and $C_2 = \langle 2 | \psi \rangle$, the amplitude to be in state $|2\rangle$. Then, using Eq. (8.8) we can write the state vector $|\psi\rangle$ as

$$|\psi\rangle = |1\rangle\langle 1 | \psi \rangle + |2\rangle\langle 2 | \psi \rangle$$

or

$$|\psi\rangle = |1\rangle C_1 + |2\rangle C_2. \quad (8.44)$$

Now the interesting thing is that if the molecule is known to be in some state at some instant, it will *not* be in the same state a little while later. The two C -coefficients will be changing with time according to the equations (8.43)—which hold for any two-state system. Suppose, for example, that you had made some observation—or had made some selection of the molecules—so that you *know* that the molecule is *initially* in the state $|1\rangle$. At some later time, there is some chance that it will be found in state $|2\rangle$. To find out what this chance is, we have to solve the differential equation which tells us how the amplitudes change with time.

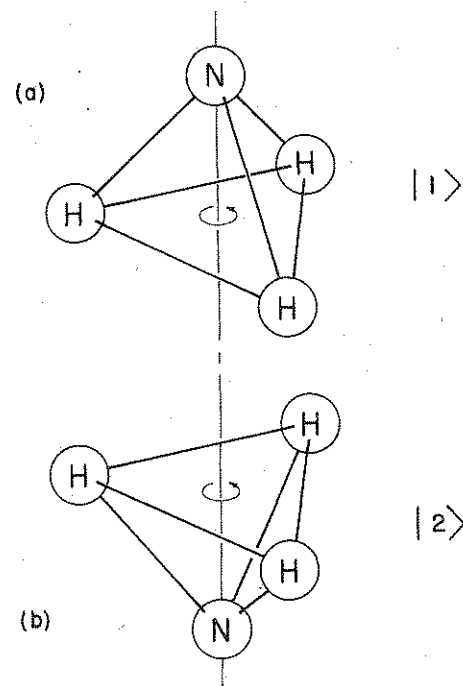


Fig. 8-1. Two equivalent geometric arrangements of the ammonia molecule.

The only trouble is that we don't know what to use for the coefficients H_{ij} in Eq. (8.43). There are some things we *can* say, however. Suppose that once the molecule was in the state $|1\rangle$ there was no chance that it could ever get into $|2\rangle$, and vice versa. Then H_{12} and H_{21} would both be zero, and Eq. (8.43) would read

$$i\hbar \frac{dC_1}{dt} = H_{11}C_1, \quad i\hbar \frac{dC_2}{dt} = H_{22}C_2.$$

We can easily solve these two equations; we get

$$C_1 = (\text{const})e^{-(i/\hbar)H_{11}t}, \quad C_2 = (\text{const})e^{-(i/\hbar)H_{22}t}. \quad (8.45)$$

These are just the amplitudes for *stationary* states with the energies $E_1 = H_{11}$ and $E_2 = H_{22}$. We note, however, that for the ammonia molecule the two states $|1\rangle$ and $|2\rangle$ have a definite symmetry. If nature is at all reasonable, the matrix elements H_{11} and H_{22} must be equal. We'll call them both E_0 , because they correspond to the energy the states would have if H_{12} and H_{21} were zero. But Eqs. (8.45) do not tell us what ammonia really does. It turns out that it is possible for the nitrogen to push its way through the three hydrogens and flip to the other side. It is quite difficult; to get half-way through requires a lot of energy. How can it get through if it hasn't got enough energy? There is *some* amplitude that it *will* penetrate the energy barrier. It is possible in quantum mechanics to sneak quickly across a region which is illegal energetically. There is, therefore, some small amplitude that a molecule which starts in $|1\rangle$ will get to the state $|2\rangle$. The coefficients H_{12} and H_{21} are not really zero. Again, by symmetry, they should both be the same—at least in magnitude. In fact, we already know that, in general, H_{ij} must be equal to the complex conjugate of H_{ji} , so they can differ only by a phase. It turns out, as you will see, that there is no loss of generality if we take them equal to each other. For later convenience we set them equal to a negative number; we take $H_{12} = H_{21} = -A$. We then have the following pair of equations:

$$i\hbar \frac{dC_1}{dt} = E_0C_1 - AC_2, \quad (8.46)$$

$$i\hbar \frac{dC_2}{dt} = E_0C_2 - AC_1. \quad (8.47)$$

These equations are simple enough and can be solved in any number of ways. One convenient way is the following. Taking the sum of the two, we get

$$i\hbar \frac{d}{dt} (C_1 + C_2) = (E_0 - A)(C_1 + C_2),$$

whose solution is

$$C_1 + C_2 = ae^{-(i/\hbar)(E_0 - A)t}. \quad (8.48)$$

Then, taking the difference of (8.46) and (8.47), we find that

$$i\hbar \frac{d}{dt} (C_1 - C_2) = (E_0 + A)(C_1 - C_2),$$

which gives

$$C_1 - C_2 = be^{-(i/\hbar)(E_0 + A)t}. \quad (8.49)$$

We have called the two integration constants a and b ; they are, of course, to be chosen to give the appropriate starting condition for any particular physical problem. Now, by adding and subtracting (8.48) and (8.49), we get C_1 and C_2 :

$$C_1(t) = \frac{a}{2} e^{-(i/\hbar)(E_0 - A)t} + \frac{b}{2} e^{-(i/\hbar)(E_0 + A)t}, \quad (8.50)$$

$$C_2(t) = \frac{a}{2} e^{-(i/\hbar)(E_0 - A)t} - \frac{b}{2} e^{-(i/\hbar)(E_0 + A)t}. \quad (8.51)$$

They are the same except for the sign of the second term.

We have the solutions; now what do they mean? (The trouble with quantum mechanics is not only in solving the equations but in understanding what the solutions mean!) First, notice that if $b = 0$, both terms have the same frequency $\omega = (E_0 - A)/\hbar$. If everything changes at one frequency, it means that the system is in a state of definite energy—here, the energy $(E_0 - A)$. So there is a stationary state of this energy in which the two amplitudes C_1 and C_2 are equal. We get the result that *the ammonia molecule has a definite energy $(E_0 - A)$ if there are equal amplitudes for the nitrogen atom to be “up” and to be “down.”*

There is another stationary state possible if $a = 0$; both amplitudes then have the frequency $(E_0 + A)/\hbar$. So there is another state with the definite energy $(E_0 + A)$ if the two amplitudes are equal but with the opposite sign; $C_2 = -C_1$. These are the only two states of definite energy. We will discuss the states of the ammonia molecule in more detail in the next chapter; we will mention here only a couple of things.

We conclude that *because* there is some chance that the nitrogen atom can flip from one position to the other, the energy of the molecule is not just E_0 , as we would have expected, but that there are *two* energy levels $(E_0 + A)$ and $(E_0 - A)$. Every one of the possible states of the molecule, whatever energy it has, is “split” into two levels. We say *every* one of the states because, you remember, we picked out one particular state of rotation, and internal energy, and so on. For each possible condition of that kind there is a doublet of energy levels because of the flip-flop of the molecule.

Let's now ask the following question about an ammonia molecule. Suppose that at $t = 0$, we *know* that a molecule is in the state $|1\rangle$ or, in other words, that $C_1(0) = 1$ and $C_2(0) = 0$. What is the probability that the molecule will be found in the state $|2\rangle$ at the time t , or will still be found in state $|1\rangle$ at the time t ? Our starting condition tells us what a and b are in Eqs. (8.50) and (8.51). Letting $t = 0$, we have that

$$C_1(0) = \frac{a + b}{2} = 1, \quad C_2(0) = \frac{a - b}{2} = 0.$$

Clearly, $a = b = 1$. Putting these values into the formulas for $C_1(t)$ and $C_2(t)$ and rearranging some terms, we have

$$C_1(t) = e^{-(i/\hbar)E_0 t} \left(\frac{e^{(i/\hbar)At} + e^{-(i/\hbar)At}}{2} \right),$$

$$C_2(t) = e^{-(i/\hbar)E_0 t} \left(\frac{e^{(i/\hbar)At} - e^{-(i/\hbar)At}}{2} \right).$$

We can rewrite these as

$$C_1(t) = e^{-(i/\hbar)E_0 t} \cos \frac{At}{\hbar}, \quad (8.52)$$

$$C_2(t) = ie^{-(i/\hbar)E_0 t} \sin \frac{At}{\hbar}. \quad (8.53)$$

The two amplitudes have a magnitude that varies harmonically with time.

The probability that the molecule is found in state $|2\rangle$ at the time t is the absolute square of $C_2(t)$:

$$|C_2(t)|^2 = \sin^2 \frac{At}{\hbar}. \quad (8.54)$$

The probability starts at zero (as it should), rises to one, and then oscillates back and forth between zero and one, as shown in the curve marked P_2 of Fig. 8-2. The probability of being in the $|1\rangle$ state does not, of course, stay at one. It “dumps” into the second state until the probability of finding the molecule in the first state is zero, as shown by the curve P_1 of Fig. 8-2. The probability sloshes back and forth between the two.

A long time ago we saw what happens when we have two equal pendulums with a slight coupling. (See Chapter 49, Vol. I.) When we lift one back and let go,

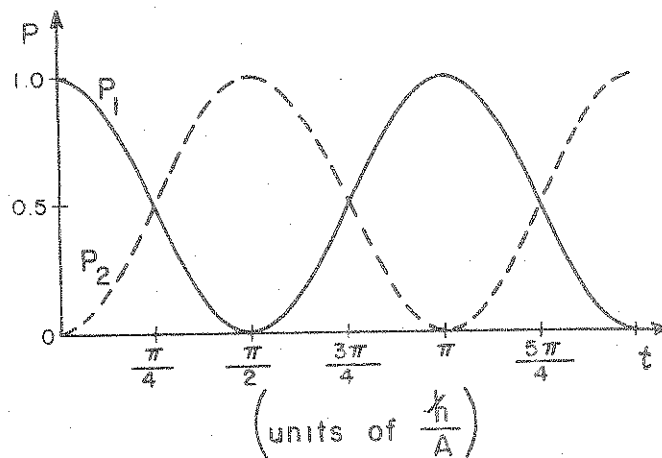


Fig. 8-2. The probability P_1 that an ammonia molecule in state $|1\rangle$ at $t = 0$ will be found in state $|1\rangle$ at t . The probability P_2 that it will be found in state $|2\rangle$.

it swings, but then gradually the other one starts to swing. Pretty soon the second pendulum has picked up all the energy. Then, the process reverses, and pendulum number one picks up the energy. It is exactly the same kind of a thing. The speed at which the energy is swapped back and forth depends on the coupling between the two pendulums—the rate at which the “oscillation” is able to leak across. Also, you remember, with the two pendulums there are two special motions—each with a definite frequency—which we call the fundamental modes. If we pull both pendulums out together, they swing together at one frequency. On the other hand, if we pull one out one way and the other out the other way, there is another stationary mode also at a definite frequency.

Well, here we have a similar situation—the ammonia molecule is mathematically like the pair of pendulums. These are the two frequencies— $(E_0 + A)/h$ and $(E_0 - A)/h$ —for when they are oscillating together, or oscillating opposite.

The pendulum analogy is not much deeper than the principle that the same equations have the same solutions. The linear equations for the amplitudes (8.39) are very much like the linear equations of harmonic oscillators. (In fact, this is the reason behind the success of our classical theory of the index of refraction, in which we replaced the quantum mechanical atom by a harmonic oscillator, even though, classically, this is not a reasonable view of electrons circulating about a nucleus.) If you pull the nitrogen to one side, then you get a *superposition* of these two frequencies, and you get a kind of *beat* note, because the system is *not* in one or the other states of definite frequency. The splitting of the energy levels of the ammonia molecule is, however, strictly a quantum mechanical effect.

The splitting of the energy levels of the ammonia molecule has important practical applications which we will describe in the next chapter. At long last we have an example of a practical physical problem that you can understand with the quantum mechanics!