

The Hamiltonian Matrix

8-1 Amplitudes and vectors

Before we begin the main topic of this chapter, we would like to describe a number of mathematical ideas that are used a lot in the literature of quantum mechanics. Knowing them will make it easier for you to read other books or papers on the subject. The first idea is the close mathematical resemblance between the equations of quantum mechanics and those of the scalar product of two vectors. You remember that if χ and ϕ are two states, the amplitude to start in ϕ and end up in χ can be written as a sum over a complete set of base states of the amplitude to go from ϕ into one of the base states and then from that base state out again into χ :

$$\langle \chi | \phi \rangle = \sum_{\text{all } i} \langle \chi | i \rangle \langle i | \phi \rangle. \quad (8.1)$$

We explained this in terms of a Stern-Gerlach apparatus, but we remind you that there is no need to have the apparatus. Equation (8.1) is a mathematical law that is just as true whether we put the filtering equipment in or not—it is not always necessary to imagine that the apparatus is there. We can think of it simply as a formula for the amplitude $\langle \chi | \phi \rangle$.

We would like to compare Eq. (8.1) to the formula for the dot product of two vectors \mathbf{B} and \mathbf{A} . If \mathbf{B} and \mathbf{A} are ordinary vectors in three dimensions, we can write the dot product this way:

$$\sum_{\text{all } i} (\mathbf{B} \cdot \mathbf{e}_i)(\mathbf{e}_i \cdot \mathbf{A}), \quad (8.2)$$

with the understanding that the symbol \mathbf{e}_i stands for the three unit vectors in the x , y , and z -directions. Then $\mathbf{B} \cdot \mathbf{e}_1$ is what we ordinarily call B_x ; $\mathbf{B} \cdot \mathbf{e}_2$ is what we ordinarily call B_y ; and so on. So Eq. (8.2) is equivalent to

$$B_x A_x + B_y A_y + B_z A_z,$$

which is the dot product $\mathbf{B} \cdot \mathbf{A}$.

Comparing Eqs. (8.1) and (8.2), we can see the following analogy: The states χ and ϕ correspond to the two vectors \mathbf{A} and \mathbf{B} . The base states i correspond to the special vectors \mathbf{e}_i to which we refer all other vectors. Any vector can be represented as a linear combination of the three “base vectors” \mathbf{e}_i . Furthermore, if you know the coefficients of each “base vector” in this combination—that is, its three components—you know everything about a vector. In a similar way, any quantum mechanical state can be described completely by the amplitude $\langle i | \phi \rangle$ to go into the base states; and if you know these coefficients, you know everything there is to know about the state. Because of this close analogy, what we have called a “state” is often also called a “state vector.”

Since the base vectors \mathbf{e}_i are all at right angles, we have the relation

$$\mathbf{e}_i \cdot \mathbf{e}_j = \delta_{ij}. \quad (8.3)$$

This corresponds to the relations (5.25) among the base states i ,

$$\langle i | j \rangle = \delta_{ij}. \quad (8.4)$$

You see now why one says that the base states i are all “orthogonal.”

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There is one minor difference between Eq. (8.1) and the dot product. We have that

$$\langle \phi | \chi \rangle = \langle \chi | \phi \rangle^*. \quad (8.5)$$

But in vector algebra,

$$\mathbf{A} \cdot \mathbf{B} = \mathbf{B} \cdot \mathbf{A}.$$

With the complex numbers of quantum mechanics we have to keep straight the order of the terms, whereas in the dot product, the order doesn't matter.

Now consider the following vector equation:

$$\mathbf{A} = \sum_i \mathbf{e}_i (\mathbf{e}_i \cdot \mathbf{A}). \quad (8.6)$$

It's a little unusual, but correct. It means the same thing as

$$\mathbf{A} = \sum_i A_i \mathbf{e}_i = A_x \mathbf{e}_x + A_y \mathbf{e}_y + A_z \mathbf{e}_z. \quad (8.7)$$

Notice, though, that Eq. (8.6) involves a quantity which is *different* from a dot product. A dot product is just a *number*, whereas Eq. (8.6) is a *vector* equation. One of the great tricks of vector analysis was to abstract away from the equations the idea of a *vector* itself. One might be similarly inclined to abstract a thing that is the analog of a "vector" from the quantum mechanical formula Eq. (8.1)—and one can indeed. We remove the $\langle \chi |$ from both sides Eq. (8.1) and write the following equation (don't get frightened—it's just a notation and in a few minutes you will find out what the symbols mean):

$$| \phi \rangle = \sum_i | i \rangle \langle i | \phi \rangle. \quad (8.8)$$

One thinks of the bracket $\langle \chi | \phi \rangle$ as being divided into two pieces. The second piece $| \phi \rangle$ is often called a *ket*, and the first piece $\langle \chi |$ is called a *bra* (put together, they make a "bra-ket"—a notation proposed by Dirac); the half-symbols $\langle \chi |$ and $| \phi \rangle$ are also called *state vectors*. In any case, they are *not* numbers, and, in general, we want the results of our calculations to come out as numbers; so such "unfinished" quantities are only part-way steps in our calculations.

It happens that until now we have written all our results in terms of numbers. How have we managed to avoid vectors? It is amusing to note that even in ordinary vector algebra we *could* make all equations involve only numbers. For instance, instead of a vector equation like

$$\mathbf{F} = m\mathbf{a},$$

we could always have written

$$\mathbf{C} \cdot \mathbf{F} = \mathbf{C} \cdot (m\mathbf{a}).$$

We have then an equation between dot products that is true for *any* vector \mathbf{C} . But if it is true for any \mathbf{C} , it hardly makes sense at all to keep writing the \mathbf{C} !

Now look at Eq. (8.1). It is an equation that is true for *any* χ . So to save writing, we should just leave *out* the χ and write Eq. (8.8) instead. It has the same information *provided* we understand that it should always be "finished" by "multiplying on the left by"—which simply means reinserting—some $\langle \chi |$ on both sides. So Eq. (8.8) means exactly the same thing as Eq. (8.1)—no more, no less. When you want numbers, you put in the $\langle \chi |$ you want.

Maybe you have already wondered about the ϕ in Eq. (8.8). Since the equation is true for *any* ϕ , why do we keep *it*? Indeed, Dirac suggests that the ϕ also can just as well be abstracted away, so that we have only

$$| = \sum_i | i \rangle \langle i |. \quad (8.9)$$

And this is the great law of quantum mechanics! (There is no analog in vector analysis.) It says that if you put *in* any two states χ and ϕ on the left and right of both sides, you *get back* Eq. (8.1). It is not really very useful, but it's a nice reminder that the equation is true for any two states.

8-2 Resolving state vectors

Let's look at Eq. (8.8) again; we can think of it in the following way. Any state vector $|\phi\rangle$ can be represented as a linear combination with suitable coefficients of a set of base "vectors"—or, if you prefer, as a superposition of "unit vectors" in suitable proportions. To emphasize that the coefficients $\langle i|\phi\rangle$ are just ordinary (complex) numbers, suppose we write

$$\langle i|\phi\rangle = C_i.$$

Then Eq. (8.8) is the same as

$$|\phi\rangle = \sum_i |i\rangle C_i. \quad (8.10)$$

We can write a similar equation for any other state vector, say $|\chi\rangle$, with, of course, different coefficients—say D_i . Then we have

$$|\chi\rangle = \sum_i |i\rangle D_i. \quad (8.11)$$

The D_i are just the amplitudes $\langle i|\chi\rangle$.

Suppose we had started by abstracting the ϕ from Eq. (8.1). We would have had

$$\langle\chi| = \sum_i \langle\chi|i\rangle\langle i|. \quad (8.12)$$

Remembering that $\langle\chi|i\rangle = \langle i|\chi\rangle^*$, we can write this as

$$\langle\chi| = \sum_i D_i^* \langle i|. \quad (8.13)$$

Now the interesting thing is that we can just *multiply* Eq. (8.13) and Eq. (8.10) to get back $\langle\chi|\phi\rangle$. When we do that, we have to be careful of the summation indices, because they are quite distinct in the two equations. Let's first rewrite Eq. (8.13) as

$$\langle\chi| = \sum_j D_j^* \langle j|,$$

which changes nothing. Then putting it together with Eq. (8.10), we have

$$\langle\chi|\phi\rangle = \sum_{ij} D_j^* \langle j|i\rangle C_i. \quad (8.14)$$

Remember, though, that $\langle j|i\rangle = \delta_{ij}$, so that in the sum we have left only the terms with $j = i$. We get

$$\langle\chi|\phi\rangle = \sum_i D_i^* C_i, \quad (8.15)$$

where, of course, $D_i^* = \langle i|\chi\rangle^* = \langle\chi|i\rangle$, and $C_i = \langle i|\phi\rangle$. Again we see the close analogy with the dot product

$$\mathbf{A} \cdot \mathbf{B} = \sum_i A_i B_i.$$

The only difference is the complex conjugate on D_i . So Eq. (8.15) says that if the state vectors $\langle\chi|$ and $|\phi\rangle$ are expanded in terms of the base vectors $\langle i|$ or $|i\rangle$, the amplitude to go from ϕ to χ is given by the kind of dot product in Eq. (8.15). This equation is, of course, just Eq. (8.1) written with different symbols. So we have just gone in a circle to get used to the new symbols.

We should perhaps emphasize again that while space vectors in three dimensions are described in terms of *three* orthogonal unit vectors, the base vectors $|i\rangle$ of the quantum mechanical states must range over the complete set applicable to any particular problem. Depending on the situation, two, or three, or five, or an infinite number of base states may be involved.

We have also talked about what happens when particles go through an apparatus. If we start the particles out in a certain state ϕ , then send them through

an apparatus, and afterward make a measurement to see if they are in state χ , the result is described by the amplitude

$$\langle \chi | A | \phi \rangle. \quad (8.16)$$

Such a symbol doesn't have a close analog in vector algebra. (It is closer to tensor algebra, but the analogy is not particularly useful.) We saw in Chapter 5, Eq. (5.32), that we could write (8.16) as

$$\langle \chi | A | \phi \rangle = \sum_{ij} \langle \chi | i \rangle \langle i | A | j \rangle \langle j | \phi \rangle. \quad (8.17)$$

This is just an example of the fundamental rule Eq. (8.9), used twice.

We also found that if another apparatus B was added in series with A , then we could write

$$\langle \chi | BA | \phi \rangle = \sum_{ijk} \langle \chi | i \rangle \langle i | B | j \rangle \langle j | A | k \rangle \langle k | \phi \rangle. \quad (8.18)$$

Again, this comes directly from Dirac's method of writing Eq. (8.9)—remember that we can always place a bar ($|$), which is just like the factor 1, between B and A .

Incidentally, we can think of Eq. (8.17) in another way. Suppose we think of the particle entering apparatus A in the state ϕ and coming out of A in the state ψ ("psi"). In other words, we could ask ourselves this question: Can we find a ψ such that the amplitude to get from ψ to χ is always identically and everywhere the same as the amplitude $\langle \chi | A | \phi \rangle$? The answer is yes. We want Eq. (8.17) to be replaced by

$$\langle \chi | \psi \rangle = \sum_i \langle \chi | i \rangle \langle i | \psi \rangle. \quad (8.19)$$

We can clearly do this if

$$\langle i | \psi \rangle = \sum_j \langle i | A | j \rangle \langle j | \phi \rangle = \langle i | A | \phi \rangle, \quad (8.20)$$

which determines ψ . "But it doesn't determine ψ ," you say; "it only determines $\langle i | \psi \rangle$." However, $\langle i | \psi \rangle$ *does* determine ψ , because if you have all the coefficients that relate ψ to the base states i , then ψ is uniquely defined. In fact, we can play with our notation and write the last term of Eq. (8.20) as

$$\langle i | \psi \rangle = \sum_j \langle i | j \rangle \langle j | A | \phi \rangle. \quad (8.21)$$

Then, since this equation is true for all i , we can write simply

$$| \psi \rangle = \sum_j | j \rangle \langle j | A | \phi \rangle. \quad (8.22)$$

Then we can say: "The state ψ is what we get if we start with ϕ and go through the apparatus A ."

One final example of the tricks of the trade. We start again with Eq. (8.17). Since it is true for any χ and ϕ , we can drop them both! We then get†

$$A = \sum_{ij} | i \rangle \langle i | A | j \rangle \langle j |. \quad (8.23)$$

What does it mean? It means no more, no less, than what you get if you put back the ϕ and χ . As it stands, it is an "open" equation and incomplete. If we multiply it "on the left" by $| \phi \rangle$, it becomes

$$A | \phi \rangle = \sum_{ij} | i \rangle \langle i | A | j \rangle \langle j | \phi \rangle, \quad (8.24)$$

† You might think we should write $|A|$ instead of just A . But then it would look like the symbol for "absolute value of A ," so the bars are usually dropped. In general, the bar ($|$) behaves much like the factor one.

which is just Eq. (8.22) all over again. In fact, we could have just dropped the j 's from that equation and written

$$|\psi\rangle = A|\phi\rangle. \quad (8.25)$$

The symbol A is neither an amplitude, nor a vector; it is a new kind of thing called an *operator*. It is something which “operates on” a state to produce a new state—Eq. (8.25) says that $|\psi\rangle$ is what results if A operates on $|\phi\rangle$. Again, it is still an open equation until it is completed with some bra like $\langle x|$ to give

$$\langle x|\psi\rangle = \langle x|A|\phi\rangle. \quad (8.26)$$

The operator A is, of course, described completely if we give the matrix of amplitudes $\langle i|A|j\rangle$ —also written A_{ij} —in terms of any set of base vectors.

We have really added nothing new with all of this new mathematical notation. One reason for bringing it all up was to show you the way of writing pieces of equations, because in many books you will find the equations written in the incomplete forms, and there's no reason for you to be paralyzed when you come across them. If you prefer, you can always add the missing pieces to make an equation between numbers that will look like something more familiar.

Also, as you will see, the “bra” and “ket” notation is a very convenient one. For one thing, we can from now on identify a state by giving its state vector. When we want to refer to a state of definite momentum p we can say: “the state $|p\rangle$ ”. Or we may speak of some arbitrary state $|\psi\rangle$. For consistency we will always use the ket, writing $|\psi\rangle$, to identify a state. (It is, of course an arbitrary choice; we could equally well have chosen to use the bra, $\langle\psi|$.)

8-3 What are the base states of the world?

We have discovered that any state in the world can be represented as a superposition—a linear combination with suitable coefficients—of base states. You may ask, first of all, *what* base states? Well, there are many different possibilities. You can, for instance, project a spin in the z -direction or in some other direction. There are many, many different *representations*, which are the analogs of the different *coordinate systems* one can use to represent ordinary vectors. Next, *what* coefficients? Well, that depends on the physical circumstances. Different sets of coefficients correspond to different physical conditions. The important thing to know about is the “space” in which you are working—in other words, what the base states mean physically. So the first thing you have to know about, in general, is what the base states are like. Then you can understand how to describe a situation in terms of these base states.

We would like to look ahead a little and speak a bit about what the general quantum mechanical description of nature is going to be—in terms of the now current ideas of physics, anyway. First, one decides on a particular representation for the base states—different representations are always possible. For example, for a spin one-half particle we can use the plus and minus states with respect to the z -axis. But there's nothing special about the z -axis—you can take any other axis you like. For consistency we'll always pick the z -axis, however. Suppose we begin with a situation with one electron. In addition to the two possibilities for the spin (“up” and “down” along the z -direction), there is also the momentum of the electron. We pick a set of base states, each corresponding to one value of the momentum. What if the electron doesn't have a definite momentum? That's all right; we're just saying what the *base* states are. If the electron hasn't got a definite momentum, it has some amplitude to have one momentum and another amplitude to have another momentum, and so on. And if it is not necessarily spinning up, it has some amplitude to be spinning up going at this momentum, and some amplitude to be spinning down going at that momentum, and so on. The complete description of an electron, *so far as we know*, requires only that the base states be described by the *momentum* and the *spin*. So one acceptable set of base states $|i\rangle$ for a single electron refer to different values of the momentum and

whether the spin is up or down. Different mixtures of amplitudes—that is, different combinations of the C 's describe different circumstances. What any particular electron is doing is described by telling with what amplitude it has an up-spin or a down-spin and one momentum or another—for all possible momenta. So you can see what is involved in a complete quantum mechanical description of a single electron.

What about systems with more than one electron? Then the base states get more complicated. Let's suppose that we have two electrons. We have, first of all, four possible states with respect to spin: both electrons spinning up, the first one down and the second one up, the first one up and the second one down, or both down. Also we have to specify that the first electron has the momentum p_1 , and the second electron, the momentum p_2 . The base states for two electrons require the specification of two momenta and two spin characters. With seven electrons, we have to specify seven of each.

If we have a proton and an electron, we have to specify the spin direction of the proton and its momentum, and the spin direction of the electron and its momentum. At least that's approximately true. *We do not really know* what the correct representation is for the world. It is all very well to start out by supposing that if you specify the spin in the electron and its momentum, and likewise for a proton, you will have the base states; but what about the "guts" of the proton? Let's look at it this way. In a hydrogen atom which has one proton and one electron, we have many different base states to describe—up and down spins of the proton and electron and the various possible momenta of the proton and electron. Then there are different combinations of amplitudes C_i which together describe the character of the hydrogen atom in different states. But suppose we look at the whole hydrogen atom as a "particle." If we didn't know that the hydrogen atom was made out of a proton and an electron, we might have started out and said: "Oh, I know what the base states are—they correspond to a particular momentum of the hydrogen atom." No, because the hydrogen atom has internal parts. It may, therefore, have various states of different internal energy, and describing the real nature requires more detail.

The question is: Does a proton have internal parts? Do we have to describe a proton by giving all possible states of protons, and mesons, and strange particles? We don't know. And even though we suppose that the electron is simple, so that all we have to tell about it is its momentum and its spin, maybe tomorrow we will discover that the electron also has inner gears and wheels. It would mean that our representation is incomplete, or wrong, or approximate—in the same way that a representation of the hydrogen atom which describes only its momentum would be incomplete, because it disregarded the fact that the hydrogen atom could have become excited inside. If an electron could become excited inside and turn into something else like, for instance, a muon, then it would be described not just by giving the states of the new particle, but presumably in terms of some more complicated internal wheels. The *main problem in the study of the fundamental particles today* is to discover what are the correct representations for the description of nature. At the present time, we *guess* that for the electron it is enough to specify its momentum and spin. We also guess that there is an idealized proton which has its π -mesons, and k -mesons, and so on, that all have to be specified. Several dozen particles—that's crazy! The question of what *is* a fundamental particle and what *is not* a fundamental particle—a subject you hear so much about these days—is the question of what is the final *representation* going to look like in the ultimate quantum mechanical description of the world. Will the electron's momentum still be the right thing with which to describe nature? Or even, should the whole question be put this way at all! This question must always come up in any scientific investigation. At any rate, we see a problem—how to find a representation. We don't know the answer. We don't even know whether we have the "right" problem, but if we do, we must first attempt to find out whether any particular particle is "fundamental" or not.

In the nonrelativistic quantum mechanics—if the energies are not too high, so that you don't disturb the inner workings of the strange particles and so forth—

you can do a pretty good job without worrying about these details. You can just decide to specify the momenta and spins of the electrons and of the nuclei; then everything will be all right. In most chemical reactions and other low-energy happenings, nothing goes on in the nuclei; they don't get excited. Furthermore, if a hydrogen atom is moving slowly and bumping quietly against other hydrogen atoms—never getting excited inside, or radiating, or anything complicated like that, but staying always in the ground state of energy for internal motion—you can use an approximation in which you talk about the hydrogen atom as one object, or particle, and not worry about the fact that it *can* do something inside. This will be a good approximation as long as the kinetic energy in any collision is well below 10 electron volts—the energy required to excite the hydrogen atom to a different internal state. We will often be making an approximation in which we do not include the possibility of inner motion, thereby decreasing the number of details that we have to put into our base states. Of course, we then omit some phenomena which would appear (usually) at some higher energy, but by making such approximations we can simplify very much the analysis of physical problems. For example, we can discuss the collision of two hydrogen atoms at low energy—or any chemical process—without worrying about the fact that the atomic nuclei could be excited. To summarize, then, when we can neglect the effects of any internal excited states of a particle we can choose a base set which are the states of definite momentum and z-component of angular momentum.

One problem then in describing nature is to find a suitable representation for the base states. But that's only the beginning. We still want to be able to say what “happens.” If we know the “condition” of the world at one moment, we would like to know the condition at a later moment. So we also have to find the laws that determine how things change with time. We now address ourselves to this second part of the framework of quantum mechanics—how states change with time.

8-4 How states change with time

We have already talked about how we can represent a situation in which we put something through an apparatus. Now one convenient, delightful “apparatus” to consider is merely a wait of a few minutes; that is, you prepare a state ϕ , and then before you analyze it, you just let it sit. Perhaps you let it sit in some particular electric or magnetic field—it depends on the physical circumstances in the world. At any rate, whatever the conditions are, you let the object sit from time t_1 to time t_2 . Suppose that it is let out of your first apparatus in the condition ϕ at t_1 . And then it goes through an “apparatus,” but the “apparatus” consists of just delay until t_2 . During the delay, various things could be going on—external forces applied or other shenanigans—so that something is happening. At the end of the delay, the amplitude to find the thing in some state χ is no longer exactly the same as it would have been without the delay. Since “waiting” is just a special case of an “apparatus,” we can describe what happens by giving an amplitude with the same form as Eq. (8.17). Because the operation of “waiting” is especially important, we'll call it U instead of A , and to specify the starting and finishing times t_1 and t_2 , we'll write $U(t_2, t_1)$. The amplitude we want is

$$\langle \chi | U(t_2, t_1) | \phi \rangle. \quad (8.27)$$

Like any other such amplitude, it can be represented in some base system or other by writing it

$$\sum_{ij} \langle \chi | i \rangle \langle i | U(t_2, t_1) | j \rangle \langle j | \phi \rangle. \quad (8.28)$$

Then U is completely described by giving the whole set of amplitudes—the matrix

$$\langle i | U(t_2, t_1) | j \rangle. \quad (8.29)$$

We can point out, incidentally, that the matrix $\langle i | U(t_2, t_1) | j \rangle$ gives much more detail than may be needed. The high-class theoretical physicist working in

high-energy physics considers problems of the following general nature (because it's the way experiments are usually done). He starts with a couple of particles, like a proton and a proton, coming together from infinity. (In the lab, usually one particle is standing still, and the other comes from an accelerator that is practically at infinity on atomic level.) The things go crash and out come, say, two k -mesons, six π -mesons, and two neutrons in certain directions with certain momenta. What's the amplitude for this to happen? The mathematics looks like this: The ϕ -state specifies the spins and momenta of the incoming particles. The χ would be the question about what comes out. For instance, with what amplitude do you get the six mesons going in such-and-such directions, and the two neutrons going off in these directions, with their spins so-and-so. In other words, χ would be specified by giving all the momenta, and spins, and so on of the final products. Then the job of the theorist is to calculate the amplitude (8.27). However, he is really only interested in the special case that t_1 is $-\infty$ and t_2 is $+\infty$. (There is no experimental evidence on the details of the process, only on what comes in and what goes out.) The limiting case of $U(t_2, t_1)$ as $t_1 \rightarrow -\infty$ and $t_2 \rightarrow +\infty$ is called S , and what he wants is

$$\langle \chi | S | \phi \rangle.$$

Or, using the form (8.28), he would calculate the matrix

$$\langle i | S | j \rangle,$$

which is called the *S-matrix*. So if you see a theoretical physicist pacing the floor and saying, "All I have to do is calculate the *S-matrix*," you will know what he is worried about.

How to analyze—how to specify the laws for—the *S-matrix* is an interesting question. In relativistic quantum mechanics for high energies, it is done one way, but in nonrelativistic quantum mechanics it can be done another way, which is very convenient. (This other way can also be done in the relativistic case, but then it is not so convenient.) It is to work out the *U-matrix* for a small interval of time—in other words for t_2 and t_1 close together. If we can find a sequence of such *U*'s for successive intervals of time we can watch how things go as a function of time. You can appreciate immediately that this way is not so good for relativity, because you don't want to have to specify how everything looks "simultaneously" everywhere. But we won't worry about that—we're just going to worry about non-relativistic mechanics.

Suppose we think of the matrix *U* for a delay from t_1 until t_3 which is greater than t_2 . In other words, let's take three successive times: t_1 less than t_2 less than t_3 . Then we claim that the matrix that goes between t_1 and t_3 is the *product* in succession of what happens when you delay from t_1 until t_2 and then from t_2 until t_3 . It's just like the situation when we had two apparatuses *B* and *A* in series. We can then write, following the notation of Section 5-6,

$$U(t_3, t_1) = U(t_3, t_2) \cdot U(t_2, t_1). \quad (8.30)$$

In other words, we can analyze any time interval if we can analyze a sequence of short time intervals in between. We just multiply together all the pieces; that's the way that quantum mechanics is analyzed nonrelativistically.

Our problem, then, is to understand the matrix $U(t_2, t_1)$ for an infinitesimal time interval—for $t_2 = t_1 + \Delta t$. We ask ourselves this: If we have a state ϕ now, what does the state look like an infinitesimal time Δt later? Let's see how we write that out. Call the state at the time t , $|\psi(t)\rangle$ (we show the time dependence of ψ to be perfectly clear that we mean the condition at the time t). Now we ask the question: What is the condition after the small interval of time Δt later? The answer is

$$|\psi(t + \Delta t)\rangle = U(t + \Delta t, t) |\psi(t)\rangle. \quad (8.31)$$

This means the same as we meant by (8.25), namely, that the amplitude to

find x at the time $t + \Delta t$, is

$$\langle x | \psi(t + \Delta t) \rangle = \langle x | U(t + \Delta t, t) | \psi(t) \rangle. \quad (8.32)$$

Since we're not yet too good at these abstract things, let's project our amplitudes into a definite representation. If we multiply both sides of Eq. (8.31) by $\langle i |$, we get

$$\langle i | \psi(t + \Delta t) \rangle = \langle i | U(t + \Delta t, t) | \psi(t) \rangle. \quad (8.33)$$

We can also resolve the $|\psi(t)\rangle$ into base states and write

$$\langle i | \psi(t + \Delta t) \rangle = \sum_j \langle i | U(t + \Delta t, t) | j \rangle \langle j | \psi(t) \rangle. \quad (8.34)$$

We can understand Eq. (8.34) in the following way. If we let $C_i(t) = \langle i | \psi(t) \rangle$ stand for the amplitude to be in the base state i at the time t , then we can think of this amplitude (just a *number*, remember!) varying with time. Each C_i becomes a function of t . And we also have some information on *how* the amplitudes C_i vary with time. Each amplitude at $(t + \Delta t)$ is proportional to *all of the other* amplitudes at t multiplied by a set of coefficients. Let's call the U -matrix U_{ij} , by which we mean

$$U_{ij} = \langle i | U | j \rangle.$$

Then we can write Eq. (8.34) as

$$C_i(t + \Delta t) = \sum_j U_{ij}(t + \Delta t, t) C_j(t). \quad (8.35)$$

This, then, is how the dynamics of quantum mechanics is going to look.

We don't know much about the U_{ij} yet, except for one thing. We know that if Δt goes to zero, nothing can happen—we should get just the original state. So, $U_{ii} \rightarrow 1$ and $U_{ij} \rightarrow 0$, if $i \neq j$. In other words, $U_{ij} \rightarrow \delta_{ij}$ for $\Delta t \rightarrow 0$. Also, we can suppose that for small Δt , each of the coefficients U_{ij} should differ from δ_{ij} by amounts proportional to Δt ; so we can write

$$U_{ij} = \delta_{ij} + K_{ij} \Delta t. \quad (8.36)$$

However, it is usual to take the factor $(-i/\hbar)^\dagger$ out of the coefficients K_{ij} , for historical and other reasons; we prefer to write

$$U_{ij}(t + \Delta t, t) = \delta_{ij} - \frac{i}{\hbar} H_{ij}(t) \Delta t. \quad (8.37)$$

It is, of course, the same as Eq. (8.36) and, if you wish, just defines the coefficients $H_{ij}(t)$. The terms H_{ij} are just the derivatives with respect to t_2 of the coefficients $U_{ij}(t_2, t_1)$, evaluated at $t_2 = t_1 = t$.

Using this form for U in Eq. (8.35), we have

$$C_i(t + \Delta t) = \sum_j \left[\delta_{ij} - \frac{i}{\hbar} H_{ij}(t) \Delta t \right] C_j(t). \quad (8.38)$$

Taking the sum over the δ_{ij} term, we get just $C_i(t)$, which we can put on the other side of the equation. Then dividing by Δt , we have what we recognize as a derivative

$$\frac{C_i(t + \Delta t) - C_i(t)}{\Delta t} = -\frac{i}{\hbar} \sum_j H_{ij}(t) C_j(t)$$

or

$$i\hbar \frac{dC_i(t)}{dt} = \sum_j H_{ij}(t) C_j(t). \quad (8.39)$$

[†] We are in a bit of trouble here with notation. In the factor $(-i/\hbar)$, the i means the imaginary unit $\sqrt{-1}$, and *not* the index i that refers to the i th base state! We hope that you won't find it too confusing.

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

$$\begin{aligned} i\hbar \frac{dC_1}{dt} &= H_{11}C_1 + H_{12}C_2, \\ i\hbar \frac{dC_2}{dt} &= H_{21}C_1 + H_{22}C_2. \end{aligned} \quad (8.43)$$

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.

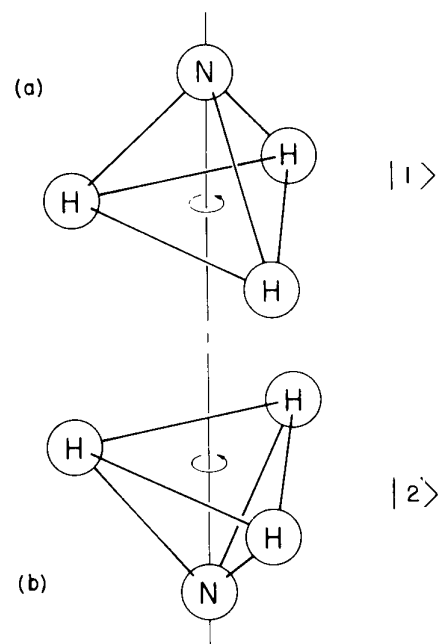


Fig. 8-1. Two equivalent geometric arrangements of the ammonia molecule.

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.

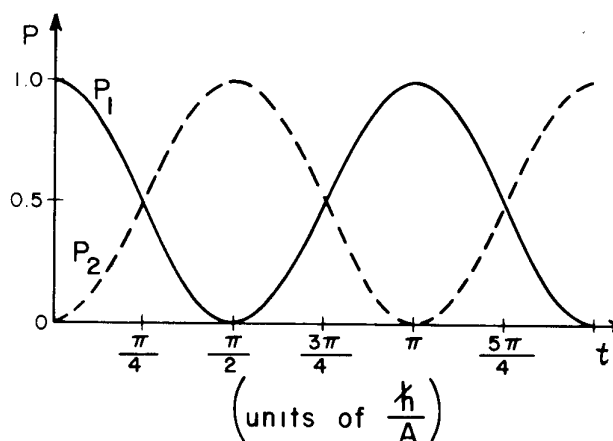
The probability that the molecule is found in state $|2\rangle$ at the time t is the absolute square of $C_2(t)$:

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

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— $(E_0 + A)/\hbar$ and $(E_0 - A)/\hbar$ —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!

The Ammonia Maser

9-1 The states of an ammonia molecule

In this chapter we are going to discuss the application of quantum mechanics to a practical device, the ammonia maser. You may wonder why we stop our formal development of quantum mechanics to do a special problem, but you will find that many of the features of this special problem are quite common in the general theory of quantum mechanics, and you will learn a great deal by considering this one problem in detail. The ammonia maser is a device for generating electromagnetic waves, whose operation is based on the properties of the ammonia molecule which we discussed briefly in the last chapter. We begin by summarizing what we found there.

The ammonia molecule has many states, but we are considering it as a two-state system, thinking now only about what happens when the molecule is in any specific state of rotation or translation. A physical model for the two states can be visualized as follows. If the ammonia molecule is considered to be rotating about an axis passing through the nitrogen atom and perpendicular to the plane of the hydrogen atoms, as shown in Fig. 9-1, there are still two possible conditions—the nitrogen may be on one side of the plane of hydrogen atoms or on the other. We call these two states $|1\rangle$ and $|2\rangle$. They are taken as a set of base states for our analysis of the behavior of the ammonia molecule.

9-1 The states of an ammonia molecule

9-2 The molecule in a static electric field

9-3 Transitions in a time-dependent field

9-4 Transitions at resonance

9-5 Transitions off resonance

9-6 The absorption of light

MASER = Microwave Amplification by Stimulated Emission of Radiation

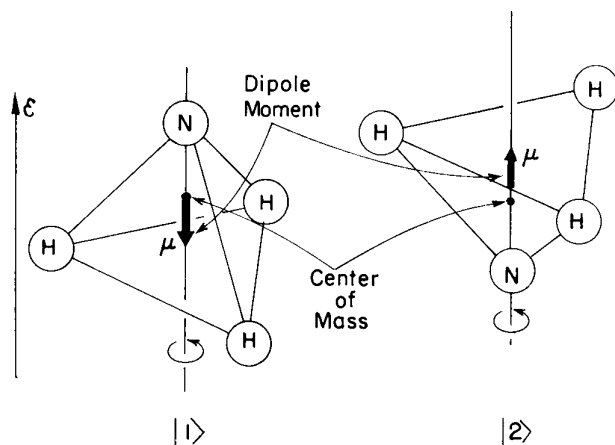


Fig. 9-1. A physical model of two base states for the ammonia molecule. These states have the electric dipole moments μ .

In a system with two base states, any state $|\psi\rangle$ of the system can always be described as a linear combination of the two base states; that is, there is a certain amplitude C_1 to be in one base state and an amplitude C_2 to be in the other. We can write its state vector as

$$|\psi\rangle = |1\rangle C_1 + |2\rangle C_2, \quad (9.1)$$

where

$$C_1 = \langle 1 | \psi \rangle \quad \text{and} \quad C_2 = \langle 2 | \psi \rangle.$$

These two amplitudes change with time according to the Hamiltonian equations, Eq. (8.43). Making use of the symmetry of the two states of the ammonia molecule, we set $H_{11} = H_{22} = E_0$, and $H_{12} = H_{21} = -A$, and get the

solution [see Eqs. (8.50) and (8.51)]

$$C_1 = \frac{a}{2} e^{-(i/\hbar)(E_0-A)t} + \frac{b}{2} e^{-(i/\hbar)(E_0+A)t}, \quad (9.2)$$

$$C_2 = \frac{a}{2} e^{-(i/\hbar)(E_0-A)t} - \frac{b}{2} e^{-(i/\hbar)(E_0+A)t}. \quad (9.3)$$

We want now to take a closer look at these general solutions. Suppose that the molecule was initially put into a state $|\psi_{II}\rangle$ for which the coefficient b was equal to zero. Then at $t = 0$ the amplitudes to be in the states $|I\rangle$ and $|2\rangle$ are identical, *and they stay that way for all time*. Their phases both vary with time in the same way—with the frequency $(E_0 - A)/\hbar$. Similarly, if we were to put the molecule into a state $|\psi_I\rangle$ for which $a = 0$, the amplitude C_2 is the negative of C_1 , and this relationship would stay that way forever. Both amplitudes would now vary with time with the frequency $(E_0 + A)/\hbar$. These are the only two possibilities of states for which the relation between C_1 and C_2 is independent of time.

We have found two special solutions in which the two amplitudes *do not vary in magnitude* and, furthermore, have phases which vary at the same frequencies. These are *stationary states* as we defined them in Section 7-1, which means that they are *states of definite energy*. The state $|\psi_{II}\rangle$ has the energy $E_{II} = E_0 - A$, and the state $|\psi_I\rangle$ has the energy $E_I = E_0 + A$. They are the only two stationary states that exist, so we find that the molecule has two energy levels, with the energy difference $2A$. (We mean, of course, two energy levels for the assumed state of rotation and vibration which we referred to in our initial assumptions.)†

If we hadn't allowed for the possibility of the nitrogen flipping back and forth, we would have taken A equal to zero and the two energy levels would be on top of each other at energy E_0 . The actual levels are not this way; their *average* energy is E_0 , but they are split apart by $\pm A$, giving a separation of $2A$ between the energies of the two states. Since A is, in fact, very small, the difference in energy is also very small.

In order to excite an *electron* inside an atom, the energies involved are relatively very high—requiring photons in the optical or ultraviolet range. To excite the *vibrations* of the molecules involves photons in the infrared. If you talk about exciting *rotations*, the energy differences of the states correspond to photons in the far infrared. But the energy difference $2A$ is lower than any of those and is, in fact, below the infrared and well into the microwave region. Experimentally, it has been found that there is a pair of energy levels with a separation of 10^{-4} electron volt—corresponding to a frequency 24,000 megacycles. Evidently this means that $2A = hf$, with $f = 24,000$ megacycles (corresponding to a wavelength of $1\frac{1}{4}$ cm). So here we have a molecule that has a transition which does not emit light in the ordinary sense, but emits microwaves.

For the work that follows we need to describe these two states of definite energy a little bit better. Suppose we were to construct an amplitude C_{II} by taking the sum of the two numbers C_1 and C_2 :

$$C_{II} = C_1 + C_2 = \langle I | \Phi \rangle + \langle 2 | \Phi \rangle. \quad (9.4)$$

What would that mean? Well, this is just the amplitude to find the state $|\Phi\rangle$ in a new state $|II\rangle$ in which the amplitudes of the original base states are equal. That is, writing $C_{II} = \langle II | \Phi \rangle$, we can abstract the $|\Phi\rangle$ away from Eq. (9.4)—because it is true for any Φ —and get

$$\langle II | = \langle I | + \langle 2 |,$$

which means the same as

$$|II\rangle = |I\rangle + |2\rangle. \quad (9.5)$$

† In what follows it is helpful—in reading to yourself or in talking to someone else—to have a handy way of distinguishing between the Arabic 1 and 2 and the Roman I and II. We find it convenient to reserve the names “one” and “two” for the Arabic numbers, and to call I and II by the names “eins” and “zwei” (although “unus” and “duo” might be more logical!).

The amplitude for the state $|II\rangle$ to be in the state $|I\rangle$ is

$$\langle I | II \rangle = \langle I | I \rangle + \langle I | 2 \rangle,$$

which is, of course, just 1, since $|I\rangle$ and $|2\rangle$ are base states. The amplitude for the state $|II\rangle$ to be in the state $|2\rangle$ is also 1, so the state $|II\rangle$ is one which has equal amplitudes to be in the two base states $|I\rangle$ and $|2\rangle$.

We are, however, in a bit of trouble. The state $|II\rangle$ has a total probability greater than one of being in *some* base state *or other*. That simply means, however, that the state vector is not properly “normalized.” We can take care of that by remembering that we should have $\langle II | II \rangle = 1$, which must be so for any state. Using the general relation that

$$\langle \chi | \Phi \rangle = \sum_i \langle \chi | i \rangle \langle i | \Phi \rangle,$$

letting both Φ and χ be the state II , and taking the sum over the base states $|I\rangle$ and $|2\rangle$, we get that

$$\langle II | II \rangle = \langle II | I \rangle \langle I | II \rangle + \langle II | 2 \rangle \langle 2 | II \rangle.$$

This will be equal to one as it should if we change our definition of C_{II} —in Eq. (9.4)—to read

$$C_{II} = \frac{1}{\sqrt{2}} [C_1 + C_2].$$

In the same way we can construct an amplitude

$$C_I = \frac{1}{\sqrt{2}} [C_1 - C_2],$$

or

$$C_I = \frac{1}{\sqrt{2}} [\langle I | \Phi \rangle - \langle 2 | \Phi \rangle]. \quad (9.6)$$

This amplitude is the projection of the state $|\Phi\rangle$ into a new state $|I\rangle$ which has opposite amplitudes to be in the states $|I\rangle$ and $|2\rangle$. Namely, Eq. (9.6) means the same as

$$\langle I | = \frac{1}{\sqrt{2}} [\langle I | - \langle 2 |],$$

or

$$|I\rangle = \frac{1}{\sqrt{2}} [|I\rangle - |2\rangle], \quad (9.7)$$

from which it follows that

$$\langle I | I \rangle = \frac{1}{\sqrt{2}} = -\langle 2 | I \rangle.$$

Now the reason we have done all this is that the states $|I\rangle$ and $|II\rangle$ *can be taken as a new set of base states* which are especially convenient for describing the stationary states of the ammonia molecule. You remember that the requirement for a set of base states is that

$$\langle i | j \rangle = \delta_{ij}.$$

We have already fixed things so that

$$\langle I | I \rangle = \langle II | II \rangle = 1.$$

You can easily show from Eqs. (9.5) and (9.7) that

$$\langle I | II \rangle = \langle II | I \rangle = 0.$$

The amplitudes $C_I = \langle I | \Phi \rangle$ and $C_{II} = \langle II | \Phi \rangle$ for any state Φ to be in our new base states $|I\rangle$ and $|II\rangle$ must also satisfy a Hamiltonian equation with the

form of Eq. (8.39). In fact, if we just subtract the two equations (9.2) and (9.3) and differentiate with respect to t , we see that

$$i\hbar \frac{dC_I}{dt} = (E_0 + A)C_I = E_I C_I. \quad (9.8)$$

And taking the sum of Eqs. (9.2) and (9.3), we see that

$$i\hbar \frac{dC_{II}}{dt} = (E_0 - A)C_{II} = E_{II} C_{II}. \quad (9.9)$$

Using $|I\rangle$ and $|II\rangle$ for base states, the Hamiltonian matrix has the simple form

$$\begin{aligned} H_{I,I} &= E_I, & H_{I,II} &= 0, \\ H_{II,I} &= 0, & H_{II,II} &= E_{II}. \end{aligned}$$

Note that each of the Eqs. (9.8) and (9.9) look just like what we had in Section 8-6 for the equation of a one-state system. They have a simple exponential time dependence corresponding to a single energy. As time goes on, the amplitudes to be in each state act independently.

The two stationary states $|\psi_I\rangle$ and $|\psi_{II}\rangle$ we found above are, of course, solutions of Eqs. (9.8) and (9.9). The state $|\psi_I\rangle$ (for which $C_1 = -C_2$) has

$$C_I = e^{-(i/\hbar)(E_0+A)t}, \quad C_{II} = 0. \quad (9.10)$$

And the state $|\psi_{II}\rangle$ (for which $C_1 = C_2$) has

$$C_I = 0, \quad C_{II} = e^{-(i/\hbar)(E_0-A)t}. \quad (9.11)$$

Remember that the amplitudes in Eq. (9.10) are

$$C_I = \langle I | \psi_I \rangle, \quad \text{and} \quad C_{II} = \langle II | \psi_I \rangle;$$

so Eq. (9.10) means the same thing as

$$|\psi_I\rangle = |I\rangle e^{-(i/\hbar)(E_0+A)t}.$$

That is, the state vector of the stationary state $|\psi_I\rangle$ is the same as the state vector of the base state $|I\rangle$ except for the exponential factor appropriate to the energy of the state. In fact at $t = 0$

$$|\psi_I\rangle = |I\rangle;$$

the state $|I\rangle$ has the same physical configuration as the stationary state of energy $E_0 + A$. In the same way, we have for the second stationary state that

$$|\psi_{II}\rangle = |II\rangle e^{-(i/\hbar)(E_0-A)t}.$$

The state $|II\rangle$ is just the stationary state of energy $E_0 - A$ at $t = 0$. Thus our two new base states $|I\rangle$ and $|II\rangle$ have physically the form of the states of definite energy, with the exponential time factor taken out so that they can be time-independent base states. (In what follows we will find it convenient not to have to distinguish always between the stationary states $|\psi_I\rangle$ and $|\psi_{II}\rangle$ and their base states $|I\rangle$ and $|II\rangle$, since they differ only by the obvious time factors.)

In summary, the state vectors $|\psi_I\rangle$ and $|\psi_{II}\rangle$ are a pair of base vectors which are appropriate for describing the definite energy states of the ammonia molecule. They are related to our original base vectors by

$$|I\rangle = \frac{1}{\sqrt{2}} [|1\rangle - |2\rangle], \quad |II\rangle = \frac{1}{\sqrt{2}} [|1\rangle + |2\rangle]. \quad (9.12)$$

The amplitudes to be in $|I\rangle$ and $|II\rangle$ are related to C_1 and C_2 by

$$C_I = \frac{1}{\sqrt{2}} [C_1 - C_2], \quad C_{II} = \frac{1}{\sqrt{2}} [C_1 + C_2]. \quad (9.13)$$

Any state at all can be represented by a linear combination of $|I\rangle$ and $|2\rangle$ —with the coefficients C_1 and C_2 —or by a linear combination of the definite energy base states $|I\rangle$ and $|II\rangle$ —with the coefficients C_I and C_{II} . Thus,

$$|\Phi\rangle = |I\rangle C_1 + |2\rangle C_2$$

or

$$|\Phi\rangle = |I\rangle C_I + |II\rangle C_{II}.$$

The second form gives us the amplitudes for finding the state $|\Phi\rangle$ in a state with the energy $E_I = E_0 + A$ or in a state with the energy $E_{II} = E_0 - A$.

9-2 The molecule in a static electric field

If the ammonia molecule is in either of the two states of definite energy and we disturb it at a frequency ω such that $\hbar\omega = E_I - E_{II} = 2A$, the system may make a transition from one state to the other. Or, if it is in the upper state, it may change to the lower state and emit a photon. But in order to induce such transitions you must have a physical connection to the states—some way of disturbing the system. There must be some external machinery for affecting the states, such as magnetic or electric fields. In this particular case, these states are sensitive to an electric field. We will, therefore, look next at the problem of the behavior of the ammonia molecule in an external electric field.

To discuss the behavior in an electric field, we will go back to the original base system $|I\rangle$ and $|2\rangle$, rather than using $|I\rangle$ and $|II\rangle$. Suppose that there is an electric field in a direction perpendicular to the plane of the hydrogen atoms. Disregarding for the moment the possibility of flipping back and forth, would it be true that the energy of this molecule is the same for the two positions of the nitrogen atom? Generally, no. The electrons tend to lie closer to the nitrogen than to the hydrogen nuclei, so the hydrogens are slightly positive. The actual amount depends on the details of electron distribution. It is a complicated problem to figure out exactly what this distribution is, but in any case the net result is that the ammonia molecule has an electric dipole moment, as indicated in Fig. 9-1. We can continue our analysis without knowing in detail the direction or amount of displacement of the charge. However, to be consistent with the notation of others, let's suppose that the electric dipole moment is μ , with its direction point *from* the nitrogen atom and perpendicular to the plane of the hydrogen atoms.

Now, when the nitrogen flips from one side to the other, the center of mass will not move, but the electric dipole moment will flip over. As a result of this moment, the energy in an electric field \mathcal{E} will depend on the molecular orientation.† With the assumption made above, the potential energy will be higher if the nitrogen atom points in the direction of the field, and lower if it is in the opposite direction; the separation in the two energies will be $2\mu\mathcal{E}$.

In the discussion up to this point, we have assumed values of E_0 and A without knowing how to calculate them. According to the correct physical theory, it should be possible to calculate these constants in terms of the positions and motions of all the nuclei and electrons. But nobody has ever done it. Such a system involves ten electrons and four nuclei and that's just too complicated a problem. As a matter of fact, there is no one who knows much more about this molecule than we do. All anyone can say is that when there is an electric field, the energy of the two states is different, the difference being proportional to the electric field. We have called the coefficient of proportionality 2μ , but its value must be determined experimentally. We can also say that the molecule has the amplitude A to flip over, but this will have to be measured experimentally. Nobody can give us accurate theoretical values of μ and A , because the calculations are too complicated to do in detail.

† We are sorry that we have to introduce a new notation. Since we have been using p and E for momentum and energy, we don't want to use them again for dipole moment and electric field. Remember, in this section μ is the *electric* dipole moment.

For the ammonia molecule in an electric field, our description must be changed. If we ignored the amplitude for the molecule to flip from one configuration to the other, we would expect the energies of the two states $|1\rangle$ and $|2\rangle$ to be $(E_0 \pm \mu\mathcal{E})$. Following the procedure of the last chapter, we take

$$H_{11} = E_0 + \mu\mathcal{E}, \quad H_{22} = E_0 - \mu\mathcal{E}. \quad (9.14)$$

Also we will assume that for the electric fields of interest the field does not affect appreciably the geometry of the molecule and, therefore, does not affect the amplitude that the nitrogen will jump from one position to the other. We can then take that H_{12} and H_{21} are not changed; so

$$H_{12} = H_{21} = -A. \quad (9.15)$$

We must now solve the Hamiltonian equations, Eq. (8.43), with these new values of H_{ij} . We could solve them just as we did before, but since we are going to have several occasions to want the solutions for two-state systems, let's solve the equations once and for all in the general case of arbitrary H_{ij} —assuming only that they do not change with time.

We want the general solution of the pair of Hamiltonian equations

$$i\hbar \frac{dC_1}{dt} = H_{11}C_1 + H_{12}C_2, \quad (9.16)$$

$$i\hbar \frac{dC_2}{dt} = H_{21}C_1 + H_{22}C_2. \quad (9.17)$$

Since these are linear differential equations with constant coefficients, we can always find solutions which are exponential functions of the dependent variable t . We will first look for a solution in which C_1 and C_2 both have the same time dependence; we can use the trial functions

$$C_1 = a_1 e^{-i\omega t}, \quad C_2 = a_2 e^{-i\omega t}.$$

Since such a solution corresponds to a state of energy $E = \hbar\omega$, we may as well write right away

$$C_1 = a_1 e^{-(i/\hbar)Et}, \quad (9.18)$$

$$C_2 = a_2 e^{-(i/\hbar)Et}, \quad (9.19)$$

where E is as yet unknown and to be determined so that the differential equations (9.16) and (9.17) are satisfied.

When we substitute C_1 and C_2 from (9.18) and (9.19) in the differential equations (9.16) and (9.17), the derivatives give us just $-iE/\hbar$ times C_1 or C_2 , so the left sides become just EC_1 and EC_2 . Cancelling the common exponential factors, we get

$$Ea_1 = H_{11}a_1 + H_{12}a_2, \quad Ea_2 = H_{21}a_1 + H_{22}a_2.$$

Or, rearranging the terms, we have

$$(E - H_{11})a_1 - H_{12}a_2 = 0, \quad (9.20)$$

$$-H_{21}a_1 + (E - H_{22})a_2 = 0. \quad (9.21)$$

With such a set of homogeneous algebraic equations, there will be nonzero solutions for a_1 and a_2 only if the determinant of the coefficients of a_1 and a_2 is zero, that is, if

$$\text{Det} \begin{pmatrix} E - H_{11} & -H_{12} \\ -H_{21} & E - H_{22} \end{pmatrix} = 0. \quad (9.22)$$

However, when there are only two equations and two unknowns, we don't need such a sophisticated idea. The two equations (9.20) and (9.21) each give a ratio for the two coefficients a_1 and a_2 , and these two ratios must be equal. From (9.20) we have that

$$\frac{a_1}{a_2} = \frac{H_{12}}{E - H_{11}}, \quad (9.23)$$

and from (9.21) that

$$\frac{a_1}{a_2} = \frac{E - H_{22}}{H_{21}}. \quad (9.24)$$

Equating these two ratios, we get that E must satisfy

$$(E - H_{11})(E - H_{22}) - H_{12}H_{21} = 0.$$

This is the same result we would get by solving Eq. (9.22). Either way, we have a quadratic equation for E which has two solutions:

$$E = \frac{H_{11} + H_{22}}{2} \pm \sqrt{\frac{(H_{11} - H_{22})^2}{4} + H_{12}H_{21}}. \quad (9.25)$$

There are two possible values for the energy E . Note that both solutions give *real numbers* for the energy, because H_{11} and H_{22} are real, and $H_{12}H_{21}$ is equal to $H_{12}H_{12}^* = |H_{12}|^2$, which is both real and positive.

Using the same convention we took before, we will call the upper energy E_I and the lower energy E_{II} . We have

$$E_I = \frac{H_{11} + H_{22}}{2} + \sqrt{\frac{(H_{11} - H_{22})^2}{4} + H_{12}H_{21}}, \quad (9.26)$$

$$E_{II} = \frac{H_{11} + H_{22}}{2} - \sqrt{\frac{(H_{11} - H_{22})^2}{4} + H_{12}H_{21}}. \quad (9.27)$$

Using each of these two energies separately in Eqs. (9.18) and (9.19), we have the amplitudes for the two stationary states (the states of definite energy). If there are no external disturbances, a system initially in one of these states will stay that way forever—only its phase changes.

We can check our results for two special cases. If $H_{12} = H_{21} = 0$, we have that $E_I = H_{11}$ and $E_{II} = H_{22}$. This is certainly correct, because then Eqs. (9.16) and (9.17) are uncoupled, and each represents a state of energy H_{11} and H_{22} . Next, if we set $H_{11} = H_{22} = E_0$ and $H_{21} = H_{12} = -A$, we get the solution we found before:

$$E_I = E_0 + A \quad \text{and} \quad E_{II} = E_0 - A.$$

For the general case, the two solutions E_I and E_{II} refer to two states—which we can again call the states

$$|\psi_I\rangle = |I\rangle e^{-(i/\hbar)E_I t} \quad \text{and} \quad |\psi_{II}\rangle = |II\rangle e^{-(i/\hbar)E_{II} t}.$$

These states will have C_1 and C_2 as given in Eqs. (9.18) and (9.19), where a_1 and a_2 are still to be determined. Their ratio is given by either Eq. (9.23) or Eq. (9.24). They must also satisfy one more condition. If the system is known to be in one of the stationary states, the sum of the probabilities that it will be found in $|I\rangle$ or $|2\rangle$ must equal one. We must have that

$$|C_1|^2 + |C_2|^2 = 1, \quad (9.28)$$

or, equivalently,

$$|a_1|^2 + |a_2|^2 = 1. \quad (9.29)$$

These conditions do not uniquely specify a_1 and a_2 ; they are still undetermined

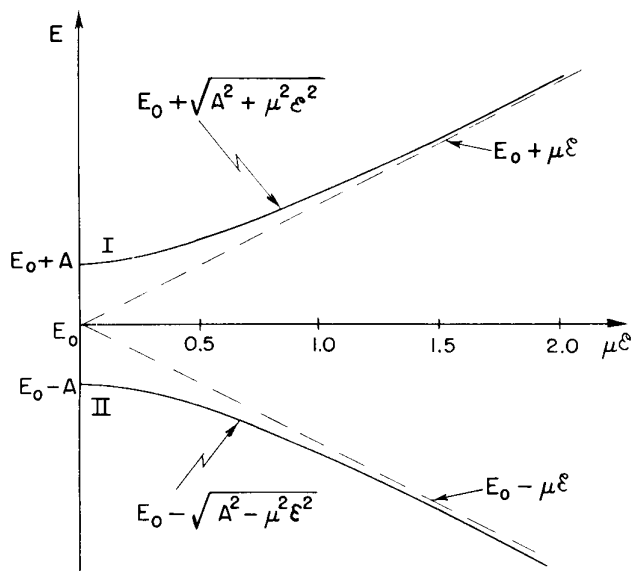


Fig. 9-2. Energy levels of the ammonia molecule in an electric field.

by an arbitrary phase—in other words, by a factor like $e^{i\delta}$. Although general solutions for the a 's can be written down,† it is usually more convenient to work them out for each special case.

Let's go back now to our particular example of the ammonia molecule in an electric field. Using the values for H_{11} , H_{22} , and H_{12} given in (9.14) and (9.15), we get for the energies of the two stationary states

$$E_I = E_0 + \sqrt{A^2 + \mu^2 \mathcal{E}^2}, \quad E_{II} = E_0 - \sqrt{A^2 + \mu^2 \mathcal{E}^2}. \quad (9.30)$$

These two energies are plotted as a function of the electric field strength \mathcal{E} in Fig. 9-2. When the electric field is zero, the two energies are, of course, just $E_0 \pm A$. When an electric field is applied, the splitting between the two levels increases. The splitting increases at first slowly with \mathcal{E} , but eventually becomes proportional to \mathcal{E} . (The curve is a hyperbola.) For enormously strong fields, the energies are just

$$E_I = E_0 + \mu \mathcal{E} = H_{11}, \quad E_{II} = E_0 - \mu \mathcal{E} = H_{22}. \quad (9.31)$$

The fact that there is an amplitude for the nitrogen to flip back and forth has little effect when the two positions have very different energies. This is an interesting point which we will come back to again later.

We are at last ready to understand the operation of the ammonia maser. The idea is the following. First, we find a way of separating molecules in the state $|I\rangle$ from those in the state $|II\rangle$.‡ Then the molecules in the higher energy state $|I\rangle$ are passed through a cavity which has a resonant frequency of 24,000 megacycles. The molecules can deliver energy to the cavity—in a way we will discuss later—and leave the cavity in the state $|II\rangle$. Each molecule that makes such a transition will deliver the energy $E = E_I - E_{II}$ to the cavity. The energy from the molecules will appear as electrical energy in the cavity.

How can we separate the two molecular states? One method is as follows. The ammonia gas is let out of a little jet and passed through a pair of slits to give a narrow beam, as shown in Fig. 9-3. The beam is then set through a

† For example, the following set is one acceptable solution, as you can easily verify:

$$a_1 = \frac{H_{12}}{[(E - H_{11})^2 + H_{12}H_{21}]^{1/2}}, \quad a_2 = \frac{E - H_{11}}{[(E - H_{11})^2 + H_{12}H_{21}]^{1/2}}.$$

‡ From now on we will write $|I\rangle$ and $|II\rangle$ instead of $|\psi_I\rangle$ and $|\psi_{II}\rangle$. You must remember that the actual states $|\psi_I\rangle$ and $|\psi_{II}\rangle$ are the energy base states multiplied by the appropriate exponential factor.

region in which there is a large transverse electric field. The electrodes to produce the field are shaped so that the electric field varies rapidly across the beam. Then the square of the electric field $\mathcal{E} \cdot \mathcal{E}$ will have a large gradient perpendicular to the beam. Now a molecule in state $|I\rangle$ has an energy which increases with \mathcal{E}^2 , and therefore this part of the beam will be deflected toward the region of lower \mathcal{E}^2 . A molecule in state $|II\rangle$ will, on the other hand, be deflected toward the region of larger \mathcal{E}^2 , since its energy decreases as \mathcal{E}^2 increases.

Incidentally, with the electric fields which can be generated in the laboratory, the energy $\mu\mathcal{E}$ is always much smaller than A . In such cases, the square root in Eqs. (9.30) can be approximated by

$$A \left(1 + \frac{1}{2} \frac{\mu^2 \mathcal{E}^2}{A^2} \right). \quad (9.32)$$

So the energy levels are, for all practical purposes,

$$E_I = E_0 + A + \frac{\mu^2 \mathcal{E}^2}{2A} \quad (9.33)$$

and

$$E_{II} = E_0 - A - \frac{\mu^2 \mathcal{E}^2}{2A}. \quad (9.34)$$

And the energies vary approximately linearly with \mathcal{E}^2 . The force on the molecules is then

$$\mathbf{F} = \frac{\mu^2}{2A} \nabla \mathcal{E}^2. \quad (9.35)$$

Many molecules have an energy in an electric field which is proportional to \mathcal{E}^2 . The coefficient is the polarizability of the molecule. Ammonia has an unusually high polarizability because of the small value of A in the denominator. Thus, ammonia molecules are unusually sensitive to an electric field. (What would you expect for the dielectric coefficient of NH_3 gas?)

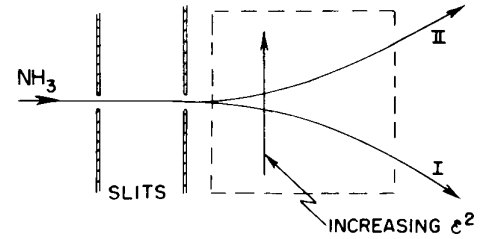


Fig. 9-3. The ammonia beam may be separated by an electric field in which \mathcal{E}^2 has a gradient perpendicular to the beam.

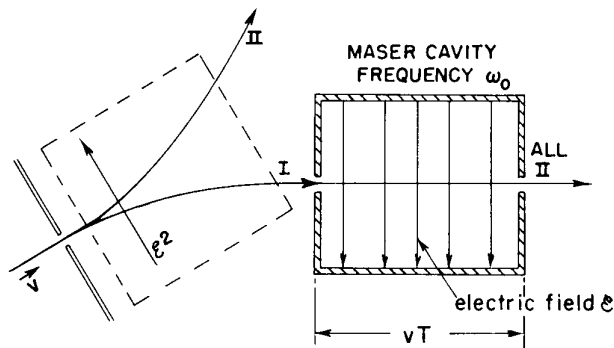


Fig. 9-4. Schematic diagram of the ammonia maser.

9-3 Transitions in a time-dependent field

In the ammonia maser, the beam with molecules in the state $|I\rangle$ and with the energy E_I is sent through a resonant cavity, as shown in Fig. 9-4. The other beam is discarded. Inside the cavity, there will be a time-varying electric field, so the next problem we must discuss is the behavior of a molecule in an electric field that varies with time. We have a completely different kind of a problem—one with a time-varying Hamiltonian. Since H_{ij} depends upon \mathcal{E} , the H_{ij} vary with time, and we must determine the behavior of the system in this circumstance.

To begin with, we write down the equations to be solved:

$$\begin{aligned} i\hbar \frac{dC_1}{dt} &= (E_0 + \mu\mathcal{E})C_1 - AC_2, \\ i\hbar \frac{dC_2}{dt} &= -AC_1 + (E_0 - \mu\mathcal{E})C_2. \end{aligned} \quad (9.36)$$

To be definite, let's suppose that the electric field varies sinusoidally; then we can write

$$\mathcal{E} = 2\mathcal{E}_0 \cos \omega t = \mathcal{E}_0(e^{i\omega t} + e^{-i\omega t}). \quad (9.37)$$

In actual operation the frequency ω will be very nearly equal to the resonant frequency of the molecular transition $\omega_0 = 2A/\hbar$, but for the time being we want to keep things general, so we'll let it have any value at all. The best way to solve our equations is to form linear combinations of C_I and C_{II} as we did before. So we add the two equations, divide by the square root of 2, and use the definitions of C_I and C_{II} that we had in Eq. (9.13). We get

$$i\hbar \frac{dC_{II}}{dt} = (E_0 - A)C_{II} + \mu\mathcal{E}C_I. \quad (9.38)$$

You'll note that this is the same as Eq. (9.9) with an extra term due to the electric field. Similarly, if we subtract the two equations (9.36), we get

$$i\hbar \frac{dC_I}{dt} = (E_0 + A)C_I + \mu\mathcal{E}C_{II}. \quad (9.39)$$

Now the question is, how to solve these equations? They are more difficult than our earlier set, because \mathcal{E} depends on t ; and, in fact, for a general $\mathcal{E}(t)$ the solution is not expressible in elementary functions. However, we can get a good approximation so long as the electric field is small. First we will write

$$\begin{aligned} C_I &= \gamma_I e^{-i(E_0+A)t/\hbar} = \gamma_I e^{-i(E_I)t/\hbar}, \\ C_{II} &= \gamma_{II} e^{-i(E_0-A)t/\hbar} = \gamma_{II} e^{-i(E_{II})t/\hbar}. \end{aligned} \quad (9.40)$$

If there were no electric field, these solutions would be correct with γ_I and γ_{II} just chosen as two complex constants. In fact, since the probability of being in state $|I\rangle$ is the absolute square of C_I and the probability of being in state $|II\rangle$ is the absolute square of C_{II} , the probability of being in state $|I\rangle$ or in state $|II\rangle$ is just $|\gamma_I|^2$ or $|\gamma_{II}|^2$. For instance, if the system were to start originally in state $|II\rangle$ so that γ_I was zero and $|\gamma_{II}|^2$ was one, this condition would go on forever. There would be no chance, if the molecule were originally in state $|II\rangle$, ever to get into state $|I\rangle$.

Now the idea of writing our equations in the form of Eq. (9.40) is that if $\mu\mathcal{E}$ is small in comparison with A , the solutions can still be written in this way, but then γ_I and γ_{II} become slowly varying functions of time—where by “slowly varying” we mean slowly *in comparison* with the exponential functions. That is the trick. We use the fact that γ_I and γ_{II} vary slowly to get an approximate solution.

We want now to substitute C_I from (9.40) in the differential equation (9.39), but we must remember that γ_I is also a function of t . We have

$$i\hbar \frac{dC_I}{dt} = E_I \gamma_I e^{-iE_I t/\hbar} + i\hbar \frac{d\gamma_I}{dt} e^{-iE_I t/\hbar}.$$

The differential equation becomes

$$\left(E_I \gamma_I + i\hbar \frac{d\gamma_I}{dt}\right) e^{-(i/\hbar)E_I t} = E_I \gamma_I e^{-(i/\hbar)E_I t} + \mu\mathcal{E} \gamma_{II} e^{-(i/\hbar)E_{II} t}. \quad (9.41)$$

Similarly, the equation in dC_{II}/dt becomes

$$\left(E_{II} \gamma_{II} + i\hbar \frac{d\gamma_{II}}{dt}\right) e^{-(i/\hbar)E_{II} t} = E_{II} \gamma_{II} e^{-(i/\hbar)E_{II} t} + \mu\mathcal{E} \gamma_I e^{-(i/\hbar)E_I t}. \quad (9.42)$$

Now you will notice that we have equal terms on both sides of each equation. We cancel these terms, and we also multiply the first equation by $e^{+iE_I t/\hbar}$ and the

second by $e^{+iE_{II}t/\hbar}$. Remembering that $(E_I - E_{II}) = 2A = \hbar\omega_0$, we have finally,

$$\begin{aligned} i\hbar \frac{d\gamma_I}{dt} &= \mu\mathcal{E}(t)e^{i\omega_0 t}\gamma_{II}, \\ i\hbar \frac{d\gamma_{II}}{dt} &= \mu\mathcal{E}(t)e^{-i\omega_0 t}\gamma_I. \end{aligned} \quad (9.43)$$

Now we have an apparently simple pair of equations—and they are still exact, of course. The derivative of one variable is a function of time $\mu\mathcal{E}(t)e^{i\omega_0 t}$, multiplied by the second variable; the derivative of the second is a similar time function, multiplied by the first. Although these simple equations cannot be solved in general, we will solve them for some special cases.

We are, for the moment at least, interested only in the case of an oscillating electric field. Taking $\mathcal{E}(t)$ as given in Eq. (9.37), we find that the equations for γ_I and γ_{II} become

$$\begin{aligned} i\hbar \frac{d\gamma_I}{dt} &= \mu\mathcal{E}_0[e^{i(\omega+\omega_0)t} + e^{-i(\omega-\omega_0)t}]\gamma_{II}, \\ i\hbar \frac{d\gamma_{II}}{dt} &= \mu\mathcal{E}_0[e^{i(\omega-\omega_0)t} + e^{-i(\omega+\omega_0)t}]\gamma_I. \end{aligned} \quad (9.44)$$

Now if \mathcal{E}_0 is sufficiently small, the rates of change of γ_I and γ_{II} are also small. The two γ 's will not vary much with t , especially in comparison with the rapid variations due to the exponential terms. These exponential terms have real and imaginary parts that oscillate at the frequency $\omega + \omega_0$ or $\omega - \omega_0$. The terms with $\omega + \omega_0$ oscillate very rapidly about an average value of zero and, therefore, do not contribute very much on the average to the rate of change of γ . So we can make a reasonably good approximation by replacing these terms by their average value, namely, zero. We will just leave them out, and take as our approximation:

$$\begin{aligned} i\hbar \frac{d\gamma_I}{dt} &= \mu\mathcal{E}_0 e^{-i(\omega-\omega_0)t}\gamma_{II}, \\ i\hbar \frac{d\gamma_{II}}{dt} &= \mu\mathcal{E}_0 e^{i(\omega-\omega_0)t}\gamma_I. \end{aligned} \quad (9.45)$$

Even the remaining terms, with exponents proportional to $(\omega - \omega_0)$, will also vary rapidly unless ω is near ω_0 . Only then will the right-hand side vary slowly enough that any appreciable amount will accumulate when we integrate the equations with respect to t . In other words, with a *weak* electric field the only significant frequencies are those near ω_0 .

With the approximation made in getting Eq. (9.45), the equations can be solved exactly, but the work is a little elaborate, so we won't do that until later when we take up another problem of the same type. Now we'll just solve them approximately—or rather, we'll find an exact solution for the case of perfect resonance, $\omega = \omega_0$, and an approximate solution for frequencies near resonance.

9-4 Transitions at resonance

Let's take the case of perfect resonance first. If we take $\omega = \omega_0$, the exponentials are equal to one in both equations of (9.45), and we have just

$$\frac{d\gamma_I}{dt} = -\frac{i\mu\mathcal{E}_0}{\hbar}\gamma_{II}, \quad \frac{d\gamma_{II}}{dt} = -\frac{i\mu\mathcal{E}_0}{\hbar}\gamma_I. \quad (9.46)$$

If we eliminate first γ_I and then γ_{II} from these equations, we find that each satisfies the differential equation of simple harmonic motion:

$$\frac{d^2\gamma}{dt^2} = -\left(\frac{\mu\mathcal{E}_0}{\hbar}\right)^2\gamma. \quad (9.47)$$

The general solutions for these equations can be made up of sines and cosines.

As you can easily verify, the following equations are a solution:

$$\begin{aligned}\gamma_I &= a \cos\left(\frac{\mu\mathcal{E}_0}{\hbar}\right)t + b \sin\left(\frac{\mu\mathcal{E}_0}{\hbar}\right)t, \\ \gamma_{II} &= ib \cos\left(\frac{\mu\mathcal{E}_0}{\hbar}\right)t - ia \sin\left(\frac{\mu\mathcal{E}_0}{\hbar}\right)t,\end{aligned}\tag{9.48}$$

where a and b are constants to be determined to fit any particular physical situation.

For instance, suppose that at $t = 0$ our molecular system was in the upper energy state $|I\rangle$, which would require—from Eq. (9.40)—that $\gamma_I = 1$ and $\gamma_{II} = 0$ at $t = 0$. For this situation we would need $a = 1$ and $b = 0$. The probability that the molecule is in the state $|I\rangle$ at some later t is the absolute square of γ_I , or

$$P_I = |\gamma_I|^2 = \cos^2\left(\frac{\mu\mathcal{E}_0}{\hbar}\right)t.\tag{9.49}$$

Similarly, the probability that the molecule will be in the state $|II\rangle$ is given by the absolute square of γ_{II} ,

$$P_{II} = \gamma_{II}^2 = \sin^2\left(\frac{\mu\mathcal{E}_0}{\hbar}\right)t.\tag{9.50}$$

So long as \mathcal{E} is small and we are on resonance, the probabilities are given by simple oscillating functions. The probability to be in state $|I\rangle$ falls from one to zero and back again, while the probability to be in the state $|II\rangle$ rises from zero to one and back. The time variation of the two probabilities is shown in Fig. 9-5. Needless to say, the sum of the two probabilities is always equal to one; the molecule is always in *some* state!

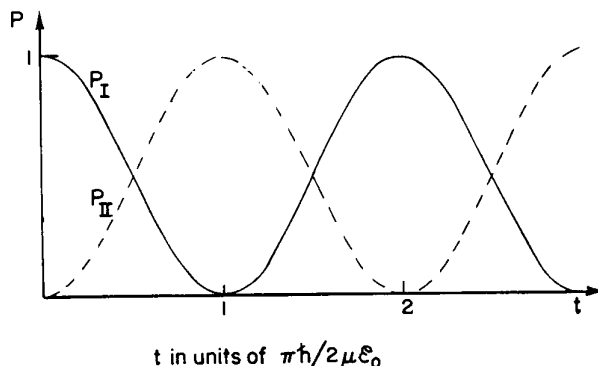


Fig. 9-5. Probabilities for the two states of the ammonia molecule in a sinusoidal electric field.

Let's suppose that it takes the molecule the time T to go through the cavity. If we make the cavity just long enough so that $\mu\mathcal{E}_0T/\hbar = \pi/2$, then a molecule which enters in state $|I\rangle$ will certainly leave it in state $|II\rangle$. If it enters the cavity in the upper state, it will leave the cavity in the lower state. In other words, its energy is decreased, and the loss of energy can't go anywhere else but into the machinery which generates the field. The details by which you can see how the energy of the molecule is fed into the oscillations of the cavity are not simple; however, we don't need to study these details, because we can use the principle of conservation of energy. (We could study them if we had to, but then we would have to deal with the quantum mechanics of the field in the cavity in addition to the quantum mechanics of the atom.)

In summary: the molecule enters the cavity, the cavity field—oscillating at exactly the right frequency—induces transitions from the upper to the lower state, and the energy released is fed into the oscillating field. In an operating maser the molecules deliver enough energy to maintain the cavity oscillations—not only providing enough power to make up for the cavity losses but even providing small amounts of excess power that can be drawn from the cavity. Thus, the molecular energy is converted into the energy of an external electromagnetic field.

Remember that before the beam enters the cavity, we have to use a filter which separates the beam so that only the upper state enters. It is easy to demonstrate that if you were to start with molecules in the lower state, the process will go the other way and take energy out of the cavity. If you put the unfiltered beam in, as many molecules are taking energy out as are putting energy in, so nothing much would happen. In actual operation it isn't necessary, of course, to make $(\mu\epsilon_0 T/\hbar)$ exactly $\pi/2$. For any other value (except an exact integral multiple of π), there is some probability for transitions from state $|I\rangle$ to state $|II\rangle$. For other values, however, the device isn't 100 percent efficient; many of the molecules which leave the cavity could have delivered some energy to the cavity but didn't.

In actual use, the velocity of all the molecules is not the same; they have some kind of Maxwell distribution. This means that the ideal periods of time for different molecules will be different, and it is impossible to get 100 percent efficiency for all the molecules at once. In addition, there is another complication which is easy to take into account, but we don't want to bother with it at this stage. You remember that the electric field in a cavity usually varies from place to place across the cavity. Thus, as the molecules drift across the cavity, the electric field at the molecule varies in a way that is more complicated than the simple sinusoidal oscillation in time that we have assumed. Clearly, one would have to use a more complicated integration to do the problem exactly, but the general idea is still the same.

There are other ways of making masers. Instead of separating the atoms in state $|I\rangle$ from those in state $|II\rangle$ by a Stern-Gerlach apparatus, one can have the atoms already in the cavity (as a gas or a solid) and shift atoms from state $|II\rangle$ to state $|I\rangle$ by some means. One way is one used in the so-called three-state maser. For it, atomic systems are used which have three energy levels, as shown in Fig. 9-6, with the following special properties. The system will absorb radiation (say, light) of frequency $\hbar\omega_1$ and go from the lowest energy level E_{II} to some high-energy level E' , and then will quickly emit photons of frequency $\hbar\omega_2$ and go to the state $|I\rangle$ with energy E_I . The state $|I\rangle$ has a long lifetime so its population can be raised, and the conditions are then appropriate for maser operation between states $|I\rangle$ and $|II\rangle$. Although such a device is called a "three-state" maser, the maser operation really works just as a two-state system such as we are describing.

A laser (*Light Amplification by Stimulated Emission of Radiation*) is just a maser working at optical frequencies. The "cavity" for a laser usually consists of just two plane mirrors between which standing waves are generated.

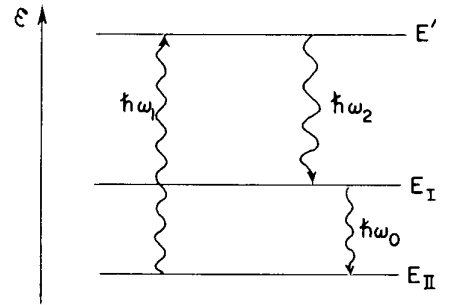


Fig. 9-6. The energy levels of a "three-state" maser.

9-5 Transitions off resonance

Finally, we would like to find out how the states vary in the circumstance that the cavity frequency is nearly, but not exactly, equal to ω_0 . We could solve this problem exactly, but instead of trying to do that, we'll take the important case that the electric field is small and also the period of time T is small, so that $\mu\epsilon_0 T/\hbar$ is much less than one. Then, even in the case of perfect resonance which we have just worked out, the probability of making a transition is small. Suppose that we start again with $\gamma_I = 1$ and $\gamma_{II} = 0$. During the time T we would expect γ_I to remain nearly equal to one, and γ_{II} to remain very small compared with unity. Then the problem is very easy. We can calculate γ_{II} from the second equation in (9.45), taking γ_I equal to one and integrating from $t = 0$ to $t = T$. We get

$$\gamma_{II} = \frac{\mu\epsilon_0}{\hbar} \left[\frac{1 - e^{i(\omega - \omega_0)T}}{\omega - \omega_0} \right]. \quad (9.51)$$

This γ_{II} , used with Eq. (9.40), gives the amplitude to have made a transition from the state $|I\rangle$ to the state $|II\rangle$ during the time interval T . The probability $P(I \rightarrow II)$ to make the transition is $|\gamma_{II}|^2$, or

$$P(I \rightarrow II) = |\gamma_{II}|^2 = \left[\frac{\mu\epsilon_0 T}{\hbar} \right]^2 \frac{\sin^2[(\omega - \omega_0)T/2]}{[(\omega - \omega_0)T/2]^2}. \quad (9.52)$$

It is interesting to plot this probability for a fixed length of time as a function of the frequency of the cavity in order to see how sensitive it is to frequencies near the resonant frequency ω_0 . We show such a plot of $P(I \rightarrow II)$ in Fig. 9-7. (The vertical scale has been adjusted to be 1 at the peak by dividing by the value of the probability when $\omega = \omega_0$.) We have seen a curve like this in the diffraction theory, so you should already be familiar with it. The curve falls rather abruptly to zero for $(\omega - \omega_0) = 2\pi/T$ and never regains significant size for large frequency deviations. In fact, by far the greatest part of the area under the curve lies within the range $\pm\pi/T$. It is possible to show† that the area under the curve is just $2\pi/T$ and is equal to the area of the shaded rectangle drawn in the figure.

Let's examine the implication of our results for a real maser. Suppose that the ammonia molecule is in the cavity for a reasonable length of time, say for one millisecond. Then for $f_0 = 24,000$ megacycles, we can calculate that the probability for a transition falls to zero for a frequency deviation of $(f - f_0)/f_0 = 1/f_0T$, which is five parts in 10^8 . Evidently the frequency must be very close to ω_0 to get a significant transition probability. Such an effect is the basis of the great precision that can be obtained with "atomic" clocks, which work on the maser principle.

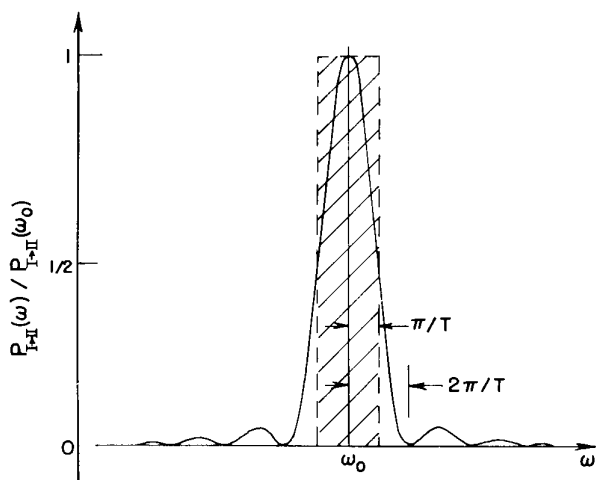


Fig. 9-7. Transition probability for the ammonia molecule as a function of frequency.

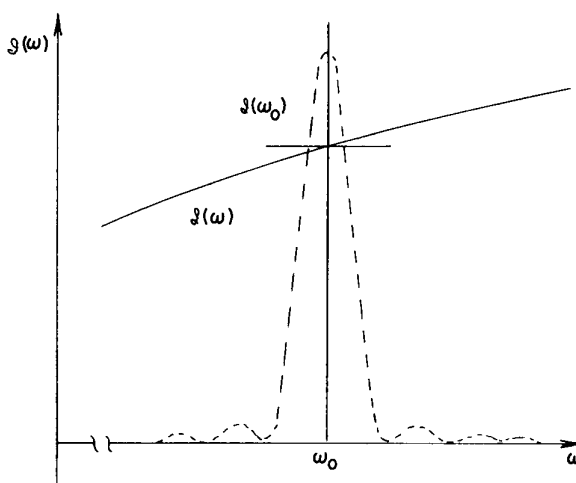


Fig. 9-8. The spectral intensity $g(\omega)$ can be approximated by its value at ω_0 .

9-6 The absorption of light

Our treatment above applies to a more general situation than the ammonia maser. We have treated the behavior of a molecule under the influence of an electric field, whether that field was confined in a cavity or not. So we could be simply shining a beam of "light"—at microwave frequencies—at the molecule and ask for the probability of emission or absorption. Our equations apply equally well to this case, but let's rewrite them in terms of the *intensity* of the radiation rather than the electric field. If we define the intensity g to be the average energy flow per unit area per second, then from Chapter 27 of Volume II, we can write

$$g = \epsilon_0 c^2 |\mathbf{E} \times \mathbf{B}|_{\text{ave}} = \frac{1}{2} \epsilon_0 c^2 (\mathbf{E} \times \mathbf{B})_{\text{max}} = 2 \epsilon_0 c \mathcal{E}_0^2.$$

(The maximum value of \mathcal{E} is $2\mathcal{E}_0$.) The transition probability now becomes:

$$P(I \rightarrow II) = 2\pi \left[\frac{\mu^2}{4\pi\epsilon_0 \hbar^2 c} \right] g T^2 \frac{\sin^2 [(\omega - \omega_0)T/2]}{[(\omega - \omega_0)T/2]^2}. \quad (9.53)$$

† Using the formula $\int_{-\infty}^{\infty} (\sin^2 x/x^2) dx = \pi$.

Ordinarily the light shining on such a system is not exactly monochromatic. It is, therefore, interesting to solve one more problem—that is, to calculate the transition probability when the light has intensity $\mathcal{J}(\omega)$ per unit frequency interval, covering a broad range which includes ω_0 . Then, the probability of going from $|I\rangle$ to $|II\rangle$ will become an integral:

$$P(I \rightarrow II) = 2\pi \left[\frac{\mu^2}{4\pi\epsilon_0\hbar^2c} \right] T^2 \int_0^\infty \mathcal{J}(\omega) \frac{\sin^2[(\omega - \omega_0)T/2]}{[(\omega - \omega_0)T/2]^2} d\omega. \quad (9.54)$$

In general, $\mathcal{J}(\omega)$ will vary much more slowly with ω than the sharp resonance term. The two functions might appear as shown in Fig. 9-8. In such cases, we can replace $\mathcal{J}(\omega)$ by its value $\mathcal{J}(\omega_0)$ at the center of the sharp resonance curve and take it outside of the integral. What remains is just the integral under the curve of Fig. 9-7, which is, as we have seen, just equal to $2\pi/T$. We get the result that

$$P(I \rightarrow II) = 4\pi^2 \left[\frac{\mu^2}{4\pi\epsilon_0\hbar^2c} \right] \mathcal{J}(\omega_0)T. \quad (9.55)$$

This is an important result, because it is the *general theory of the absorption of light by any molecular or atomic system*. Although we began by considering a case in which state $|I\rangle$ had a higher energy than state $|II\rangle$, none of our arguments depended on that fact. Equation (9.55) still holds if the state $|I\rangle$ has a *lower* energy than the state $|II\rangle$; then $P(I \rightarrow II)$ represents the probability for a transition with the *absorption* of energy from the incident electromagnetic wave. The absorption of light by any atomic system always involves the amplitude for a transition in an oscillating electric field between two states separated by an energy $E = \hbar\omega_0$. For any particular case, it is always worked out in just the way we have done here and gives an expression like Eq. (9.55). We, therefore, emphasize the following features of this result. First, the probability is proportional to T . In other words, there is a constant probability per unit time that transitions will occur. Second, this probability is proportional to the *intensity* of the light incident on the system. Finally, the transition probability is proportional to μ^2 , where, you remember, $\mu\mathcal{E}$ defined the shift in energy due to the electric field \mathcal{E} . Because of this, $\mu\mathcal{E}$ also appeared in Eqs. (9.38) and (9.39) as the coupling term that is responsible for the transition between the otherwise stationary states $|I\rangle$ and $|II\rangle$. In other words, for the small \mathcal{E} we have been considering, $\mu\mathcal{E}$ is the so-called “perturbation term” in the Hamiltonian matrix element which connects the states $|I\rangle$ and $|II\rangle$. In the general case, we would have that $\mu\mathcal{E}$ gets replaced by the matrix element $\langle II|H|I\rangle$ (see Section 5-6).

In Volume I (Section 42-5) we talked about the relations among light absorption, induced emission, and spontaneous emission in terms of the Einstein A - and B -coefficients. Here, we have at last the quantum mechanical procedure for computing these coefficients. What we have called $P(I \rightarrow II)$ for our two-state ammonia molecule corresponds precisely to the absorption coefficient B_{nm} of the Einstein radiation theory. For the complicated ammonia molecule—which is too difficult for anyone to calculate—we have taken the matrix element $\langle II|H|I\rangle$ as $\mu\mathcal{E}$, saying that μ is to be gotten from experiment. For simpler atomic systems, the μ_{mn} which belongs to any particular transition can be calculated from the *definition*

$$\mu_{mn}\mathcal{E} = \langle m|H|n\rangle = H_{mn}, \quad (9.56)$$

where H_{mn} is the matrix element of the Hamiltonian which includes the effects of a weak electric field. The μ_{mn} calculated in this way is called the *electric dipole matrix element*. The quantum mechanical theory of the absorption and emission of light is, therefore, reduced to a calculation of these matrix elements for particular atomic systems.

Our study of a simple two-state system has thus led us to an understanding of the general problem of the absorption and emission of light.

Other Two-State Systems

10-1 The hydrogen molecular ion

In the last chapter we discussed some aspects of the ammonia molecule under the approximation that it can be considered as a two-state system. It is, of course, not really a two-state system—there are many states of rotation, vibration, translation, and so on—but each of these states of motion must be analyzed in terms of two internal states because of the flip-flop of the nitrogen atom. Here we are going to consider other examples of systems which, to some approximation or other, can be considered as two-state systems. Lots of things will be approximate because there are always many other states, and in a more accurate analysis they would have to be taken into account. But in each of our examples we will be able to understand a great deal by just thinking about two states.

Since we will only be dealing with two-state systems, the Hamiltonian we need will look just like the one we used in the last chapter. When the Hamiltonian is independent of time, we know that there are two stationary states with definite—and usually different—energies. Generally, however, we start our analysis with a set of base states which are *not* these stationary states, but states which may, perhaps, have some other simple physical meaning. Then, the stationary states of the system will be represented by a linear combination of these base states.

For convenience, we will summarize the important equations from Chapter 9. Let the original choice of base states be $|I\rangle$ and $|2\rangle$. Then any state $|\psi\rangle$ is represented by the linear combination

$$|\psi\rangle = |I\rangle\langle I|\psi\rangle + |2\rangle\langle 2|\psi\rangle = |I\rangle C_1 + |2\rangle C_2. \quad (10.1)$$

The amplitudes C_i (by which we mean either C_1 or C_2) satisfy the two linear differential equations

$$i\hbar \frac{dC_i}{dt} = \sum_j H_{ij} C_j, \quad (10.2)$$

where both i and j take on the values 1 and 2.

When the terms of the Hamiltonian H_{ij} do not depend on t , the two states of definite energy (the stationary states), which we call

$$|\psi_I\rangle = |I\rangle e^{-(i/\hbar)E_I t} \quad \text{and} \quad |\psi_{II}\rangle = |II\rangle e^{-(i/\hbar)E_{II} t},$$

have the energies

$$\begin{aligned} E_I &= \frac{H_{11} + H_{22}}{2} + \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12}H_{21}}, \\ E_{II} &= \frac{H_{11} + H_{22}}{2} - \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12}H_{21}}. \end{aligned} \quad (10.3)$$

The two C 's for each of these states have the same time dependence. The state vectors $|I\rangle$ and $|II\rangle$ which go with the stationary states are related to our original base states $|I\rangle$ and $|2\rangle$ by

$$\begin{aligned} |I\rangle &= |I\rangle a_1 + |2\rangle a_2, \\ |II\rangle &= |I\rangle a'_1 + |2\rangle a'_2. \end{aligned} \quad (10.4)$$

10-1 The hydrogen molecular ion

10-2 Nuclear forces

10-3 The hydrogen molecule

10-4 The benzene molecule

10-5 Dyes

10-6 The Hamiltonian of a spin one-half particle in a magnetic field

10-7 The spinning electron in a magnetic field

The a 's are complex constants, which satisfy

$$|a_1|^2 + |a_2|^2 = 1,$$

$$\frac{a_1}{a_2} = \frac{H_{12}}{E_I - H_{11}}, \quad (10.5)$$

$$|a'_1|^2 + |a'_2|^2 = 1,$$

$$\frac{a'_1}{a'_2} = \frac{H_{12}}{E_{II} - H_{11}}. \quad (10.6)$$

If H_{11} and H_{22} are equal—say both are equal to E_0 —and $H_{12} = H_{21} = -A$, then $E_I = E_0 + A$, $E_{II} = E_0 - A$, and the states $|I\rangle$ and $|II\rangle$ are particularly simple:

$$|I\rangle = \frac{1}{\sqrt{2}} [|1\rangle - |2\rangle], \quad |II\rangle = \frac{1}{\sqrt{2}} [|1\rangle + |2\rangle]. \quad (10.7)$$

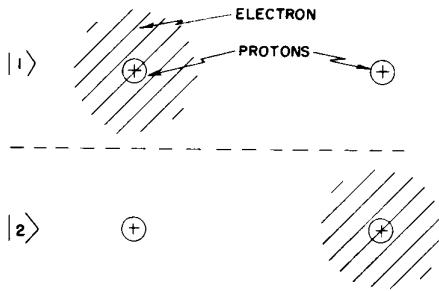


Fig. 10-1. A set of base states for two protons and an electron.

Now we will use these results to discuss a number of interesting examples taken from the fields of chemistry and physics. The first example is the hydrogen molecular ion. A positively ionized hydrogen molecule consists of two protons with one electron worming its way around them. If the two protons are very far apart, what states would we expect for this system? The answer is pretty clear: The electron will stay close to one proton and form a hydrogen atom in its lowest state, and the other proton will remain alone as a positive ion. So, if the two protons are far apart, we can visualize one physical state in which the electron is “attached” to one of the protons. There is, clearly, another state symmetric to that one in which the electron is near the other proton, and the first proton is the one that is an ion. We will take these two as our base states, and we’ll call them $|1\rangle$ and $|2\rangle$. They are sketched in Fig. 10-1. Of course, there are really many states of an electron near a proton, because the combination can exist as any one of the excited states of the hydrogen atom. We are not interested in that variety of states now; we will consider only the situation in which the hydrogen atom is in the lowest state—its ground state—and we will, for the moment, disregard spin of the electron. We can just suppose that for all our states the electron has its spin “up” along the z -axis.[†]

Now to remove an electron from a hydrogen atom requires 13.6 electron volts of energy. So long as the two protons of the hydrogen molecular ion are far apart, it still requires about this much energy—which is for our present considerations a great deal of energy—to get the electron somewhere near the midpoint between the protons. So it is impossible, classically, for the electron to jump from one proton to the other. However, in quantum mechanics it is possible—though not very likely. There is some small amplitude for the electron to move from one proton to the other. As a first approximation, then, each of our base states $|1\rangle$ and $|2\rangle$ will have the energy E_0 , which is just the energy of one hydrogen atom plus one proton. We can take that the Hamiltonian matrix elements H_{11} and H_{22} are both approximately equal to E_0 . The other matrix elements H_{12} and H_{21} , which are the amplitudes for the electron to go back and forth, we will again write as $-A$.

You see that this is the same game we played in the last two chapters. If we disregard the fact that the electron can flip back and forth, we have two states of exactly the same energy. This energy will, however, be split into two energy levels by the possibility of the electron going back and forth—the greater the probability of the transition, the greater the split. So the two energy levels of the system are $E_0 + A$ and $E_0 - A$, and the states which have these definite energies are given by Eqs. (10.7).

[†] This is satisfactory so long as there are no important magnetic fields. We will discuss the effects of magnetic fields on the electron later in this chapter, and the very small effects of spin in the hydrogen atom in Chapter 12.

From our solution we see that if a proton and a hydrogen ion are put anywhere near together, the electron will not stay on one of the protons but will flip back and forth between the two protons. If it starts on one of the protons, it will oscillate back and forth between the states $|I\rangle$ and $|II\rangle$ —giving a time-varying solution. In order to have the lowest energy solution (which does not vary with time), it is necessary to start the system with equal amplitudes for the electron to be around each proton. Remember, there are not two electrons—we are not saying that there is an electron around each proton. There is only *one* electron, and it has the same amplitude— $1/\sqrt{2}$ in magnitude—to be in either position.

Now the amplitude A for an electron which is near one proton to get to the other one depends on the separation between the protons. The closer the protons are together, the larger the amplitude. You remember that we talked in Chapter 7 about the amplitude for an electron to “penetrate a barrier,” which it could not do classically. We have the same situation here. The amplitude for an electron to get across decreases roughly exponentially with the distance—for large distances. Since the transition probability, and therefore A , gets larger when the protons are closer together, the separation of the energy levels will also get larger. If the system is in the state $|I\rangle$, the energy $E_0 + A$ increases with decreasing distance, so these quantum mechanical effects make a *repulsive* force tending to keep the protons apart. On the other hand, if the system is in the state $|II\rangle$, the total energy *decreases* if the protons are brought closer together; there is an *attractive* force pulling the protons together. The variation of the two energies with the distance between the two protons should be roughly as shown in Fig. 10-2. We have, then, a quantum-mechanical explanation of the binding force that holds the H_2^+ ion together.

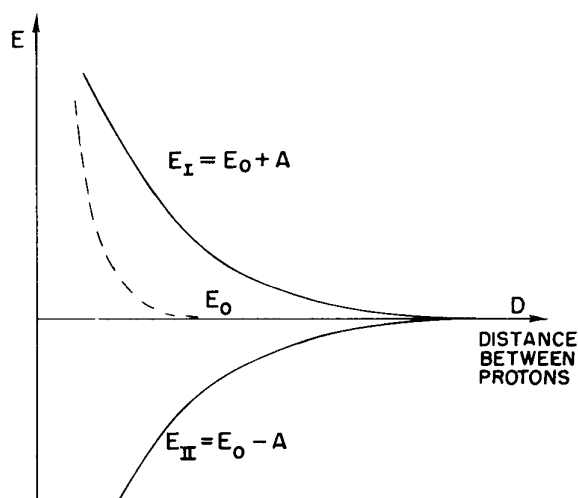


Fig. 10-2. The energies of the two stationary states of the H_2^+ ion as a function of the distance between the two protons.

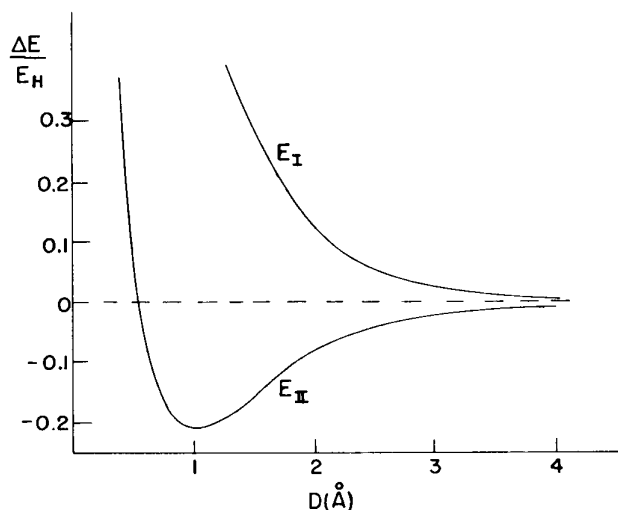


Fig. 10-3. The energy levels of the H_2^+ ion as a function of the interproton distance D . ($E_h = 13.6$ ev.)

We have, however, forgotten one thing. In addition to the force we have just described, there is also an electrostatic repulsive force between the two protons. When the two protons are far apart—as in Fig. 10-1—the “bare” proton sees only a neutral atom, so there is a negligible electrostatic force. At very close distances, however, the “bare” proton begins to get “inside” the electron distribution—that is, it is closer to the proton on the average than to the electron. So there begins to be some extra electrostatic energy which is, of course, positive. This energy—which also varies with the separation—should be included in E_0 . So for E_0 we should take something like the broken-line curve in Fig. 10-2 which rises rapidly for distances less than the radius of a hydrogen atom. We should add and subtract the flip-flop energy A from this E_0 . When we do that, the energies E_I and E_{II} will vary with the interproton distance D as shown in Fig. 10-3. [In this figure, we have plotted the results of a more detailed calculation. The interproton distance

is given in units of $1 \text{ A}(10^{-8} \text{ cm})$, and the excess energy over a proton plus a hydrogen atom is given in units of the binding energy of the hydrogen atom—the so-called “Rydberg” energy, 13.6 ev.] We see that the state $|II\rangle$ has a minimum-energy point. This will be the equilibrium configuration—the lowest energy condition—for the H_2^+ ion. The energy at this point is lower than the energy of a separated proton and hydrogen ion, so the system is bound. A single electron acts to hold the two protons together. A chemist would call it a “one-electron bond.”

This kind of chemical binding is also often called “quantum mechanical resonance” (by analogy with the two coupled pendulums we have described before). But that really sounds more mysterious than it is, it’s only a “resonance” if you start out by making a poor choice for your base states—as we did also! If you picked the state $|II\rangle$, you would have the lowest energy state—that’s all.

We can see in another way why such a state should have a lower energy than a proton and a hydrogen atom. Let’s think about an electron near two protons with some fixed, but not too large, separation. You remember that with a single proton the electron is “spread out” because of the uncertainty principle. It seeks a balance between having a low coulomb *potential* energy and not getting confined into too small a space, which would make a high *kinetic* energy (because of the uncertainty relation $\Delta p \Delta x \approx \hbar$). Now if there are two protons, there is more space where the electron can have a low potential energy. It can spread out—lowering its kinetic energy—without increasing its potential energy. The net result is a lower energy than a hydrogen atom. Then why does the other state $|I\rangle$ have a higher energy? Notice that this state is the *difference* of the states $|I\rangle$ and $|2\rangle$. Because of the symmetry of $|I\rangle$ and $|2\rangle$, the difference must have zero amplitude to find the electron half-way between the two protons. This means that the electron is somewhat more confined, which leads to a larger energy.

We should say that our approximate treatment of the H_2^+ ion as a two-state system breaks down pretty badly once the protons get as close together as they are at the minimum in the curve of Fig. 10-3, and so, will not give a good value for the actual binding energy. For small separations, the energies of the two “states” we imagined in Fig. 6-1 are not really equal to E_0 ; a more refined quantum mechanical treatment is needed.

Suppose we ask now what would happen if instead of two protons, we had two different objects—as, for example, one proton and one lithium positive ion (both particles still with a single positive charge). In such a case, the two terms H_{11} and H_{22} of the Hamiltonian would no longer be equal; they would, in fact, be quite different. If it should happen that the difference ($H_{11} - H_{22}$) is, in absolute value, much greater than $A = -H_{12}$, the attractive force gets very weak, as we can see in the following way.

If we put $H_{12}H_{21} = A^2$ into Eqs. (10.3) we get

$$E = \frac{H_{11} + H_{22}}{2} \pm \frac{H_{11} - H_{22}}{2} \sqrt{1 + \frac{4A^2}{(H_{11} - H_{22})^2}}.$$

When $H_{11} - H_{22}$ is much greater than A^2 , the square root is very nearly equal to

$$1 + \frac{2A^2}{(H_{11} - H_{22})^2}.$$

The two energies are then

$$\begin{aligned} E_I &= H_{11} + \frac{A^2}{(H_{11} - H_{22})}, \\ E_{II} &= H_{22} - \frac{A^2}{(H_{11} - H_{22})}. \end{aligned} \quad (10.8)$$

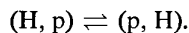
They are now very nearly just the energies H_{11} and H_{22} of the isolated atoms, pushed apart only slightly by the flip-flop amplitude A .

The energy difference $E_I - E_{II}$ is

$$(H_{11} - H_{22}) + \frac{2A^2}{H_{11} - H_{22}}.$$

The *additional* separation from the flip-flop of the electron is no longer equal to $2A$; it is smaller by the factor $A/(H_{11} - H_{22})$, which we are now taking to be much less than one. Also, the dependence of $E_I - E_{II}$ on the separation of the two nuclei is much smaller than for the H_2^+ ion—it is also reduced by the factor $A/(H_{11} - H_{22})$. We can now see why the binding of unsymmetric diatomic molecules is generally very weak.

In our theory of the H_2^+ ion we have discovered an explanation for the mechanism by which an electron shared by two protons provides, in effect, an attractive force between the two protons which can be present even when the protons are at large distances. The attractive force comes from the reduced energy of the system due to the possibility of the electron jumping from one proton to the other. In such a jump the system changes from the configuration (hydrogen atom, proton) to the configuration (proton, hydrogen atom), or switches back. We can write the process symbolically as



The energy shift due to this process is proportional to the amplitude A that an electron whose energy is $-W_H$ (its binding energy in the hydrogen atom) can get from one proton to the other.

For large distances R between the two protons, the electrostatic potential energy of the electron is nearly zero over most of the space it must go when it makes its jump. In this space, then, the electron moves nearly like a free particle in empty space—but with a *negative* energy! We have seen in Chapter 3 [Eq. (3.7)] that the amplitude for a particle of definite energy to get from one place to another a distance r away is proportional to

$$\frac{e^{(i/\hbar)pr}}{r},$$

where p is the momentum corresponding to the definite energy. In the present case (using the nonrelativistic formula), p is given by

$$\frac{p^2}{2m} = -W_H. \quad (10.9)$$

This means that p is an imaginary number,

$$p = i\sqrt{2mW_H}$$

(the other sign for the radical gives nonsense here).

We should expect, then, that the amplitude A for the H_2^+ ion will vary as

$$A \sim \frac{e^{-(\sqrt{2mW_H}/\hbar)R}}{R} \quad (10.10)$$

for large separations R between the two protons. The energy shift due to the electron binding is proportional to A , so there is a force pulling the two protons together which is proportional—for large R —to the derivative of (10.10) with respect to R .

Finally, to be complete, we should remark that in the two-proton, one-electron system there is still one other effect which gives a dependence of the energy on R . We have neglected it until now because it is usually rather unimportant—the exception is just for those very large distances where the energy of the exchange term A has decreased exponentially to very small values. The new effect we are thinking of is the electrostatic attraction of the proton for the hydrogen atom, which comes about in the same way any charged object attracts a neutral object. The bare proton makes an electric field \mathcal{E} (varying as $1/R^2$) at the neutral hydrogen atom. The atom becomes polarized, taking on an induced dipole moment μ proportional to \mathcal{E} . The energy of the dipole is $\mu\mathcal{E}$, which is proportional to \mathcal{E}^2 —or to $1/R^4$. So there is a term in the energy of the system which decreases with the fourth power of the distance. (It is a correction to E_0 .) This energy falls off with

distance more slowly than the shift A given by (10.10); at some large separation R it becomes the only remaining important term giving a variation of energy with R —and, therefore, the only remaining force. Note that the electrostatic term has the same sign for both of the base states (the force is attractive, so the energy is negative) and so also for the two stationary states, whereas the electron exchange term A gives opposite signs for the two stationary states.

10-2 Nuclear forces

We have seen that the system of a hydrogen atom and a proton has an energy of interaction due to the exchange of the single electron which varies at large separations R as

$$\frac{e^{-\alpha R}}{R}, \quad (10.11)$$

with $\alpha = \sqrt{2mW_H}/\hbar$. (One usually says that there is an exchange of a “virtual” electron when—as here—the electron has to jump across a space where it would have a negative energy. More specifically, a “virtual exchange” means that the phenomenon involves a quantum mechanical interference between an exchanged state and a nonexchanged state.)

Now we might ask the following question: Could it be that forces between other kinds of particles have an analogous origin? What about, for example, the nuclear force between a neutron and a proton, or between two protons? In an attempt to explain the nature of nuclear forces, Yukawa proposed that the force between two nucleons is due to a similar exchange effect—only, in this case, due to the virtual exchange, not of an electron, but of a new particle, which he called a “meson.” Today, we would identify Yukawa’s meson with the π -meson (or “pion”) produced in high-energy collisions of protons or other particles.

Let’s see, as an example, what kind of a force we would expect from the exchange of a positive pion (π^+) of mass m_π between a proton and a neutron. Just as a hydrogen atom H^0 can go into a proton p^+ by giving up an electron e^-



a proton p^+ can go into a neutron n^0 by giving up a π^+ meson:



So if we have a proton at a and a neutron at b separated by the distance R , the proton can become a neutron by emitting a π^+ which is then absorbed by the neutron at b , turning it into a proton. There is an energy of interaction of the two-nucleon (plus pion) system which depends on the amplitude A for the pion exchange—just as we found for the electron exchange in the H_2^+ ion.

In the process (10.12), the energy of the H^0 atom is less than that of the proton by W_H (calculating nonrelativistically, and omitting the rest energy mc^2 of the electron), so the electron has a negative *kinetic* energy—or imaginary momentum—as in Eq. (10.9). In the nuclear process (10.13), the proton and neutron have almost equal masses, so the π^+ will have zero *total* energy. The relation between the total energy E and the momentum p for a pion of mass m_π is

$$E^2 = p^2c^2 + m_\pi^2c^4$$

Since E is zero (or at least negligible in comparison with m_π), the momentum is again imaginary:

$$p = im_\pi c.$$

Using the same arguments we gave for the amplitude that a bound electron would penetrate the barrier in the space between two protons, we get for the nuclear case an exchange amplitude A which should—for large R —go as

$$\frac{e^{-(m_\pi c/\hbar)R}}{R}. \quad (10.14)$$

The interaction energy is proportional to A , and so varies in the same way. We get an energy variation in the form of the so-called *Yukawa potential* between two nucleons. Incidentally, we obtained this same formula earlier directly from the differential equation for the motion of a pion in free space [see Chapter 28, Vol. II, Eq. (28.18)].

We can, following the same line of argument, discuss the interaction between two protons (or between two neutrons) which results from the exchange of a *neutral pion* (π^0). The basic process is now

$$p^+ \rightarrow p^+ + \pi^0. \quad (10.15)$$

A proton can emit a virtual π^0 , but then it remains still a proton. If we have two protons, proton No. 1 can emit a virtual π^0 which is absorbed by proton No. 2. At the end, we still have two protons. This is somewhat different from the H_2^+ ion. There the H^0 went into a different condition—the proton—after emitting the electron. Now we are assuming that a proton can emit a π^0 without changing its character. Such processes are, in fact, observed in high-energy collisions. The process is analogous to the way that an electron emits a photon and ends up still an electron:

$$e \rightarrow e + \text{photon}. \quad (10.16)$$

We do not “see” the photons inside the electrons before they are emitted or after they are absorbed, and their emission does not change the “nature” of the electron.

Going back to the two protons, there is an interaction energy which arises from the amplitude A that one proton emits a neutral pion which travels across (with imaginary momentum) to the other proton and is absorbed there. This amplitude is again proportional to (10.14), with m_π the mass of the neutral pion. All the same arguments give an equal interaction energy for two neutrons. Since the nuclear forces (disregarding electrical effects) between neutron and proton, between proton and proton, between neutron and neutron are the same, we conclude that the masses of the charged and neutral pions should be the same. Experimentally, the masses are indeed very nearly equal, and the small difference is about what one would expect from electric self-energy corrections (see Chapter 28, Vol. II).

There are other kinds of particles—like K-mesons—which can be exchanged between two nucleons. It is also possible for two pions to be exchanged at the same time. But all of these other exchanged “objects” have a rest mass m_x higher than the pion mass m_π , and lead to terms in the exchange amplitude which vary as

$$\frac{e^{-(m_x c/\hbar)R}}{R}.$$

These terms die out faster with increasing R than the one-meson term. No one knows, today, how to calculate these higher-mass terms, but for large enough values of R only the one-pion term survives. And, indeed, those experiments which involve nuclear interactions only at large distances do show that the interaction energy is as predicted from the one-pion exchange theory.

In the classical theory of electricity and magnetism, the coulomb electrostatic interaction and the radiation of light by an accelerating charge are closely related—both come out of the Maxwell equations. We have seen in the quantum theory that light can be represented as the quantum excitations of the harmonic oscillations of the classical electromagnetic fields in a box. Alternatively, the quantum theory can be set up by describing light in terms of particles—photons—which obey Bose statistics. We emphasized in Section 4–5 that the two alternative points of view always give identical predictions. Can the second point of view be carried through completely to include *all* electromagnetic effects? In particular, if we want to describe the electromagnetic field purely in terms of Bose particles—that is, in terms of photons—what is the coulomb force due to?

From the “particle” point of view the coulomb interaction between two electrons *comes from the exchange of a virtual photon*. One electron emits a photon—as in reaction (10.16)—which goes over to the second electron, where it is absorbed in the reverse of the same reaction. The interaction energy is again given

by a formula like (10.14), but now with m_π replaced by the rest mass of the photon—which is zero. So the virtual exchange of a photon between two electrons gives an interaction energy that varies simply inversely as R , the distance between the two electrons—just the normal coulomb potential energy! In the “particle” theory of electromagnetism, the process of a virtual photon exchange gives rise to all the phenomena of electrostatics.

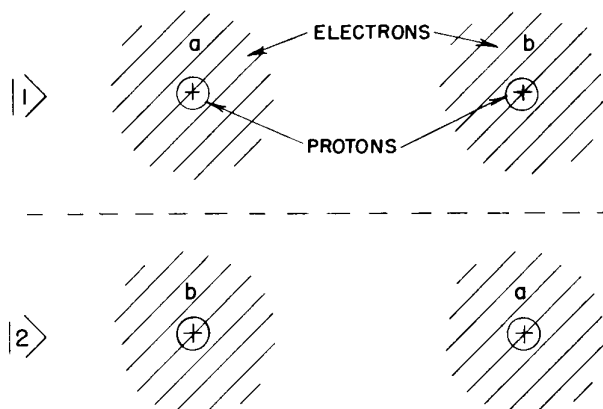


Fig. 10-4. A set of base states for the H_2 molecule.

10-3 The hydrogen molecule

As our next two-state system we will look at the neutral hydrogen molecule H_2 . It is, naturally, more complicated to understand because it has two electrons. Again, we start by thinking of what happens when the two protons are well separated. Only now we have two electrons to add. To keep track of them, we'll call one of them “electron a ” and the other “electron b .” We can again imagine two possible states. One possibility is that “electron a ” is around the first proton and “electron b ” is around the second, as shown in Fig. 10-4(a). We have simply two hydrogen atoms. We will call this state $|1\rangle$. There is also another possibility: that “electron b ” is around the first proton and that “electron a ” is around the second. We call this state $|2\rangle$. From the symmetry of the situation, those two possibilities should be energetically equivalent, but, as we will see, the energy of the system is *not* just the energy of two hydrogen atoms. We should mention that there are many other possibilities. For instance, “electron a ” might be near the first proton and “electron b ” might be in another state around the *same* proton. We'll disregard such a case, since it will certainly have higher energy (because of the large coulomb repulsion between the two electrons). For greater accuracy, we would have to include such states, but we can get the essentials of the molecular binding by considering just the two states of Fig. 10.4. To this approximation we can describe any state by giving the amplitude $\langle 1 | \phi \rangle$ to be in the state $|1\rangle$ and an amplitude $\langle 2 | \phi \rangle$ to be in state $|2\rangle$. In other words, the state vector $|\phi\rangle$ can be written as the linear combination

$$|\phi\rangle = \sum_i |i\rangle \langle i | \phi \rangle.$$

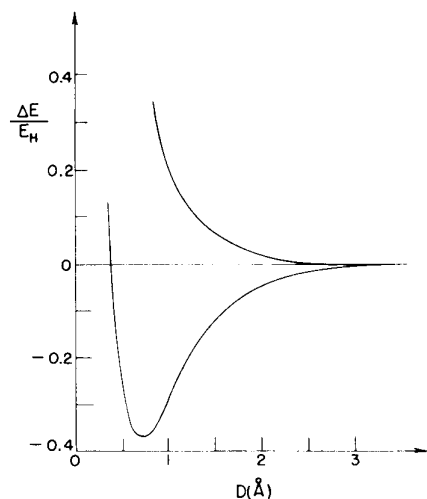


Fig. 10-5. The energy levels of the H_2 molecule for different interproton distances D . ($E_h = 13.6$ ev.)

To proceed, we assume—as usual—that there is some amplitude A that the electrons can move through the intervening space and exchange places. This possibility of exchange means that the energy of the system is split, as we have seen for other two-state systems. As for the hydrogen molecular ion, the splitting is very small when the distance between the protons is large. As the protons approach each other, the amplitude for the electrons to go back and forth increases, so the splitting increases. The decrease of the lower energy state means that there is an attractive force which pulls the atoms together. Again the energy levels rise when the protons get very close together because of the coulomb repulsion. The net final result is that the two stationary states have energies which vary with the separation as shown in Fig. 10-5. At a separation of about 0.74 Å, the lower energy

level reaches a minimum; this is the proton-proton distance of the true hydrogen molecule.

Now you have probably been thinking of an objection. What about the fact that the two electrons are identical particles? We have been calling them “electron *a*” and “electron *b*,” but there really is no way to tell which is which. And we have said in Chapter 4 that for electrons—which are Fermi particles—if there are two ways something can happen by exchanging the electrons, the two amplitudes will interfere with a *negative* sign. This means that if we switch which electron is which, the sign of the amplitude must reverse. We have just concluded, however, that the bound state of the hydrogen molecule would be (at $t = 0$)

$$|II\rangle = \frac{1}{\sqrt{2}} (|I\rangle + |2\rangle).$$

However, according to our rules of Chapter 4, this state is not allowed. If we reverse which electron is which, we get the state

$$\frac{1}{\sqrt{2}} (|2\rangle + |I\rangle),$$

and we get the same sign instead of the opposite one.

These arguments are correct *if both electrons have the same spin*. It is true that if both electrons have spin up (or both have spin down), the only state that is permitted is

$$|I\rangle = \frac{1}{\sqrt{2}} (|I\rangle - |2\rangle).$$

For this state, an interchange of the two electrons gives

$$(|2\rangle - |I\rangle),$$

which is $-|I\rangle$, as required. So if we bring two hydrogen atoms near to each other with their electrons spinning in the same direction, they can go into the state $|I\rangle$ and not state $|II\rangle$. But notice that state $|I\rangle$ is the *upper* energy state. Its curve of energy versus separation has no minimum. The two hydrogens will always repel and will not form a molecule. So we conclude that the hydrogen molecule cannot exist with parallel electron spins. And that is right.

On the other hand, our state $|II\rangle$ is perfectly symmetric for the two electrons. In fact, if we interchange which electron we call *a* and which we call *b* we get back exactly the same state. We saw in Section 4-7 that if two Fermi particles are in the same state, they *must* have opposite spins. So, the bound hydrogen molecule must have one electron with spin up and one with spin down.

The whole story of the hydrogen molecule is really somewhat more complicated if we want to include the proton spins. It is then no longer right to think of the molecule as a *two-state* system. It should really be looked at as an *eight-state* system—there are four possible spin arrangements for each of our states $|I\rangle$ and $|2\rangle$ —so we were cutting things a little short by neglecting the spins. Our final conclusions are, however, correct.

We find that the lowest energy state—the only bound state—of the H_2 molecule has the two electrons with spins opposite. The total spin angular momentum of the electrons is zero. On the other hand, two nearby hydrogen atoms with spins parallel—and so with a total angular momentum \hbar —must be in a higher (unbound) energy state; the atoms repel each other. There is an interesting correlation between the spins and the energies. It gives another illustration of something we mentioned before, which is that there appears to be an “interaction” energy between two spins because the case of parallel spins has a higher energy than the opposite case. In a certain sense you could say that the spins try to reach an antiparallel condition and, in doing so, have the potential to liberate energy—not because there is a large magnetic force, but because of the exclusion principle.

We saw in Section 10-1 that the binding of two *different* ions by a *single* electron is likely to be quite weak. This is *not* true for binding by *two* electrons. Suppose the two protons in Fig. 10-4 were replaced by any two ions (with closed inner electron shells and a single ionic charge), and that the binding energies of an electron at the two ions are different. The energies of states $|1\rangle$ and $|2\rangle$ would still be equal because in each of these states we have one electron bound to each ion. Therefore, we always have the splitting proportional to A . Two-electron binding is ubiquitous—it is the most common valence bond. Chemical binding usually involves this flip-flop game played by two electrons. Although two atoms can be bound together by only one electron, it is relatively rare—because it requires just the right conditions.

Finally, we want to mention that if the energy of attraction for an electron to one nucleus is much greater than to the other, then what we have said earlier about ignoring other possible states is no longer right. Suppose nucleus a (or it may be a positive ion) has a much stronger attraction for an electron than does nucleus b . It may then happen that the total energy is still fairly low even when both electrons are at nucleus a , and no electron is at nucleus b . The strong attraction may more than compensate for the mutual repulsion of the two electrons. If it does, the lowest energy state may have a large amplitude to find both electrons at a (making a negative ion) and a small amplitude to find any electron at b . The state looks like a negative ion with a positive ion. This is, in fact, what happens in an “ionic” molecule like NaCl. You can see that all the gradations between covalent binding and ionic binding are possible.

You can now begin to see how it is that many of the facts of chemistry can be most clearly understood in terms of a quantum mechanical description.

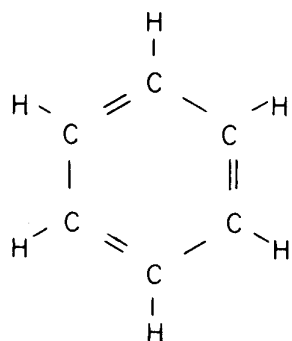


Fig. 10-6. The benzene molecule, C_6H_6 .

10-4 The benzene molecule

Chemists have invented nice diagrams to represent complicated organic molecules. Now we are going to discuss one of the most interesting of them—the benzene molecule shown in Fig. 10-6. It contains six carbon and six hydrogen atoms in a symmetrical array. Each bar of the diagram represents a *pair* of electrons, with spins opposite, doing the covalent bond dance. Each hydrogen atom contributes one electron and each carbon atom contributes four electrons to make up the total of 30 electrons involved. (There are two more electrons close to the nucleus of the carbon which form the first, or K, shell. These are not shown since they are so tightly bound that they are not appreciably involved in the covalent binding.) So each bar in the figure represents a *bond*, or pair of electrons, and the double bonds mean that there are *two pairs* of electrons between alternate pairs of carbon atoms.

There is a mystery about this benzene molecule. We can calculate what energy should be required to form this chemical compound, because the chemists have measured the energies of various compounds which involve pieces of the ring—for instance, they know the energy of a double bond by studying ethylene, and so on. We can, therefore, calculate the total energy we should expect for the benzene

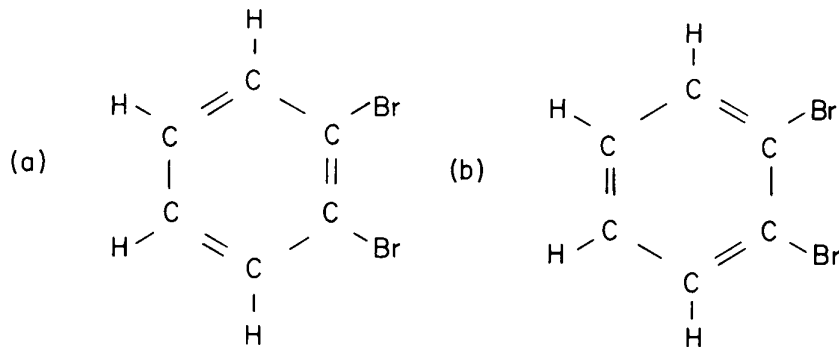


Fig. 10-7. Two possibilities of orthodibromobenzene. The two bromines could be separated by a single bond or by a double bond.

molecule. The actual energy of the benzene ring, however, is much lower than we get by such a calculation; it is more tightly bound than we would expect from what is called an “unsaturated double bond system.” Usually a double bond system which is not in such a ring is easily attacked chemically because it has a relatively high energy—the double bonds can be easily broken by the addition of other hydrogens. But in benzene the ring is quite permanent and hard to break up. In other words, benzene has a much lower energy than you would calculate from the bond picture.

Then there is another mystery. Suppose we replace two adjacent hydrogens by bromine atoms to make ortho-dibromobenzene. There are two ways to do this, as shown in Fig. 10-7. The bromines could be on the opposite ends of a double bond as shown in part (a) of the figure, or could be on the opposite ends of a single bond as in (b). One would think that ortho-dibromobenzene should have two different forms, but it doesn't. There is only one such chemical.†

Now we want to resolve these mysteries—and perhaps you have already guessed how: by noticing, of course, that the “ground state” of the benzene ring is really a two-state system. We could imagine that the bonds in benzene could be in either of the two arrangements shown in Fig. 10-8. You say, “But they are really the same; they should have the same energy.” Indeed, they should. And for that reason they must be analyzed as a two-state system. Each state represents a different configuration of the whole set of electrons, and there is some amplitude A that the whole bunch can switch from one arrangement to the other—there is a chance that the electrons can flip from one dance to the other.

As we have seen, this chance of flipping makes a mixed state whose energy is lower than you would calculate by looking separately at either of the two pictures in Fig. 10-8. Instead, there are two stationary states—one with an energy above and one with an energy below the expected value. So actually, the true normal state (lowest energy) of benzene is neither of the possibilities shown in Fig. 10-8, but it has the amplitude $1/\sqrt{2}$ to be in each of the states shown. It is the only state that is involved in the chemistry of benzene at normal temperatures. Incidentally, the upper state also exists; we can tell it is there because benzene has a strong absorption for ultraviolet light at the frequency $\omega = (E_I - E_{II})/\hbar$. You will remember that in ammonia, where the object flipping back and forth was three protons, the energy separation was in the microwave region. In benzene, the objects are electrons, and because they are much lighter, they find it easier to flip back and forth, which makes the coefficient A very much larger. The result is that the energy difference is much larger—about 1.5 eV, which is the energy of an ultraviolet photon.‡

What happens if we substitute bromine? Again the two “possibilities” (a) and (b) in Fig. 10-7 represent the two different electron configurations. The only difference is that the two base states we start with would have slightly different energies. The lowest energy stationary state will still involve a linear combination of the two states, but with unequal amplitudes. The amplitude for state $|1\rangle$ might have a value something like $\sqrt{2/3}$, say, whereas state $|2\rangle$ would have the magnitude

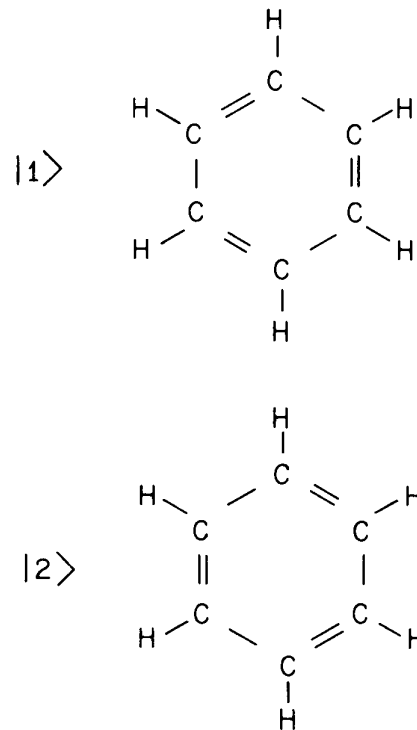


Fig. 10-8. A set of base states for the benzene molecule.

† We are oversimplifying a little. Originally, the chemists thought that there should be *four* forms of dibromobenzene: two forms with the bromines on adjacent carbon atoms (ortho-dibromobenzene), a third form with the bromines on next-nearest carbons (meta-dibromobenzene), and a fourth form with the bromines opposite to each other (para-dibromobenzene). However, they found only three forms—there is only *one* form of the ortho-molecule.

‡ What we have said is a little misleading. Absorption of ultraviolet light would be very weak in the two-state system we have taken for benzene, because the dipole moment matrix element between the two states is zero. [The two states are electrically symmetric, so in our formula Eq. (9.55) for the probability of a transition, the dipole moment μ is zero and no light is absorbed.] If these were the only states, the existence of the upper state would have to be shown in other ways. A more complete theory of benzene, however, which begins with more base states (such as those having adjacent double bonds) shows that the true stationary states of benzene are slightly distorted from the ones we have found. The resulting dipole moments permit the transition we mentioned in the text to occur by the absorption of ultraviolet light.

$\sqrt{1/3}$. We can't say for sure without more information, but once the two energies H_{11} and H_{22} are no longer equal, then the amplitudes C_1 and C_2 no longer have equal magnitudes. This means, of course, that one of the two possibilities in the figure is more likely than the other, but the electrons are mobile enough so that there is some amplitude for both. The other state has different amplitudes (like $\sqrt{1/3}$ and $-\sqrt{2/3}$) but lies at a higher energy. There is only one lowest state, not two as the naive theory of fixed chemical bonds would suggest.

10-5 Dyes

We will give you one more chemical example of the two-state phenomenon—this time on a larger molecular scale. It has to do with the theory of dyes. Many dyes—in fact, most artificial dyes—have an interesting characteristic; they have a kind of symmetry. Figure 10-9 shows an ion of a particular dye called magenta, which has a purplish red color. The molecule has three ring structures—two of which are benzene rings. The third is not exactly the same as a benzene ring because it has only two double bonds inside the ring. The figure shows two equally satisfactory pictures, and we would guess that they should have equal energies. But there is a certain amplitude that all the electrons can flip from one condition to the other, shifting the position of the “unfilled” position to the opposite end. With so many electrons involved, the flipping amplitude is somewhat lower than it is in the case of benzene, and the difference in energy between the two stationary states is smaller. There are, nevertheless, the usual two stationary states $|I\rangle$ and $|II\rangle$ which are the sum and difference combinations of the two base states shown in the figure. The energy separation of $|I\rangle$ and $|II\rangle$ comes out to be equal to the energy of a photon in the optical region. If one shines light on the molecule, there is a very strong absorption at one frequency, and it appears to be brightly colored. That's why it's a dye!

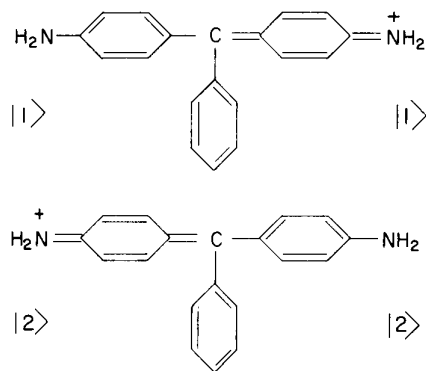


Fig. 10-9. Two base states for the molecule of the dye magenta.

Another interesting feature of such a dye molecule is that in the two base states shown, the center of electric charge is located at different places. As a result, the molecule should be strongly affected by an external electric field. We had a similar effect in the ammonia molecule. Evidently we can analyze it by using exactly the same mathematics, provided we know the numbers E_0 and A . Generally, these are obtained by gathering experimental data. If one makes measurements with many dyes, it is often possible to guess what will happen with some related dye molecule. Because of the large shift in the position of the center of electric charge the value of μ in formula (9.55) is large and the material has a high probability for absorbing light of the characteristic frequency $2A/\hbar$. Therefore, it is not only colored but very strongly so—a small amount of substance absorbs a lot of light.

The rate of flipping—and, therefore, A —is very sensitive to the complete structure of the molecule. By changing A , the energy splitting, and with it the color of the dye, can be changed. Also, the molecules do not have to be perfectly symmetrical. We have seen that the same basic phenomenon exists with slight modifications, even if there is some small asymmetry present. So, one can get some modification of the colors by introducing slight asymmetries in the molecules. For example, another important dye, malachite green, is very similar to magenta, but has two of the hydrogens replaced by CH_3 . It's a different color because the A is shifted and the flip-flop rate is changed.

10-6 The Hamiltonian of a spin one-half particle in a magnetic field

Now we would like to discuss a two-state system involving an object of spin one-half. Some of what we will say has been covered in earlier chapters, but doing it again may help to make some of the puzzling points a little clearer. We can think of an electron at rest as a two-state system. Although we will be talking in this section about “an electron,” what we find out will be true for *any* spin one-half particle. Suppose we choose for our base states $|I\rangle$ and $|2\rangle$ the states in which the z -component of the electron spin is $+\hbar/2$ and $-\hbar/2$.

These states are, of course, the same ones we have called (+) and (−) in earlier chapters. To keep the notation of this chapter consistent, though, we call the “plus” spin state $|1\rangle$ and the “minus” spin state $|2\rangle$ —where “plus” and “minus” refer to the angular momentum in the z -direction.

Any possible state ψ for the electron can be described as in Eq. (10.1) by giving the amplitude C_1 that the electron is in state $|1\rangle$, and the amplitude C_2 that it is in state $|2\rangle$. To treat this problem, we will need to know the Hamiltonian for this two-state system—that is, for an electron in a magnetic field. We begin with the special case of a magnetic field in the z -direction.

Suppose that the vector \mathbf{B} has only a z -component B_z . From the definition of the two base states (that is, spins parallel and antiparallel to \mathbf{B}) we know that they are already stationary states with a definite energy in the magnetic field. State $|1\rangle$ corresponds to an energy† equal to $-\mu B_z$ and state $|2\rangle$ to $+\mu B_z$. The Hamiltonian must be very simple in this case since C_1 , the amplitude to be in state $|1\rangle$, is not affected by C_2 , and vice versa:

$$\begin{aligned} i\hbar \frac{dC_1}{dt} &= E_1 C_1 = -\mu B_z C_1, \\ i\hbar \frac{dC_2}{dt} &= E_2 C_2 = +\mu B_z C_2. \end{aligned} \quad (10.17)$$

For this special case, the Hamiltonian is

$$\begin{aligned} H_{11} &= -\mu B_z, & H_{12} &= 0, \\ H_{21} &= 0, & H_{22} &= +\mu B_z. \end{aligned} \quad (10.18)$$

So we know what the Hamiltonian is for the magnetic field in the z -direction, and we know the energies of the stationary states.

Now suppose the field is *not* in the z -direction. What is the Hamiltonian? How are the matrix elements changed if the field is not in the z -direction? We are going to make an assumption that there is a kind of superposition principle for the terms of the Hamiltonian. More specifically, we want to assume that if two magnetic fields are superposed, the terms in the Hamiltonian simply add—if we know the H_{ij} for a pure B_z and we know the H_{ij} for a pure B_x , then the H_{ij} for both B_z and B_x together is simply the sum. This is certainly true if we consider only fields in the z -direction—if we double B_z , then all the H_{ij} are doubled. So let's assume that H is linear in the field \mathbf{B} . That's all we need to be able to find the H_{ij} for any magnetic field.

Suppose we have a constant field \mathbf{B} . We *could* have chosen our z -axis in its direction, and we *would* have found two stationary states with the energies $\mp\mu B$. Just choosing our axes in a different direction won't change the *physics*. Our *description* of the stationary states will be different, but their energies *will still be* $\mp\mu B$ —that is,

$$\begin{aligned} E_I &= -\mu\sqrt{B_x^2 + B_y^2 + B_z^2} \\ \text{and} \\ E_{II} &= +\mu\sqrt{B_x^2 + B_y^2 + B_z^2}. \end{aligned} \quad (10.19)$$

The rest of the game is easy. We have here the formulas for the energies. We want a Hamiltonian which is linear in B_x , B_y , and B_z , and which will give these energies when used in our general formula of Eq. (10.3). The problem: find the Hamiltonian. First, notice that the energy splitting is symmetric, with an average value of zero. Looking at Eq. (10.3), we can see directly that that requires

$$H_{22} = -H_{11}.$$

(Note that this checks with what we already know when B_x and B_y are both zero;

† We are taking the rest energy $m_0 c^2$ as our “zero” of energy and treating the magnetic moment μ of the electron as a *negative* number, since it points opposite to the spin.

in that case $H_{11} = -\mu B_z$ and $H_{22} = \mu B_z$.) Now if we equate the energies of Eq. (10.3) with what we know from Eq. (10.19), we have

$$\left(\frac{H_{11} - H_{22}}{2}\right)^2 + |H_{12}|^2 = \mu^2(B_x^2 + B_y^2 + B_z^2). \quad (10.20)$$

(We have also made use of the fact that $H_{21} = H_{12}^*$, so that $H_{12}H_{21}$ can also be written as $|H_{12}|^2$.) Again for the special case of a field in the z -direction, this gives

$$\mu^2 B_z^2 + |H_{12}|^2 = \mu^2 B_z^2.$$

Clearly, $|H_{12}|$ must be zero in this special case, which means that H_{12} cannot have any terms in B_z . (Remember, we have said that all terms must be linear in B_x , B_y , and B_z .)

So far, then, we have discovered that H_{11} and H_{22} have terms in B_z , while H_{12} and H_{21} do not. We can make a simple guess that will satisfy Eq. (10.20) if we say that

$$\begin{aligned} H_{11} &= -\mu B_z, \\ H_{22} &= \mu B_z, \end{aligned} \quad (10.21)$$

and

$$|H_{12}|^2 = \mu^2(B_x^2 + B_y^2).$$

And it turns out that that's the *only* way it can be done!

“Wait”—you say—“ H_{12} is not linear in B ; Eq. (10.21) gives $H_{12} = \mu\sqrt{B_x^2 + B_y^2}$.” Not necessarily. There is another possibility which *is* linear, namely,

$$H_{12} = \mu(B_x + iB_y).$$

There are, in fact, several such possibilities—most generally, we could write

$$H_{12} = \mu(B_x \pm iB_y)e^{i\delta},$$

where δ is some arbitrary phase. Which sign and phase should we use? It turns out that you can choose either sign, and any phase you want, and the physical results will always be the same. So the choice is a matter of convention. People ahead of us have chosen to use the minus sign and to take $e^{i\delta} = -1$. We might as well follow suit and write

$$H_{12} = -\mu(B_x - iB_y), \quad H_{21} = -\mu(B_x + iB_y).$$

(Incidentally, these conventions are related to, and consistent with, some of the arbitrary choices we made in Chapter 6.)

The complete Hamiltonian for an electron in an arbitrary magnetic field is, then

$$\begin{aligned} H_{11} &= -\mu B_z, & H_{12} &= -\mu(B_x - iB_y), \\ H_{21} &= -\mu(B_x + iB_y), & H_{22} &= +\mu B_z. \end{aligned} \quad (10.22)$$

And the equations for the amplitudes C_1 and C_2 are

$$\begin{aligned} i\hbar \frac{dC_1}{dt} &= -\mu[B_z C_1 + (B_x - iB_y)C_2], \\ i\hbar \frac{dC_2}{dt} &= -\mu[(B_x + iB_y)C_1 - B_z C_2]. \end{aligned} \quad (10.23)$$

So we have discovered the “equations of motion for the spin states” of an electron in a magnetic field. We guessed at them by making some physical argument, but the real test of any Hamiltonian is that it should give predictions in agreement with experiment. According to any tests that have been made, these equations are right. In fact, although we made our arguments only for constant fields, the Hamiltonian we have written is also right for magnetic fields which vary with time. So we can now use Eq. (10.23) to look at all kinds of interesting problems.

10-7 The spinning electron in a magnetic field

Example number one: We start with a constant field in the z -direction. There are just the two stationary states with energies $\mp\mu B_z$. Suppose we add a small field in the x -direction. Then the equations look like our old two-state problem. We get the flip-flop business once more, and the energy levels are split a little farther apart. Now let's let the x -component of the field vary with time—say, as $\cos \omega t$. The equations are then the same as we had when we put an oscillating electric field on the ammonia molecule in Chapter 9. You can work out the details in the same way. You will get the result that the oscillating field causes transitions from the $+z$ -state to the $-z$ -state—and vice versa—when the horizontal field oscillates near the resonant frequency $\omega_0 = 2\mu B_z/\hbar$. *This gives the quantum mechanical theory of the magnetic resonance phenomena we described in Chapter 35 of Volume II (see Appendix).*

It is also possible to make a maser which uses a spin one-half system. A Stern-Gerlach apparatus is used to produce a beam of particles polarized in, say, the $+z$ -direction, which are sent into a cavity in a constant magnetic field. The oscillating fields in the cavity can couple with the magnetic moment and induce transitions which give energy to the cavity.

Now let's look at the following question. Suppose we have a magnetic field \mathbf{B} which points in the direction whose polar angle is θ and azimuthal angle is ϕ , as in Fig. 10-10. Suppose, additionally, that there is an electron which has been prepared with its spin pointing along this field. What are the amplitudes C_1 and C_2 for such an electron? In other words, calling the state of the electron $|\psi\rangle$, we want to write

$$|\psi\rangle = |1\rangle C_1 + |2\rangle C_2,$$

where C_1 and C_2 are

$$C_1 = \langle 1 | \psi \rangle, \quad C_2 = \langle 2 | \psi \rangle,$$

where by $|1\rangle$ and $|2\rangle$ we mean the same thing we used to call $|+\rangle$ and $|-\rangle$ (referred to our chosen z -axis).

The answer to this question is also in our general equations for two-state systems. First, we know that since the electron's spin is parallel to \mathbf{B} it is in a stationary state with energy $E_I = -\mu B$. Therefore, both C_1 and C_2 must vary as $e^{-iE_I t/\hbar}$, as in (9.18); and their coefficients a_1 and a_2 are given by (10.5), namely,

$$\frac{a_1}{a_2} = \frac{H_{12}}{E_I - H_{11}}. \quad (10.24)$$

An additional condition is that a_1 and a_2 should be normalized so that $|a_1|^2 + |a_2|^2 = 1$. We can take H_{11} and H_{12} from (10.22) using

$$B_z = B \cos \theta, \quad B_x = B \sin \theta \cos \phi, \quad B_y = B \sin \theta \sin \phi.$$

So we have

$$\begin{aligned} H_{11} &= -\mu B \cos \theta, \\ H_{12} &= -\mu B \sin \theta (\cos \phi - i \sin \phi). \end{aligned} \quad (10.25)$$

The last factor in the second equation is, incidentally, $e^{-i\phi}$, so it is simpler to write

$$H_{12} = -\mu B \sin \theta e^{-i\phi}. \quad (10.26)$$

Using these matrix elements in Eq. (10.16)—and canceling $-\mu B$ from numerator and denominator—we find

$$\frac{a_1}{a_2} = \frac{\sin \theta e^{-i\phi}}{1 - \cos \theta}. \quad (10.27)$$

With this ratio and the normalization condition, we can find both a_1 and a_2 . That's not hard, but we can make a short cut with a little trick. Notice that

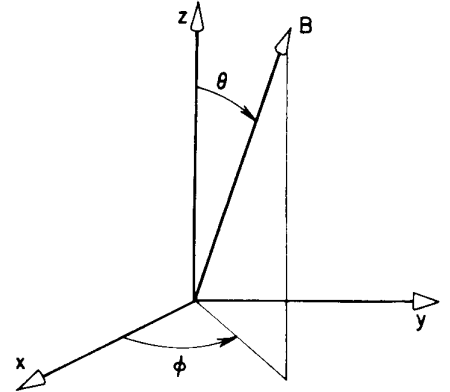


Fig. 10-10. The direction of \mathbf{B} is defined by the polar angle θ and the azimuthal angle ϕ .

$1 - \cos \theta = 2 \sin^2 (\theta/2)$, and that $\sin \theta = 2 \sin (\theta/2) \cos (\theta/2)$. Then Eq. (10.27) is equivalent to

$$\frac{a_1}{a_2} = \frac{\cos \frac{\theta}{2} e^{-i\phi}}{\sin \frac{\theta}{2}}. \quad (10.28)$$

So one possible answer is

$$a_1 = \cos \frac{\theta}{2} e^{-i\phi}, \quad a_2 = \sin \frac{\theta}{2}, \quad (10.29)$$

since it fits with (10.28) and also makes

$$|a_1|^2 + |a_2|^2 = 1.$$

As you know, multiplying both a_1 and a_2 by an arbitrary phase factor doesn't change anything. People generally prefer to make Eqs. (10.29) more symmetric by multiplying both by $e^{i\phi/2}$. So the form usually used is

$$a_1 = \cos \frac{\theta}{2} e^{-i\phi/2}, \quad a_2 = \sin \frac{\theta}{2} e^{+i\phi/2}, \quad (10.30)$$

and this is the answer to our question. The numbers a_1 and a_2 are the amplitudes to find an electron with its spin up or down along the z -axis when we know that its spin is along the axis at θ and ϕ . (The amplitudes C_1 and C_2 are just a_1 and a_2 times $e^{-iE_I t/\hbar}$.)

Now we notice an interesting thing. The strength B of the magnetic field does not appear anywhere in (10.30). The result is clearly the same in the limit that B goes to zero. This means that we have answered *in general* the question of how to represent a particle whose spin is along an arbitrary axis. The amplitudes of (10.30) are the projection amplitudes for spin one-half particles corresponding to the projection amplitudes we gave in Chapter 5 [Eqs. (5.38)] for spin-one particles. We can now find the amplitudes for filtered beams of spin one-half particles to go through any particular Stern-Gerlach filter.

Let $|+z\rangle$ represent a state with spin up along the z -axis, and $|-z\rangle$ represent the spin down state. If $|+z'\rangle$ represents a state with spin up along a z' -axis which makes the polar angles θ and ϕ with the z -axis, then in the notation of Chapter 5, we have

$$\langle +z | +z' \rangle = \cos \frac{\theta}{2} e^{-i\phi/2}, \quad \langle -z | +z' \rangle = \sin \frac{\theta}{2} e^{+i\phi/2}. \quad (10.31)$$

These results are equivalent to what we found in Chapter 6, Eq. (6.36), by purely geometrical arguments. (So if you decided to skip Chapter 6, you now have the essential results anyway.)

As our final example let's look again at one which we've already mentioned a number of times. Suppose that we consider the following problem. We start with an electron whose spin is in some given direction, then turn on a magnetic field in the z -direction for 25 minutes, and then turn it off. What is the final state? Again let's represent the state by the linear combination $|\psi\rangle = |1\rangle C_1 + |2\rangle C_2$. For this problem, however, the states of definite energy are also our base states $|1\rangle$ and $|2\rangle$. So C_1 and C_2 only vary in phase. We know that

$$C_1(t) = C_1(0) e^{-iE_I t/\hbar} = C_1(0) e^{+i\mu B t/\hbar},$$

and

$$C_2(t) = C_2(0) e^{-iE_{II} t/\hbar} = C_2(0) e^{-i\mu B t/\hbar}.$$

Now initially we said the electron spin was set in a given direction. That means that initially C_1 and C_2 are two numbers given by Eqs. (10.30). After we wait for a period of time T , the new C_1 and C_2 are the same two numbers multiplied respectively by $e^{i\mu B_z T/\hbar}$ and $e^{-i\mu B_z T/\hbar}$. What state is that? That's easy. It's exactly the same as if the angle ϕ had been changed by the subtraction of $2\mu B_z T/\hbar$ and the angle θ had been left unchanged. That means that at the end of the time

T , the state $|\psi\rangle$ represents an electron lined up in a direction which differs from the original direction only by a *rotation* about the z -axis through the angle $\Delta\phi = 2\mu B_z T/\hbar$. Since this angle is proportional to T , we can also say the direction of the spin *precesses* at the angular velocity $2\mu B_z/\hbar$ around the z -axis. This result we discussed several times previously in a less complete and rigorous manner. Now we have obtained a complete and accurate quantum mechanical description of the precession of atomic magnets.

It is interesting that the mathematical ideas we have just gone over for the spinning electron in a magnetic field can be applied to *any* two-state system. That means that by making a mathematical *analogy* to the spinning electron, *any problem* about two-state systems can be solved by pure geometry. It works like this. First you shift the zero of energy so that $(H_{11} + H_{22})$ is equal to zero so that $H_{11} = -H_{22}$. Then any two-state problem is *formally* the same as the electron in a magnetic field. All you have to do is *identify* $-\mu B_z$ with H_{11} and $-\mu(B_x - iB_y)$ with H_{12} . No matter what the physics is originally—an ammonia molecule, or whatever—you can translate it into a corresponding electron problem. So if we can solve the electron problem *in general*, we have solved *all* two-state problems.

And we have the general solution for the electron! Suppose you have some state to start with that has spin “up” in some direction, and you have a magnetic field \mathbf{B} that points in some other direction. You just rotate the spin direction around the axis of \mathbf{B} with the *vector* angular velocity $\boldsymbol{\omega}(t)$ equal to a constant times the vector \mathbf{B} (namely $\boldsymbol{\omega} = 2\mu\mathbf{B}/\hbar$). As \mathbf{B} varies with time, you keep moving the axis of the rotation to keep it parallel with \mathbf{B} , and keep changing the speed of rotation so that it is always proportional to the strength of \mathbf{B} . See Fig. 10-11. If you keep doing this, you will end up with a certain final orientation of the spin axis, and the amplitudes C_1 and C_2 are just given by the projections—using (10.30)—into your coordinate frame. You see, it’s just a geometric problem to keep track of where you end up after all the rotating. Although it’s easy to see what’s involved, this geometric problem (of finding the net result of a rotation with a varying angular velocity vector) is not easy to solve explicitly in the general case. Anyway, we see, *in principle*, the general solution to any two-state problem. In the next chapter we will look some more into the mathematical techniques for handling the important case of a spin one-half particle—and, therefore, for handling two-state systems in general.

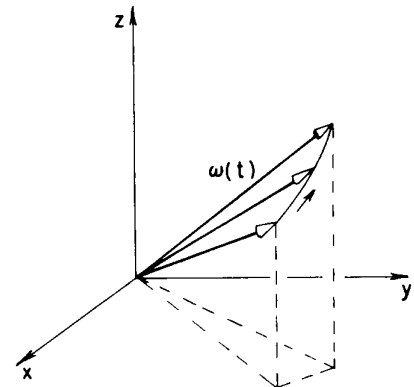


Fig. 10-11. The spin direction of an electron in a varying magnetic field $\mathbf{B}(t)$ precesses at the frequency $\omega(t)$ about an axis parallel to \mathbf{B} .

More Two-State Systems

11-1 The Pauli spin matrices

We continue our discussion of two-state systems. At the end of the last chapter we were talking about a spin one-half particle in a magnetic field. We described the spin state by giving the amplitude C_1 that the z -component of spin angular momentum is $+\hbar/2$ and the amplitude C_2 that it is $-\hbar/2$. In earlier chapters we have called these base states $|+\rangle$ and $|-\rangle$. We will now go back to that notation, although we may occasionally find it convenient to use $|+\rangle$ or $|1\rangle$, and $|-\rangle$ or $|2\rangle$, interchangeably.

We saw in the last chapter that when a spin one-half particle with a magnetic moment μ is in a magnetic field $\mathbf{B} = (B_x, B_y, B_z)$, the amplitudes $C_+ (= C_1)$ and $C_- (= C_2)$ are connected by the following differential equations:

$$i\hbar \frac{dC_+}{dt} = -\mu[B_z C_+ + (B_x - iB_y)C_-], \quad (11.1)$$

$$i\hbar \frac{dC_-}{dt} = -\mu[(B_x + iB_y)C_+ - B_z C_-].$$

In other words, the Hamiltonian matrix H_{ij} is

$$\begin{aligned} H_{11} &= -\mu B_z, & H_{12} &= -\mu(B_x - iB_y), \\ H_{21} &= -\mu(B_x + iB_y), & H_{22} &= +\mu B_z. \end{aligned} \quad (11.2)$$

And Eqs. (11.1) are, of course, the same as

$$i\hbar \frac{dC_i}{dt} = \sum_j H_{ij} C_j, \quad (11.3)$$

where i and j take on the values $+$ and $-$ (or 1 and 2).

The two-state system of the electron spin is so important that it is very useful to have a neater way of writing things. We will now make a little mathematical digression to show you how people usually write the equations of a two-state system. It is done this way: First, note that each term in the Hamiltonian is proportional to μ and to some component of \mathbf{B} ; we can then—*purely formally*—write that

$$H_{ij} = -\mu[\sigma_{ij}^x B_x + \sigma_{ij}^y B_y + \sigma_{ij}^z B_z]. \quad (11.4)$$

There is no new physics here; this equation just means that the coefficients σ_{ij}^x , σ_{ij}^y , and σ_{ij}^z —there are $4 \times 3 = 12$ of them—can be figured out so that (11.4) is identical with (11.2).

Let's see what they have to be. We start with B_z . Since B_z appears only in H_{11} and H_{22} , everything will be O.K. if

$$\begin{aligned} \sigma_{11}^z &= 1, & \sigma_{12}^z &= 0, \\ \sigma_{21}^z &= 0, & \sigma_{22}^z &= -1. \end{aligned}$$

We often write the matrix H_{ij} as a little table like this:

$$H_{ij} = \begin{matrix} & \begin{matrix} \xrightarrow{j} \\ \downarrow i \end{matrix} \\ \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \end{matrix}.$$

11-1 The Pauli spin matrices

11-2 The spin matrices as operators

11-3 The solution of the two-state equations

11-4 The polarization states of the photon

11-5 The neutral K-meson†

11-6 Generalization to N -state systems

Review: Chapter 35, Vol. I, *Polarization*

† This section should be omitted on the first reading of this book. It is more advanced than is appropriate in a first course.

For the Hamiltonian of a spin one-half particle in the magnetic field B_z , this is the same as

$$H_{ij} = \overset{i \downarrow}{\underset{j \rightarrow}{\begin{pmatrix} -\mu B_z & -\mu(B_x - iB_y) \\ -\mu(B_x + iB_y) & +\mu B_z \end{pmatrix}}}.$$

In the same way, we can write the coefficients σ_{ij}^z as the matrix

$$\sigma_{ij}^z = \overset{i \downarrow}{\underset{j \rightarrow}{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}}. \quad (11.5)$$

Working with the coefficients of B_x , we get that the terms of σ_x have to be

$$\begin{aligned} \sigma_{11}^x &= 0, & \sigma_{12}^x &= 1, \\ \sigma_{21}^x &= 1, & \sigma_{22}^x &= 0. \end{aligned}$$

Or, in shorthand,

$$\sigma_{ij}^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \quad (11.6)$$

Finally, looking at B_y , we get

$$\begin{aligned} \sigma_{11}^y &= 0, & \sigma_{12}^y &= -i, \\ \sigma_{21}^y &= i, & \sigma_{22}^y &= 0; \end{aligned}$$

or

$$\sigma_{ij}^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \quad (11.7)$$

Table 11-1
The Pauli spin matrices

$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$
$1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

With these three sigma matrices, Eqs. (11.2) and (11.4) are identical. To leave room for the subscripts i and j , we have shown which σ goes with which component of \mathbf{B} by putting x , y , and z as superscripts. Usually, however, the i and j are omitted—it's easy to imagine they are there—and the x , y , z are written as subscripts. Then Eq. (11.4) is written

$$H = -\mu[\sigma_x B_x + \sigma_y B_y + \sigma_z B_z]. \quad (11.8)$$

Because the sigma matrices are so important—they are used all the time by the professionals—we have gathered them together in Table 11-1. (Anyone who is going to work in quantum physics really has to memorize them.) They are also called the *Pauli spin matrices* after the physicist who invented them.

In the table we have included one more two-by-two matrix which is needed if we want to be able to take care of a system which has two spin states of the same energy, or if we want to choose a different zero energy. For such situations we must add $E_0 C_+$ to the first equation in (11.1) and $E_0 C_-$ to the second equation. We can include this in the new notation if we define the *unit matrix* "1" as δ_{ij} ,

$$1 = \delta_{ij} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad (11.9)$$

and rewrite Eq. (11.8) as

$$H = E_0 \delta_{ij} - \mu(\sigma_x B_x + \sigma_y B_y + \sigma_z B_z). \quad (11.10)$$

Usually, it is *understood* that any constant like E_0 is automatically to be multiplied by the unit matrix; then one writes simply

$$H = E_0 - \mu(\sigma_x B_x + \sigma_y B_y + \sigma_z B_z). \quad (11.11)$$

One reason the spin matrices are useful is that *any* two-by-two matrix at all can be written in terms of them. Any matrix you can write has four numbers in it, say,

$$M = \begin{pmatrix} a & b \\ c & d \end{pmatrix}.$$

It can always be written as a linear combination of four matrices. For example,

$$M = a \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + b \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} + c \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} + d \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$

There are many ways of doing it, but one special way is to say that M is a certain amount of σ_x , plus a certain amount of σ_y , and so on, like this:

$$M = \alpha I + \beta \sigma_x + \gamma \sigma_y + \delta \sigma_z,$$

where the “amounts” α , β , γ , and δ may, in general, be complex numbers.

Since any two-by-two matrix can be represented in terms of the unit matrix and the sigma matrices, we have all that we ever need for *any* two-state system. No matter what the two-state system—the ammonia molecule, the magenta dye, anything—the Hamiltonian equation can be written in terms of the sigmas. Although the sigmas seem to have a geometrical significance in the physical situation of an electron in a magnetic field, they can also be thought of as just useful matrices, which can be used for any two-state problem.

For instance, in one way of looking at things a proton and a neutron can be thought of as the same particle in either of two states. We say the *nucleon* (proton or neutron) is a two-state system—in this case, two states with respect to its charge. When looked at that way, the $|1\rangle$ state can represent the proton and the $|2\rangle$ state can represent the neutron. People say that the nucleon has two “isotopic-spin” states.

Since we will be using the sigma matrices as the “arithmetic” of the quantum mechanics of two-state systems, let’s review quickly the conventions of matrix algebra. By the “sum” of any two or more matrices we mean just what was obvious in Eq. (11.4). In general, if we “add” two matrices A and B , the “sum” C means that each term C_{ij} is given by

$$C_{ij} = A_{ij} + B_{ij}.$$

Each term of C is the sum of the terms in the same slots of A and B .

In Section 5–6 we have already encountered the idea of a matrix “product.” The same idea will be useful in dealing with the sigma matrices. In general, the “product” of two matrices A and B (in that order) is defined to be a matrix C whose elements are

$$C_{ij} = \sum_k A_{ik} B_{kj}. \quad (11.12)$$

It is the sum of products of terms taken in pairs from the i th row of A and the k th column of B . If the matrices are written out in tabular form as in Fig. 11–1, there is a good “system” for getting the terms of the product matrix. Suppose you are calculating C_{23} . You run your left index finger *along* the *second row* of A and your right index finger *down* the *third column* of B , multiplying each pair and adding as you go. We have tried to indicate how to do it in the figure.

$$\begin{pmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ A_{21} & A_{22} & A_{23} & A_{24} \\ A_{31} & A_{32} & A_{33} & A_{34} \\ A_{41} & A_{42} & A_{43} & A_{44} \end{pmatrix} \cdot \begin{pmatrix} B_{11} & B_{12} & B_{13} & B_{14} \\ B_{21} & B_{22} & B_{23} & B_{24} \\ B_{31} & B_{32} & B_{33} & B_{34} \\ B_{41} & B_{42} & B_{43} & B_{44} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} \\ C_{21} & C_{22} & C_{23} & C_{24} \\ C_{31} & C_{32} & C_{33} & C_{34} \\ C_{41} & C_{42} & C_{43} & C_{44} \end{pmatrix}$$

$$C_{ik} = \sum_j A_{ij} B_{jk}$$

$$\text{Example: } C_{23} = A_{21} B_{13} + A_{22} B_{23} + A_{23} B_{33} + A_{24} B_{43}$$

Fig. 11–1. Multiplying two matrices.

It is, of course, particularly simple for two-by-two matrices. For instance, if we multiply σ_x times σ_x , we get

$$\sigma_x^2 = \sigma_x \cdot \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},$$

which is just the unit matrix 1. Or, for another example, let's work out $\sigma_x \sigma_y$:

$$\sigma_x \sigma_y = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}.$$

Referring to Table 11-1, you see that the product is just i times the matrix σ_z . (Remember that a number times a matrix just multiplies each term of the matrix.) Since the products of the sigmas taken two at a time are important—as well as rather amusing—we have listed them all in Table 11-2. You can work them out as we have done for σ_x^2 and $\sigma_x \sigma_y$.

There's another very important and interesting point about these σ matrices. We can imagine, if we wish, that the three matrices σ_x , σ_y , and σ_z are analogous to the three components of a vector—it is sometimes called the “sigma vector” and is written σ . It is really a “matrix vector” or a “vector matrix.” It is three different matrices—one matrix associated with each axis, x , y , and z . With it, we can write the Hamiltonian of the system in a nice form which works in any coordinate system:

$$H = -\mu \sigma \cdot B. \quad (11.13)$$

Although we have written our three matrices in the representation in which “up” and “down” are in the z -direction—so that σ_z has a particular simplicity—we could figure out what the matrices would look like in some other representation. Although it takes a lot of algebra, you can show that they change among themselves like the components of a vector. (We won't, however, worry about proving it right now. You can check it if you want.) You can use σ in different coordinate systems as though it is a vector.

You remember that the H is related to energy in quantum mechanics. It is, in fact, just equal to the energy in the simple situation where there is only one state. Even for two-state systems of the electron spin, when we write the Hamiltonian as in Eq. (11.13), it looks very much like the *classical* formula for the energy of a little magnet with magnetic moment μ in a magnetic field. B Classically, we would say

$$U = -\mu \cdot B, \quad (11.14)$$

where μ is the property of the object and B is an external field. We can imagine that Eq. (11.14) can be converted to (11.13) if we replace the classical energy by the Hamiltonian and the classical μ by the matrix $\mu \sigma$. Then, after this purely formal substitution, we interpret the result as a matrix equation. It is sometimes said that to each quantity in classical physics there corresponds a matrix in quantum mechanics. It is really more correct to say that the Hamiltonian matrix corresponds to the energy, and any quantity that can be defined via energy has a corresponding matrix.

For example, the magnetic moment can be defined via energy by saying that the energy in an external field B is $-\mu \cdot B$. This *defines* the magnetic moment vector μ . Then we look at the formula for the Hamiltonian of a real (quantum) object in a magnetic field and try to identify whatever the matrices are that correspond to the various quantities in the classical formula. That's the trick by which *sometimes* classical quantities have their quantum counterparts.

You may try, if you want, to understand how a classical vector is equal to a matrix $\mu \sigma$, and maybe you will discover something—but don't break your head on it. That's not the idea—they are *not equal*. Quantum mechanics is a different kind of a theory to represent the world. It just happens that there are certain correspondences which are hardly more than mnemonic devices—things to remember with. That is, you remember Eq. (11.14) when you learn classical physics;

Table 11-2

Products of the spin matrices

$\sigma_x^2 = 1$
$\sigma_y^2 = 1$
$\sigma_z^2 = 1$
$\sigma_x \sigma_y = -\sigma_y \sigma_x = i \sigma_z$
$\sigma_y \sigma_z = -\sigma_z \sigma_y = i \sigma_x$
$\sigma_z \sigma_x = -\sigma_x \sigma_z = i \sigma_y$

then if you remember the correspondence $\mu \rightarrow \mu\sigma$, you have a handle for remembering Eq. (11.13). Of course, nature knows the quantum mechanics, and the classical mechanics is only an approximation; so there is no mystery in the fact that in classical mechanics there is some shadow of quantum mechanical laws—which are truly the ones underneath. To reconstruct the original object from the shadow is not possible in any direct way, but the shadow does help you to remember what the object looks like. Equation (11.13) is the truth, and Eq. (11.14) is the shadow. Because we learn classical mechanics first, we would like to be able to get the quantum formula from it, but there is no sure-fire scheme for doing that. We must always go back to the real world and discover the correct quantum mechanical equations. When they come out looking like something in classical physics, we are in luck.

If the warnings above seem repetitious and appear to you to be belaboring self-evident truths about the relation of classical physics to quantum physics, please excuse the conditioned reflexes of a professor who has usually taught quantum mechanics to students who hadn't heard about Pauli spin matrices until they were in graduate school. Then they always seemed to be hoping that, somehow, quantum mechanics could be seen to follow as a logical consequence of classical mechanics which they had learned thoroughly years before. (Perhaps they wanted to avoid having to learn something new.) You have learned the classical formula, Eq. (11.14), only a few months ago—and then with warnings that it was inadequate—so maybe you will not be so unwilling to take the quantum formula, Eq. (11.13), as the basic truth.

11-2 The spin matrices as operators

While we are on the subject of mathematical notation, we would like to describe still *another* way of writing things—a way which is used very often because it is so compact. It follows directly from the notation introduced in Chapter 8. If we have a system in a state $|\psi(t)\rangle$, which varies with time, we can—as we did in Eq. (8.31)—write the amplitude that the system would be in the state $|i\rangle$ at $t + \Delta t$ as

$$\langle i | \psi(t + \Delta t) \rangle = \sum_j \langle i | U(t, t + \Delta t) | j \rangle \langle j | \psi(t) \rangle.$$

The matrix element $\langle i | U(t, t + \Delta t) | j \rangle$ is the amplitude that the base state $|j\rangle$ will be converted into the base state $|i\rangle$ in the time interval Δt . We then *defined* H_{ij} by writing

$$\langle i | U(t, t + \Delta t) | j \rangle = \delta_{ij} - \frac{i}{\hbar} H_{ij}(t) \Delta t,$$

and we showed that the amplitudes $C_i(t) = \langle i | \psi(t) \rangle$ were related by the differential equations

$$i\hbar \frac{dC_i}{dt} = \sum_j H_{ij} C_j. \quad (11.15)$$

If we write out the amplitudes C_i explicitly, the same equation appears as

$$i\hbar \frac{d}{dt} \langle i | \psi \rangle = \sum_j H_{ij} \langle j | \psi \rangle. \quad (11.16)$$

Now the matrix elements H_{ij} are also amplitudes which we can write as $\langle i | H | j \rangle$; our differential equation looks like this:

$$i\hbar \frac{d}{dt} \langle i | \psi \rangle = \sum_j \langle i | H | j \rangle \langle j | \psi \rangle. \quad (11.17)$$

We see that $-i/\hbar \langle i | H | j \rangle$ is the amplitude that—under the physical conditions described by H —a state $|j\rangle$ will, during the time dt , “generate” the state $|i\rangle$. (All of this is implicit in the discussion of Section 8-4.)

Now following the ideas of Section 8-2, we can drop out the common term $\langle i |$ in Eq. (11.17)—since it is true for any state $|i\rangle$ —and write that equation simply as

$$i\hbar \frac{d}{dt} |\psi\rangle = \sum_j H |j\rangle \langle j | \psi\rangle. \quad (11.18)$$

Or, going one step further, we can also remove the j and write

$$i\hbar \frac{d}{dt} |\psi\rangle = H |\psi\rangle. \quad (11.19)$$

In Chapter 8 we pointed out that when things are written this way, the H in $H |j\rangle$ or $H |\psi\rangle$ is called an *operator*. From now on we will put the little hat (^) over an operator to remind you that it *is* an operator and not just a number. We will write $\hat{H} |\psi\rangle$. Although the two equations (11.18) and (11.19) *mean exactly the same thing* as Eq. (11.17) or Eq. (11.15), we can *think* about them in a different way. For instance, we would describe Eq. (11.18) in this way: “The time derivative of the *state vector* $|\psi\rangle$ is equal to what you get by operating with the Hamiltonian *operator* \hat{H} on each base state, multiplying by the amplitude $\langle j | \psi\rangle$ that ψ is in the state j , and summing over all j .” Or Eq. (11.19) is described this way. “The time derivative (times $i\hbar$) of a state $|\psi\rangle$ is equal to what you get if you operate with the Hamiltonian \hat{H} on the state vector $|\psi\rangle$.” It’s just a shorthand way of saying what is in Eq. (11.17), but, as you will see, it can be a great convenience.

If we wish, we can carry the “abstraction” idea one more step. Equation (11.19) is true for *any state* $|\psi\rangle$. Also the left-hand side, $i\hbar d/dt$, is also an operator—it’s the operation “differentiate by t and multiply by $i\hbar$.” Therefore, Eq. (11.19) can also be thought of as an equation between operators—the operator equation

$$i\hbar \frac{d}{dt} = \hat{H}.$$

The Hamiltonian operator (within a constant) produces the same result as does d/dt when acting on any state. Remember that this equation—as well as Eq. (11.19)—is *not* a statement that the \hat{H} operator is just the identical *operation* as d/dt . The equations are the dynamical law of nature—the law of motion—for a quantum system.

Just to get some practice with these ideas, we will show you another way we could get to Eq. (11.18). You know that we can write any state $|\psi\rangle$ in terms of its projections into some base set [see Eq. (8.8)],

$$|\psi\rangle = \sum_i |i\rangle \langle i | \psi\rangle. \quad (11.20)$$

How does $|\psi\rangle$ change with time? Well, just take its derivative:

$$\frac{d}{dt} |\psi\rangle = \frac{d}{dt} \sum_i |i\rangle \langle i | \psi\rangle. \quad (11.21)$$

Now the base states $|i\rangle$ do not change with time (at least *we* are always taking them as definite fixed states), but the amplitudes $\langle i | \psi\rangle$ are numbers which may vary. So Eq. (11.21) becomes

$$\frac{d}{dt} |\psi\rangle = \sum_i |i\rangle \frac{d}{dt} \langle i | \psi\rangle. \quad (11.22)$$

Since we know $d\langle i | \psi\rangle/dt$ from Eq. (11.16), we get

$$\begin{aligned} \frac{d}{dt} |\psi\rangle &= -\frac{i}{\hbar} \sum_i |i\rangle \sum_j H_{ij} \langle j | \psi\rangle \\ &= -\frac{i}{\hbar} \sum_{ij} |i\rangle \langle i | H | j\rangle \langle j | \psi\rangle = -\frac{i}{\hbar} \sum_j H |j\rangle \langle j | \psi\rangle. \end{aligned}$$

This is Eq. (11.18) all over again.

So we have many ways of looking at the Hamiltonian. We can think of the set of coefficients H_{ij} as just a bunch of numbers, or we can think of the “amplitudes” $\langle i | H | j \rangle$, or we can think of the “matrix” H_{ij} , or we can think of the operator” \hat{H} . It all means the same thing.

Now let’s go back to our two-state systems. If we write the Hamiltonian in terms of the sigma matrices (with suitable numerical coefficients like B_x , etc.), we can clearly also think of σ_{ij}^x as an amplitude $\langle i | \sigma_x | j \rangle$ or, for short, as the operator $\hat{\sigma}_x$. If we use the operator idea, we can write the equation of motion of a state $|\psi\rangle$ in a magnetic field as

$$i\hbar \frac{d}{dt} |\psi\rangle = -\mu(B_x \hat{\sigma}_x + B_y \hat{\sigma}_y + B_z \hat{\sigma}_z) |\psi\rangle. \quad (11.23)$$

When we want to “use” such an equation we will normally have to express $|\psi\rangle$ in terms of base vectors (just as we have to find the components of space vectors when we want specific numbers). So we will usually want to put Eq. (11.23) in the somewhat expanded form:

$$i\hbar \frac{d}{dt} |\psi\rangle = -\mu \sum_i (B_x \hat{\sigma}_x + B_y \hat{\sigma}_y + B_z \hat{\sigma}_z) |i\rangle \langle i | \psi \rangle. \quad (11.24)$$

Now you will see why the operator idea is so neat. To use Eq. (11.24) we need to know what happens when the $\hat{\sigma}$ operators work on each of the base states. Let’s find out. Suppose we have $\hat{\sigma}_z |+\rangle$; it is some vector $|?\rangle$, but what? Well, let’s multiply it on the left by $\langle + |$; we have

$$\langle + | \hat{\sigma}_z | + \rangle = \sigma_{11} = 1$$

(using Table 11-1). So we know that

$$\langle + | ? \rangle = 1. \quad (11.25)$$

Now let’s multiply $\hat{\sigma}_z |+\rangle$ on the left by $\langle - |$. We get

$$\langle - | \hat{\sigma}_z | + \rangle = \sigma_{21} = 0;$$

so

$$\langle - | ? \rangle = 0. \quad (11.26)$$

There is only one state vector that satisfies both (11.25) and (11.26); it is $|+\rangle$. We discover then that

$$\hat{\sigma}_z |+\rangle = |+\rangle. \quad (11.27)$$

By this kind of argument you can easily show that all of the properties of the sigma matrices can be described in the operator notation by the set of rules given in Table 11-3.

If we have products of sigma matrices, they go over into products of operators. When two operators appear together as a product, you carry out first the operation with the operator which is farthest to the right. For instance, by $\hat{\sigma}_x \hat{\sigma}_y |+\rangle$ we are to understand $\hat{\sigma}_x(\hat{\sigma}_y |+\rangle)$. From Table 11-3, we get $\hat{\sigma}_y |+\rangle = i |-\rangle$, so

$$\hat{\sigma}_x \hat{\sigma}_y |+\rangle = \hat{\sigma}_x(i |-\rangle). \quad (11.28)$$

Now any number—like i —just moves through an operator (operators work only on state vectors); so Eq. (11.28) is the same as

$$\hat{\sigma}_x \hat{\sigma}_y |+\rangle = i \hat{\sigma}_x |-\rangle = i |+\rangle.$$

If you do the same thing for $\hat{\sigma}_x \hat{\sigma}_y |-\rangle$, you will find that

$$\hat{\sigma}_x \hat{\sigma}_y |-\rangle = -i |-\rangle.$$

Looking at Table 11-3, you see that $\hat{\sigma}_x \hat{\sigma}_y$ operating on $|+\rangle$ or $|-\rangle$ gives just what you get if you operate with $\hat{\sigma}_z$ and multiply by $-i$. We can, therefore, say

Table 11-3

Properties of the $\hat{\sigma}$ -operator

$\sigma_z +\rangle = +\rangle$
$\sigma_z -\rangle = - -\rangle$
$\sigma_x +\rangle = -\rangle$
$\sigma_x -\rangle = +\rangle$
$\sigma_y +\rangle = i -\rangle$
$\sigma_y -\rangle = -i +\rangle$

that the operation $\hat{\sigma}_x \hat{\sigma}_y$ is identical with the operation $i\hat{\sigma}_z$, and write this statement as an operator equation:

$$\hat{\sigma}_x \hat{\sigma}_y = i\hat{\sigma}_z. \quad (11.29)$$

Notice that this equation is identical with one of our matrix equations of Table 11-2. So again we see the correspondence between the matrix and operator points of view. Each of the equations in Table 11-2 can, therefore, also be considered as equations about the sigma operators. You can check that they do indeed follow from Table 11-3. It is best, when working with these things, *not* to keep track of whether a quantity like σ or H is an operator or a matrix. All the equations are the same either way, so Table 11-2 is for sigma operators, or for sigma matrices, as you wish.

11-3 The solution of the two-state equations

We can now write our two-state equation in various forms, for example, either as

$$i\hbar \frac{dC_i}{dt} = \sum_j H_{ij} C_j \quad (11.30)$$

or

$$i\hbar \frac{d|\psi\rangle}{dt} = \hat{H}|\psi\rangle.$$

They both mean the same thing. For a spin one-half particle in a magnetic field, the Hamiltonian H is given by Eq. (11.8) or by Eq. (11.13).

If the field is in the z -direction, then—as we have seen several times by now—the solution is that the state $|\psi\rangle$, whatever it is, precesses around the z -axis (just as if you were to take the physical object and rotate it bodily around the z -axis) at an angular velocity equal to twice the magnetic field times μ/\hbar . The same is true, of course, for a magnetic field along any other direction, because the physics is independent of the coordinate system. If we have a situation where the magnetic field varies from time to time in a complicated way, then we can analyze the situation in the following way. Suppose you start with the spin in the $+z$ -direction and you have an x -magnetic field. The spin starts to turn. Then if the x -field is turned off, the spin stops turning. Now if a z -field is turned on, the spin precesses about z , and so on. So depending on how the fields vary in time, you can figure out what the final state is—along what axis it will point. Then you can refer that state back to the original $|+\rangle$ and $|-\rangle$ with respect to z by using the projection formulas we had in Chapter 10 (or Chapter 6). If the state ends up with its spin in the direction (θ, ϕ) , it will have an up-amplitude $\cos(\theta/2)e^{-i\phi/2}$ and a down-amplitude $\sin(\theta/2)e^{+i\phi/2}$. That solves any problem. It is a word description of the solution of the differential equations.

The solution just described is sufficiently general to take care of *any two-state system*. Let's take our example of the ammonia molecule—including the effects of an electric field. If we describe the system in terms of the states $|I\rangle$ and $|II\rangle$, the equations look like this:

$$\begin{aligned} i\hbar \frac{dC_I}{dt} &= +AC_I + \mu\mathcal{E}C_{II}, \\ i\hbar \frac{dC_{II}}{dt} &= -AC_{II} + \mu\mathcal{E}C_I. \end{aligned} \quad (11.31)$$

You say, "No, I remember there was an E_0 in there." Well, we have shifted the origin of energy to make the E_0 zero. (You can always do that by changing both amplitudes by the same factor— $e^{iE_0 T/\hbar}$ —and get rid of any constant energy.) Now if corresponding equations always have the same solutions, then we really don't have to do it twice. If we look at these equations and look at Eq. (11.1), then we can make the following identification. Let's call $|I\rangle$ the state $|+\rangle$ and $|II\rangle$ the state $|-\rangle$. That *does not mean* that we are lining-up the ammonia in space, or that $|+\rangle$ and $|-\rangle$ has anything to do with the z -axis. It is purely artificial.

We have an artificial space that we might “call the ammonia molecule representative space,” or something—a three-dimensional “diagram” in which being “up” corresponds to having the molecule in the state $|I\rangle$ and being “down” along this false z -axis represents having a molecule in the state $|II\rangle$. Then, the equations will be identified as follows. First of all, you see that the Hamiltonian can be written in terms of the sigma matrices as

$$H = +A\sigma_z + \mu\mathcal{E}\sigma_x. \quad (11.32)$$

Or, putting it another way, μB_z in Eq. (11.1) corresponds to $-A$ in Eq. (11.32), and μB_x corresponds to $-\mu\mathcal{E}$. In our “model” space, then, we have a constant B field along the z -direction. If we have an electric field \mathcal{E} which is changing with time, then we have a B field along the x -direction which varies in proportion. *So the behavior of an electron in a magnetic field with a constant component in the z -direction and an oscillating component in the x -direction is mathematically analogous and corresponds exactly to the behavior of an ammonia molecule in an oscillating electric field.* Unfortunately, we do not have the time to go any further into the details of this correspondence, or to work out any of the technical details. We only wished to make the point that *all* systems of two states can be made analogous to a spin one-half object precessing in a magnetic field.

11-4 The polarization states of the photon

There are a number of other two-state systems which are interesting to study, and the first new one we would like to talk about is the photon. To describe a photon we must first give its vector momentum. For a free photon, the frequency is determined by the momentum, so we don’t have to say also what the frequency is. After that, though, we still have a property called the polarization. Imagine that there is a photon coming at you with a definite monochromatic frequency (which will be kept the same throughout all this discussion so that we don’t have a variety of momentum states). Then there are two directions of polarization. In the classical theory, light can be described as having an electric field which oscillates horizontally or an electric field which oscillates vertically (for instance); these two kinds of light are called x -polarized and y -polarized light. The light can also be polarized in some other direction, which can be made up from the superposition of a field in the x -direction and one in the y -direction. Or if you take the x - and the y -components out of phase by 90° , you get an electric field that rotates—the light is elliptically polarized. (This is just a quick reminder of the classical theory of polarized light that we studied in Chapter 35, Vol. I.)

Now, however, suppose we have a *single* photon—just one. There is no electric field that we can discuss in the same way. All we have is *one photon*. But a photon has to have the analog of the classical phenomena of polarization. There must be at least two different kinds of photons. At first, you might think there should be an infinite variety—after all, the electric vector can point in all sorts of directions. We can, however, describe the polarization of a photon as a two-state system. A photon can be in the state $|x\rangle$ or in the state $|y\rangle$. By $|x\rangle$ we mean the polarization state of each one of the photons in a beam of light which *classically* is x -polarized light. On the other hand, by $|y\rangle$ we mean the polarization state of each of the photons in a y -polarized beam. And we can take $|x\rangle$ and $|y\rangle$ as our base states of a photon of given momentum pointing at you—in what we will call the z -direction. So there are two base states $|x\rangle$ and $|y\rangle$, and they are all that are needed to describe any photon at all.

For example, if we have a piece of polaroid set with its axis to pass light polarized in what we call the x -direction, and we send in a photon which we know is in the state $|y\rangle$, it will be absorbed by the polaroid. If we send in a photon which we know is in the state $|x\rangle$, it will come right through as $|x\rangle$. If we take a piece of calcite which takes a beam of polarized light and splits it into an $|x\rangle$ beam and a $|y\rangle$ beam, that piece of calcite is the complete analog of a Stern-Gerlach apparatus which splits a beam of silver atoms into the two states $|+\rangle$ and $|-\rangle$. So every-

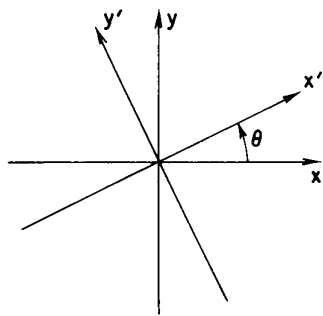


Fig. 11-2. Coordinates at right angles to the momentum vector of the photon.

thing we did before with particles and Stern-Gerlach apparatuses, we can do again with light and pieces of calcite. And what about light filtered through a piece of polaroid set at an angle θ ? Is that another state? Yes, indeed, it *is* another state. Let's call the axis of the polaroid x' to distinguish it from the axes of our base states. See Fig. 11-2. A photon that comes out will be in the state $|x'\rangle$. However, any state can be represented as a linear combination of base states, and the formula for the combination is, here,

$$|x'\rangle = \cos \theta |x\rangle + \sin \theta |y\rangle. \quad (11.33)$$

That is, if a photon comes through a piece of polaroid set at the angle θ (with respect to x), it can still be resolved into $|x\rangle$ and $|y\rangle$ beams—by a piece of calcite, for example. Or you can, if you wish, just analyze it into x - and y -components in your imagination. Either way, you will find the amplitude $\cos \theta$ to be in the $|x\rangle$ state and the amplitude $\sin \theta$ to be in the $|y\rangle$ state.

Now we ask this question: Suppose a photon is polarized in the x' -direction by a piece of polaroid set at the angle θ and arrives at a polaroid at the angle zero—as in Fig. 11-3; what will happen? With what probability will it get through? The answer is the following. After it gets through the first polaroid, it is definitely in the state $|x'\rangle$. The second polaroid will let the photon through if it is in the state $|x\rangle$ (but absorb it if it is the state $|y\rangle$). So we are asking with what probability does the photon appear to be in the state $|x\rangle$? We get that probability from the absolute square of amplitude $\langle x | x' \rangle$ that a photon in the state $|x'\rangle$ is also in the state $|x\rangle$. What is $\langle x | x' \rangle$? Just multiply Eq. (11.33) by $\langle x |$ to get

$$\langle x | x' \rangle = \cos \theta \langle x | x \rangle + \sin \theta \langle x | y \rangle.$$

Now $\langle x | y \rangle = 0$, from the physics—as they *must* be if $|x\rangle$ and $|y\rangle$ are base states—and $\langle x | x \rangle = 1$. So we get

$$\langle x | x' \rangle = \cos \theta,$$

and the probability is $\cos^2 \theta$. For example, if the first polaroid is set at 30° , a photon will get through $3/4$ of the time, and $1/4$ of the time it will heat the polaroid by being absorbed therein.

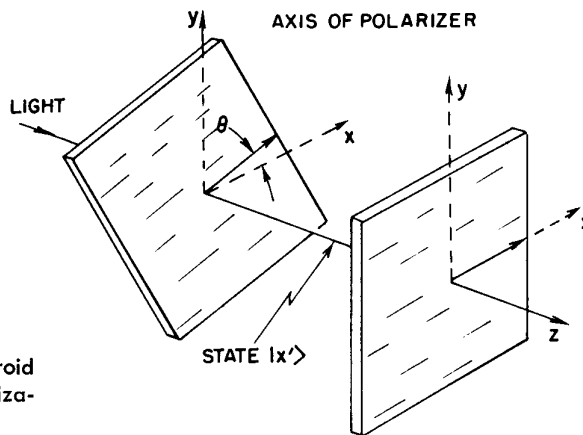


Fig. 11-3. Two sheets of polaroid with angle θ between planes of polarization.

Now let us see what happens classically in the same situation. We would have a beam of light with an electric field which is varying in some way or another—say “unpolarized.” After it gets through the first polaroid, the electric field is oscillating in the x' -direction with a size \mathcal{E} ; we would draw the field as an oscillating vector with a peak value \mathcal{E}_0 in a diagram like Fig. 11-4. Now when the light arrives at the second polaroid, only the x -component, $\mathcal{E}_0 \cos \theta$, of the electric field gets through. The *intensity* is proportional to the square of the field and, therefore, to $\mathcal{E}_0^2 \cos^2 \theta$. So the energy coming through is $\cos^2 \theta$ weaker than the energy which was entering the last polaroid.

The classical picture and the quantum picture give similar results. If you were to throw 10 billion photons at the second polaroid, and the average probability of each one going through is, say, 3/4, you would expect 3/4 of 10 billion would get through. Likewise, the energy that they would carry would be 3/4 of the energy that you attempted to put through. The classical theory says nothing about the statistics of the thing—it simply says that the energy that comes through will be precisely 3/4 of the energy which you were sending in. That is, of course, impossible if there is only one photon. There is no such thing as 3/4 of a photon. It is either *all* there, or it isn't there at all. Quantum mechanics tells us it is *all* there 3/4 of the time. The relation of the two theories is clear.

What about the other kinds of polarization? For example, right-hand circular polarization? In the classical theory, right-hand circular polarization has equal components in x and y which are 90° out of phase. In the quantum theory, a right-hand circularly polarized (RHC) photon has equal amplitudes to be polarized $|x\rangle$ or $|y\rangle$, and the *amplitudes* are 90° out of phase. Calling a RHC photon a state $|R\rangle$ and a LHC photon a state $|L\rangle$, we can write (see Vol. I, Section 33-1)

$$\begin{aligned} |R\rangle &= \frac{1}{\sqrt{2}} (|x\rangle + i|y\rangle), \\ |L\rangle &= -\frac{1}{\sqrt{2}} (|x\rangle - i|y\rangle). \end{aligned} \quad (11.34)$$

—the $1/\sqrt{2}$ is put in to get normalized states. With these states you can calculate any filtering or interference effects you want, using the laws of quantum theory. If you want, you can also choose $|R\rangle$ and $|L\rangle$ as base states and represent everything in terms of them. You only need to show first that $\langle R|L\rangle = 0$ —which you can do by taking the conjugate form of the first equation above [see Eq. (8.13)] and multiplying it by the other. You can resolve light into x - and y -polarizations, or into x' - and y' -polarizations, or into right and left polarizations as a basis.

Just as an example, let's try to turn our formulas around. Can we represent the state $|x\rangle$ as a linear combination of right and left? Yes, here it is:

$$\begin{aligned} |x\rangle &= \frac{1}{\sqrt{2}} (|R\rangle + |L\rangle), \\ |y\rangle &= -\frac{i}{\sqrt{2}} (|R\rangle - |L\rangle). \end{aligned} \quad (11.35)$$

Proof: Add and subtract the two equations in (11.34). It is easy to go from one base to the other.

One curious point has to be made, though. If a photon is right circularly polarized, it shouldn't have anything to do with the x - and y -axes. If we were to look at the same thing from a coordinate system turned at some angle about the direction of flight, the light would still be right circularly polarized—and similarly for left. The right and left circularly polarized light are the same for any such rotation; the definition is independent of any choice of the x -direction (except that the photon direction is given). Isn't that nice—it doesn't take any axes to define it. Much better than x and y . On the other hand, isn't it rather a miracle that when you *add* the right and left together you can find out which direction x was? If "right" and "left" do not depend on x in any way, how is it that we can put them back together again and get x ? We can answer that question in part by writing out the state $|R'\rangle$, which represents a photon RHC polarized in the frame x', y' . In that frame, you would write

$$|R'\rangle = \frac{1}{\sqrt{2}} (|x'\rangle + i|y'\rangle).$$

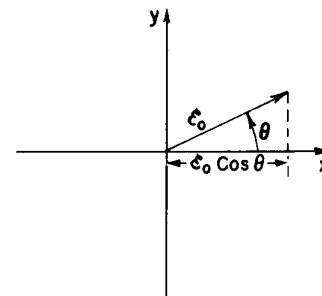


Fig. 11-4. The classical picture of the electric vector \mathcal{E} .

How does such a state look in the frame x, y ? Just substitute x' from Eq.(11. 33) and the corresponding $|y'\rangle$ —we didn't write it down, but it is $(-\sin \theta) |x\rangle + (\cos \theta) |y\rangle$. Then

$$\begin{aligned} |R'\rangle &= \frac{1}{\sqrt{2}} [\cos \theta |x\rangle + \sin \theta |y\rangle - i \sin \theta |x\rangle + i \cos \theta |y\rangle] \\ &= \frac{1}{\sqrt{2}} [(\cos \theta - i \sin \theta) |x\rangle + i(\cos \theta - i \sin \theta) |y\rangle] \\ &= \frac{1}{\sqrt{2}} (|x\rangle + i |y\rangle)(\cos \theta - i \sin \theta). \end{aligned}$$

The first term is just $|R\rangle$, and the second is $e^{+i\theta}$; our result is that

$$|R'\rangle = e^{-i\theta} |R\rangle. \quad (11.36)$$

The states $|R'\rangle$ and $|R\rangle$ are the same except for the phase factor $e^{-i\theta}$. If you work out the same thing for $|L'\rangle$, you get that†

$$|L'\rangle = e^{+i\theta} |L\rangle. \quad (11.37)$$

Now you see what happens. If we add $|R\rangle$ and $|L\rangle$, we get something different from what we get when we add $|R'\rangle$ and $|L'\rangle$. For instance, an x -polarized photon is [Eq. (11.35)] the sum of $|R\rangle$ and $|L\rangle$, but a y -polarized photon is the sum with the phase of one shifted 90° backward and the other 90° forward. That is just what we would get from the sum of $|R'\rangle$ and $|L'\rangle$ for the special angle $\theta = 90^\circ$, and that's right. An x -polarization in the *prime* frame is the same as a y -polarization in the original frame. So it is not exactly true that a circularly polarized photon looks the same for any set of axes. Its *phase* (the phase relation of the right and left circularly polarized states) keeps track of the x -direction.

11-5 The neutral K-meson‡

We will now describe a two-state system in the world of the strange particles—a system for which quantum mechanics gives a most remarkable prediction. To describe it completely would involve us in a lot of stuff about strange particles, so we will, unfortunately, have to cut some corners. We can only give an outline of how a certain discovery was made—to show you the kind of reasoning that was involved. It begins with the discovery by Gell-Mann and Nishijima of the concept of *strangeness* and of a new law of *conservation of strangeness*. It was when Gell-Mann and Pais were analyzing the consequences of these new ideas that they came across the prediction of a most remarkable phenomenon we are going to describe. First, though, we have to tell you a little about “strangeness.”

We must begin with what are called the *strong interactions* of nuclear particles. These are the interactions which are responsible for the strong nuclear forces—as distinct, for instance, from the relatively weaker electromagnetic interactions. The interactions are “strong” in the sense that if two particles get close enough to interact at all, they interact in a big way and produce other particles very easily.

† It's similar to what we found (in Chapter 6) for a spin one-half particle when we rotated the coordinates about the z -axis—then we got the phase factors $e^{\pm i\phi/2}$. It is, in fact, exactly what we wrote down in Section 5-7 for the $|+\rangle$ and $|-\rangle$ states of a spin-one particle—which is no coincidence. The photon is a spin-one particle which has, however, no “zero” state.

‡ We now feel that the material of this section is longer and harder than is appropriate at this point in our development. We suggest that you skip it and continue with Section 11-6. If you are ambitious and have time you may wish to come back to it later. We leave it here, because it is a beautiful example—taken from recent work in high-energy physics—of what can be done with our formulation of the quantum mechanics of two-state systems.

The nuclear particles have also what is called a “weak interaction” by which certain things can happen, such as beta decay, but always very slowly on a nuclear time scale—the weak interactions are many, many orders of magnitude weaker than the strong interactions and even much weaker than electromagnetic interactions.

When the strong interactions were being studied with the big accelerators, people were surprised to find that certain things that “should” happen—that were expected to happen—did not occur. For instance, in some interactions a particle of a certain type did not appear when it was expected. Gell-Mann and Nishijima noticed that many of these peculiar happenings could be explained at once by inventing a new conservation law: the *conservation of strangeness*. They proposed that there was a new kind of attribute associated with each particle—which they called its “strangeness” number—and that in any strong interaction the “quantity of strangeness” is conserved.

Suppose, for instance, that a high-energy negative K-meson—with, say, an energy of many Bev—collides with a proton. Out of the interaction may come many other particles: π -mesons, K-mesons, lambda particles, sigma particles—any of the mesons or baryons listed in Table 2-2 of Vol. I. It is observed, however, that only *certain combinations* appear, and never others. Now certain conservation laws were already known to apply. First, energy and momentum are always conserved. The total energy and momentum after an event must be the same as before the event. Second, there is the conservation of electric charge which says that the total charge of the outgoing particles must be equal to the total charge carried by the original particles. In our example of a K-meson and a proton coming together, the following reactions *do* occur:

$$\begin{aligned} & \text{or} \quad K^- + p \rightarrow p + K^- + \pi^+ + \pi^- + \pi^0 \\ & \quad K^- + p \rightarrow \Sigma^- + \pi^+ \end{aligned} \quad (11.38)$$

We would never get:

$$K^- + p \rightarrow p + K^- + \pi^+ \quad \text{or} \quad K^- + p \rightarrow \Lambda_0 + \pi^+ \quad (11.39)$$

because of the conservation of charge. It was also known that the *number of baryons* is conserved. The number of baryons *out* must be equal to the number of baryons *in*. For this law, an *antiparticle* of a baryon is counted as *minus* one baryon. This means that we can—and *do*—see

$$\begin{aligned} & \text{or} \quad K^- + p \rightarrow \Lambda^0 + \pi^0 \\ & \quad K^- + p \rightarrow p + K^- + p + \bar{p} \end{aligned} \quad (11.40)$$

(where \bar{p} is the antiproton, which carries a negative charge). But we *never* see

$$\begin{aligned} & \text{or} \quad K^- + p \rightarrow K^- + \pi^+ + \pi^0 \\ & \quad K^- + p \rightarrow p + K^- + n \end{aligned} \quad (11.41)$$

(even when there is plenty of energy), because baryons would not be conserved.

These laws, however, do *not* explain the strange fact that the following reactions—which do not immediately appear to be especially different from some of those in (11.38) or (11.40)—are also never observed:

$$\begin{aligned} & \text{or} \quad K^- + p \rightarrow p + K^- + K^0 \\ & \quad K^- + p \rightarrow p + \pi^- \\ & \text{or} \quad K^- + p \rightarrow \Lambda^0 + K^0 \end{aligned} \quad (11.42)$$

The explanation is the conservation of strangeness. With each particle goes a number—its *strangeness S*—and there is a law that in any *strong* interaction, the

Table 11-4

The strangeness numbers of the strongly interacting particles

	S			
	-2	-1	0	+1
Baryons	Ξ^0 Ξ^-	Σ^+ Λ^0, Σ^0 Σ^-	p n	
Mesons		\bar{K}^0 K ⁻	π^+ π^0 π^-	K ⁺ K ⁰

Note: The π^- is the antiparticle of the π^+ (or *vice versa*).

total strangeness *out* must equal the total strangeness that went *in*. The proton and antiproton (p, \bar{p}), the neutron and antineutron (n, \bar{n}), and the π -mesons (π^+, π^0, π^-) all have the strangeness number *zero*; the K^+ and K^0 mesons have strangeness $+1$; the K^- and \bar{K}^0 (the anti- K^0),† the Λ^0 and the Σ -particles ($+, 0, -$) have strangeness -1 . There is also a particle with strangeness -2 —the Ξ -particle (capital “ksi”)—and perhaps others as yet unknown. We have made a list of these strangenesses in Table 11-4.

Let’s see how the strangeness conservation works in some of the reactions we have written down. If we start with a K^- and a proton, we have a total strangeness of $(-1 + 0) = -1$. The conservation of strangeness says that the strangeness of products *after* the reaction must also add up to -1 . You see that that is so for the reactions of (11.38) and (11.40). But in the reactions of (11.42) the strangeness of the right-hand side is *zero* in each case. Such reactions do not conserve strangeness, and do not occur. Why? Nobody knows. Nobody knows any more than what we have just told you about this. Nature just works that way.

Now let’s look at the following reaction: a π^- hits a proton. You might, for instance, get a Λ^0 particle plus a neutral K-particle—two neutral particles. Now which neutral K do you get? Since the Λ -particle has a strangeness -1 and the π and p^+ have a strangeness zero, and since this is a fast production reaction, the strangeness must not change. The K-particle must have strangeness $+1$ —it must therefore be the K^0 . The reaction is

$$\pi^- + p \rightarrow \Lambda^0 + K^0,$$

with

$$S = 0 + 0 = -1 + +1 \quad (\text{conserved}).$$

If the \bar{K}^0 were there instead of the K^0 , the strangeness on the right would be -2 —which nature does not permit, since the strangeness on the left side is zero. On the other hand, a \bar{K}^0 can be produced in other reactions, such as

$$n + n \rightarrow n + p + \bar{K}^0 + K^+,$$

$$S = 0 + 0 = 0 + 0 + +1 + -1$$

or

$$K^- + p \rightarrow n + \bar{K}^0,$$

$$S = -1 + 0 = 0 + -1.$$

You may be thinking, “That’s all a lot of stuff, because how do you *know* whether it is a \bar{K}^0 or a K^0 ? They look exactly the same. They are antiparticles of each other, so they have exactly the same mass, and both have zero electric charge.

† Read as: “K-naught-bar,” or “K-zero-bar.”

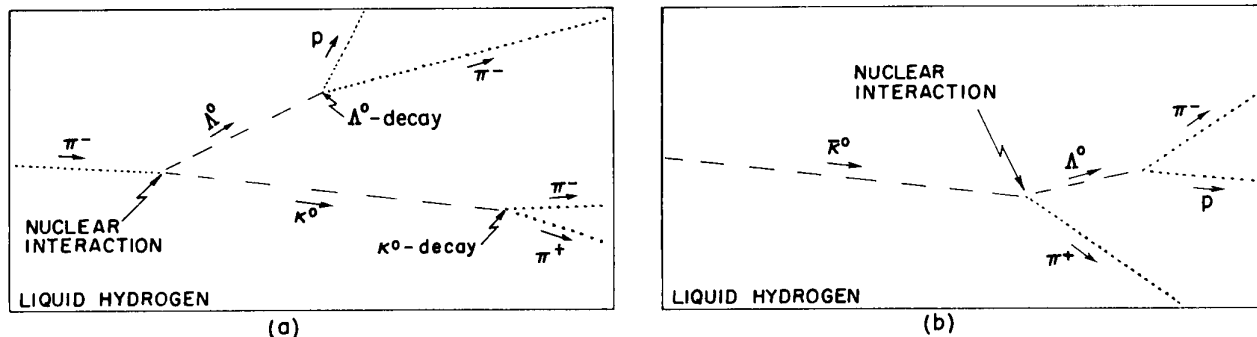
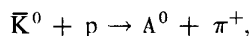


Fig. 11-5. High-energy events as seen in a hydrogen bubble chamber. (a) A π^- meson interacts with a hydrogen nucleus (proton) producing a Λ^0 particle and a K^0 meson. Both particles decay in the chamber. (b) A K^0 meson interacts with a proton producing a π^+ meson and a Λ^0 particle which then decays. (The neutral particles leave no tracks. Their inferred trajectories are indicated here by light dashed lines.)

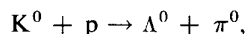
How do you distinguish them?" By the reactions *they* produce. For example, a \bar{K}^0 can interact with matter to produce a Λ -particle, like this:



but a K^0 cannot. There is *no* way a K^0 can produce a Λ -particle when it interacts with ordinary matter (protons and neutrons).† So the experimental distinction between the K^0 and the \bar{K}^0 would be that one of them will and one of them will not produce Λ 's.

One of the predictions of the strangeness theory is then this—if, in an experiment with high-energy pions, a Λ -particle is produced with a neutral K -meson, then *that* neutral K -meson going into other pieces of matter will never produce a Λ . The experiment might run something like this. You send a beam of π^- -mesons into a large hydrogen bubble chamber. A π^- track disappears, but somewhere else a pair of tracks appear (a proton and a π^-) indicating that a Λ -particle has disintegrated‡—see Fig. 11-5. Then you know that there is a K^0 somewhere which you cannot see.

You can, however, figure out where it is going by using the conservation of momentum and energy. [It could reveal itself later by disintegrating into two charged particles, as shown in Fig. 11-5(a).] As the K^0 goes flying along, it may interact with one of the hydrogen nuclei (protons), producing perhaps some other particles. The prediction of the strangeness theory is that it will *never* produce a Λ -particle in a simple reaction like, say,



although a \bar{K}^0 can do just that. That is, in a bubble chamber a \bar{K}^0 might produce the event sketched in Fig. 11-5(b)—in which the Λ^0 is seen because it decays—but a K^0 will not. That's the first part of our story. That's the conservation of strangeness.

The conservation of strangeness is, however, *not perfect*. There are very slow disintegrations of the strange particles—decays taking a long¶ time like 10^{-10} second in which the strangeness is *not* conserved. These are called the "weak" decays. For example, the K^0 disintegrates into a pair of π -mesons (+ and -)

† Except, of course, if it *also* produces *two* K^+ 's or other particles with a total strangeness of +2. We can think here of reactions in which there is insufficient energy to produce these additional strange particles.

‡ The free Λ -particle decays slowly via a *weak* interaction (so strangeness need not be conserved). The decay products are either a p and a π^- , or an n and a π^0 . The lifetime is 2.2×10^{-10} sec.

¶ A typical time for strong interactions is more like 10^{-23} sec.

with a lifetime of 10^{-10} second. That was, in fact, the way K-particles were first seen. Notice that the decay reaction

$$K^0 \rightarrow \pi^+ + \pi^-$$

does not conserve strangeness, so it cannot go “fast” by the strong interaction; it can only go through the weak decay process.

Now the \bar{K}^0 also disintegrates *in the same way*—into a π^+ and a π^- — and also with the same lifetime

$$\bar{K}^0 \rightarrow \pi^- + \pi^+.$$

Again we have a weak decay because it does not conserve strangeness. There is a principle that for any reaction there is the corresponding reaction with “matter” replaced by “antimatter” and *vice versa*. Since the \bar{K}^0 is the antiparticle of the K^0 , it should decay into the antiparticles of the π^+ and π^- , but the antiparticle of a π^+ is the π^- . (Or, if you prefer, *vice versa*. It turns out that for the π -mesons it doesn’t matter which one you call “matter.”) So as a consequence of the weak decays, the K^0 and \bar{K}^0 can go into the same final products. When “seen” through their decays—as in a bubble chamber—they look like the same particle. Only their strong interactions are different.

At last we are ready to describe the work of Gell-Mann and Pais. They first noticed that since the K^0 and the \bar{K}^0 can both turn into states of two π -mesons there must be some amplitude that a K^0 can turn into a \bar{K}^0 , and also that a \bar{K}^0 can turn into a K^0 . Writing the reactions as one does in chemistry, we would have

$$K^0 \rightleftharpoons \pi^- + \pi^+ \rightleftharpoons \bar{K}^0. \quad (11.43)$$

These reactions imply that there is some amplitude per unit time, say $-i/\hbar$ times $\langle \bar{K}^0 | W | K^0 \rangle$, that a K^0 will turn into a \bar{K}^0 through the weak interaction responsible for the decay into two π -mesons. And there is the corresponding amplitude $\langle K^0 | W | \bar{K}^0 \rangle$ for the reverse process. Because matter and antimatter behave in exactly the same way, these two amplitudes are numerically equal; we’ll call them both A :

$$\langle \bar{K}^0 | W | K^0 \rangle = \langle K^0 | W | \bar{K}^0 \rangle = A. \quad (11.44)$$

Now—said Gell-Mann and Pais—here is an interesting situation. What people have been calling two distinct states of the world—the K^0 and the \bar{K}^0 —should really be considered as *one* two-state *system*, because there is an amplitude to go from one state to the other. For a complete treatment, one would, of course, have to deal with more than two states, because there are also the states of 2π ’s, and so on; but since they were mainly interested in the relation of K^0 and \bar{K}^0 , they did not have to complicate things and could make the approximation of a two-state system. The other states *were* taken into account to the extent that their effects appeared implicitly in the amplitudes of Eq. (11.44).

Accordingly, Gell-Mann and Pais analyzed the neutral particle as a two-state system. They began by choosing as their two base states the states $|K^0\rangle$ and $|\bar{K}^0\rangle$. (From here on, the story goes very much as it did for the ammonia molecule.) Any state $|\psi\rangle$ of the neutral K-particle could then be described by giving the amplitudes that it was in either base state. We’ll call these amplitudes

$$C_+ = \langle K^0 | \psi \rangle, \quad C_- = \langle \bar{K}^0 | \psi \rangle. \quad (11.45)$$

The next step was to write the Hamiltonian equations for this two-state system. If there were no coupling between the K^0 and the \bar{K}^0 , the equations would be simply

$$\begin{aligned} i\hbar \frac{dC_+}{dt} &= E_0 C_+, \\ i\hbar \frac{dC_-}{dt} &= E_0 C_-. \end{aligned} \quad (11.46)$$

But since there is the amplitude $\langle \bar{K}^0 | W | K^0 \rangle$ for the K^0 to turn into a \bar{K}^0 there should be the additional term

$$\langle \bar{K}^0 | W | K^0 \rangle C_- = AC_-$$

added to the right-hand side of the first equation. And similarly, the term AC_+ should be inserted in the equation for the rate of change of C_- .

But that's not all. When the two-pion effect is taken into account there is an *additional* amplitude for the K^0 to turn into *itself* through the process

$$K^0 \rightarrow \pi^- + \pi^+ \rightarrow K^0.$$

The additional amplitude, which we would write $\langle K^0 | W | K^0 \rangle$, is just equal to the amplitude $\langle \bar{K}^0 | W | K^0 \rangle$, since the amplitudes to go to and from a pair of π -mesons are identical for the K^0 and the \bar{K}^0 . If you wish, the argument can be written out in detail like this. First write†

$$\langle \bar{K}^0 | W | K^0 \rangle = \langle \bar{K}^0 | W | 2\pi \rangle \langle 2\pi | W | K^0 \rangle$$

and

$$\langle K^0 | W | K^0 \rangle = \langle K^0 | W | 2\pi \rangle \langle 2\pi | W | K^0 \rangle.$$

Because of the symmetry of matter and antimatter

$$\langle 2\pi | W | K^0 \rangle = \langle 2\pi | W | \bar{K}^0 \rangle,$$

and also

$$\langle K^0 | W | 2\pi \rangle = \langle \bar{K}^0 | W | 2\pi \rangle.$$

It then follows that $\langle K^0 | W | K^0 \rangle = \langle \bar{K}^0 | W | K^0 \rangle$, and also that $\langle \bar{K}^0 | W | K^0 \rangle = \langle K^0 | W | \bar{K}^0 \rangle$, as we said earlier. Anyway, there are the two additional amplitudes $\langle K^0 | W | K^0 \rangle$ and $\langle \bar{K}^0 | W | \bar{K}^0 \rangle$, both equal to A , which should be included in the Hamiltonian equations. The first gives a term AC_+ on the right-hand side of the equation for dC_+/dt , and the second gives a new term AC_- in the equation for dC_-/dt . Reasoning this way, Gell-Mann and Pais concluded that the Hamiltonian equations for the $K^0 \bar{K}^0$ system should be

$$\begin{aligned} i\hbar \frac{dC_+}{dt} &= E_0 C_+ + AC_- + AC_+, \\ i\hbar \frac{dC_-}{dt} &= E_0 C_- + AC_+ + AC_-. \end{aligned} \tag{11.47}$$

We must now correct something we have said in earlier chapters: that two amplitudes like $\langle K^0 | W | \bar{K}^0 \rangle$ and $\langle \bar{K}^0 | W | K^0 \rangle$ which are the reverse of each other, are always complex conjugates. That was true when we were talking about particles that did not decay. But if particles can decay—and can, therefore, become “lost”—the two amplitudes are not necessarily complex conjugates. So the equality of (11.44) does not mean that the amplitudes are real numbers; they are in fact complex numbers. The coefficient A is, therefore, complex; and we can't just incorporate it into the energy E_0 .

Having played often with electron spins and such, our heroes knew that the Hamiltonian equations of (11.47) meant that there was *another* pair of base states which could also be used to represent the K -particle system and which would have especially simple behaviors. They said, “Let's take the sum and difference of these two equations. Also, let's measure all our energies from E_0 , and use units for

† We are making a simplification here. The 2π -system can have many states corresponding to various momenta of the π -mesons, and we should make the right-hand side of this equation into a sum over the various base states of the π 's. The complete treatment still leads to the same conclusions.

energy and time that make $\hbar = 1$." (That's what modern theoretical physicists always do. It doesn't change the physics but makes the equations take on a simple form.) Their result:

$$i \frac{d}{dt} (C_+ + C_-) = 2A(C_+ + C_-), \quad i \frac{d}{dt} (C_+ - C_-) = 0. \quad (11.48)$$

It is apparent that the combinations of amplitudes $(C_+ + C_-)$ and $(C_+ - C_-)$ act independently from each other (corresponding, of course, to the stationary states we have been studying earlier). So they concluded that it would be more convenient to use a different representation for the K-particle. They defined the two states

$$|K_1\rangle = \frac{1}{\sqrt{2}} (|K^0\rangle + |\bar{K}^0\rangle), \quad |K_2\rangle = \frac{1}{\sqrt{2}} (|K^0\rangle - |\bar{K}^0\rangle). \quad (11.49)$$

They said that instead of thinking of the K^0 and \bar{K}^0 mesons, we can equally well think in terms of the two "particles" (that is, "states") K_1 and K_2 . (These correspond, of course, to the states we have usually called $|I\rangle$ and $|II\rangle$). We are not using our old notation because we want now to follow the notation of the original authors—and the one you will see in physics seminars.)

Now Gell-Mann and Pais didn't do all this just to get different names for the particles—there is also some strange new physics in it. Suppose that C_1 and C_2 are the amplitudes that some state $|\psi\rangle$ will be either a K_1 or a K_2 meson:

$$C_1 = \langle K_1 | \psi \rangle, \quad C_2 = \langle K_2 | \psi \rangle.$$

From the equations of (11.49),

$$C_1 = \frac{1}{\sqrt{2}} (C_+ + C_-), \quad C_2 = \frac{1}{\sqrt{2}} (C_+ - C_-). \quad (11.50)$$

Then the Eqs. (11.48) become

$$i \frac{dC_1}{dt} = 2AC_1, \quad i \frac{dC_2}{dt} = 0. \quad (11.51)$$

The solutions are

$$C_1(t) = C_1(0)e^{-i2At}, \quad C_2(t) = C_2(0), \quad (11.52)$$

where, of course, $C_1(0)$ and $C_2(0)$ are the amplitudes at $t = 0$.

These equations say that if a neutral K-particle starts out in the state $|K_1\rangle$ at $t = 0$ [then $C_1(0) = 1$ and $C_2(0) = 0$], the amplitudes at the time t are

$$C_1(t) = e^{-i2At}, \quad C_2(t) = 0.$$

Remembering that A is a complex number, it is convenient to take $A = \alpha - i\beta$. (Since the imaginary part of $2A$ turns out to be negative, we write it as *minus* $i\beta$.) With this substitution, $C_1(t)$ reads

$$C_1(t) = C_1(0)e^{-\beta t}e^{-i\alpha t}. \quad (11.53)$$

The probability of finding a K_1 particle at t is the absolute square of this amplitude, which is $e^{-2\beta t}$. And, from Eqs. (11.52), the probability of finding the K_2 state at any time is zero. That means that if you make a K-particle in the state $|K_1\rangle$, the probability of finding it in the same state decreases exponentially with time—but you will never find it in state $|K_2\rangle$. Where does it go? It disintegrates into two π -mesons with the mean life $\tau = 1/2\beta$ which is, experimentally, 10^{-10} sec. We made provisions for that when we said that A was complex.

On the other hand, Eq. (11.52) says that if we make a K-particle completely in the K_2 state, it stays that way forever. Well, that's not really true. It is observed experimentally to disintegrate into *three* π -mesons, but 600 times slower than the

two-pion decay we have described. So there are some other small terms we have left out in our approximation. But so long as we are considering only the two-pion decay, the K_2 lasts “forever.”

Now to finish the story of Gell-Mann and Pais. They went on to consider what happens when a K-particle is produced *with a Λ^0 particle* in a *strong* interaction. Since it must then have a strangeness of +1, it must be produced in the K^0 state. So at $t = 0$ it is neither a K_1 nor a K_2 but a *mixture*. The initial conditions are

$$C_+(0) = 1, \quad C_-(0) = 0.$$

But that means—from Eq. (11.50)—that

$$C_1(0) = \frac{1}{\sqrt{2}}, \quad C_2(0) = \frac{1}{\sqrt{2}},$$

and—from Eq. (11.51)—that

$$C_1(t) = \frac{1}{\sqrt{2}} e^{-\beta t} e^{-i\alpha t}, \quad C_2(t) = \frac{1}{\sqrt{2}}. \quad (11.54)$$

Now remember that K_1 and K_2 are each linear combinations of K^0 and \bar{K}^0 . In Eqs. (11.54) the amplitudes have been chosen so that at $t = 0$ the \bar{K}^0 parts cancel each other out by interference, leaving only a K^0 state. But the $|K_1\rangle$ state *changes with time*, and the $|K_2\rangle$ state *does not*. After $t = 0$ the interference of C_1 and C_2 will give finite amplitudes for both K^0 and \bar{K}^0 .

What does all this mean? Let’s go back and think of the experiment we sketched in Fig. 11-5. A π^- meson has produced a Λ^0 particle and a K^0 meson which is tooting along through the hydrogen in the chamber. As it goes along, there is some small but uniform chance that it will collide with a hydrogen nucleus. At first, we thought that strangeness conservation would prevent the K-particle from making a Λ^0 in such an interaction. Now, however, we see that that is not right. For although our K-particle *starts out* as a K^0 —which cannot make a Λ^0 —it does not *stay* this way. After a while, there *is some amplitude* that it will have flipped to the \bar{K}^0 state. We can, therefore, sometimes expect to see a Λ^0 produced along the K-particle track. The chance of this happening is given by the amplitude C_- , which we can [by using Eq. (11.50) backwards] relate to C_1 and C_2 . The relation is

$$C_- = \frac{1}{\sqrt{2}} (C_1 - C_2) = \frac{1}{2}(e^{-\beta t} e^{-i\alpha t} - 1). \quad (11.55)$$

As our K-particle goes along, the probability that it will “act like” a \bar{K}^0 is equal to $|C_-|^2$, which is

$$|C_-|^2 = \frac{1}{4}(1 + e^{-2\beta t} - 2e^{-\beta t} \cos \alpha t). \quad (11.56)$$

A complicated and strange result!

This, then, is the remarkable prediction of Gell-Mann and Pais: when a K^0 is produced, the chance that it will turn into a \bar{K}^0 —as it can demonstrate by being able to produce a Λ^0 —varies with time according to Eq. (11.56). This prediction came from using only sheer logic and the basic principles of the quantum mechanics—with no knowledge at all of the inner workings of the K-particle. Since nobody knows anything about the inner machinery, that is as far as Gell-Mann and Pais could go. They could not give any theoretical values for α and β . And nobody has been able to do so to this date. They were able to give a value of β obtained from the experimentally observed rate of decay into two π ’s ($2\beta = 10^{10}$ sec), but they could say nothing about α .

We have plotted the function of Eq. (11.56) for two values of α in Fig. 11-6. You can see that the form depends very much on the ratio of α to β . There is no \bar{K}^0 probability at first; then it builds up. If α is large, the probability would have

large oscillations. If α is small, there will be little or no oscillation—the probability will just rise smoothly to $1/4$.

Now, typically, the K-particle will be travelling at a constant speed near the speed of light. The curves of Fig. 11-6 then also represent the probability along the track of observing a \bar{K}^0 —with typical distances of several centimeters. You can see why this prediction is so remarkably peculiar. You produce a single particle and instead of just disintegrating, it does something else. Sometimes it disintegrates, and other times it turns into a different kind of a particle. Its characteristic probability of producing an effect varies in a strange way as it goes along. There is nothing else quite like it in nature. And this most remarkable prediction was made solely by arguments about the interference of amplitudes.

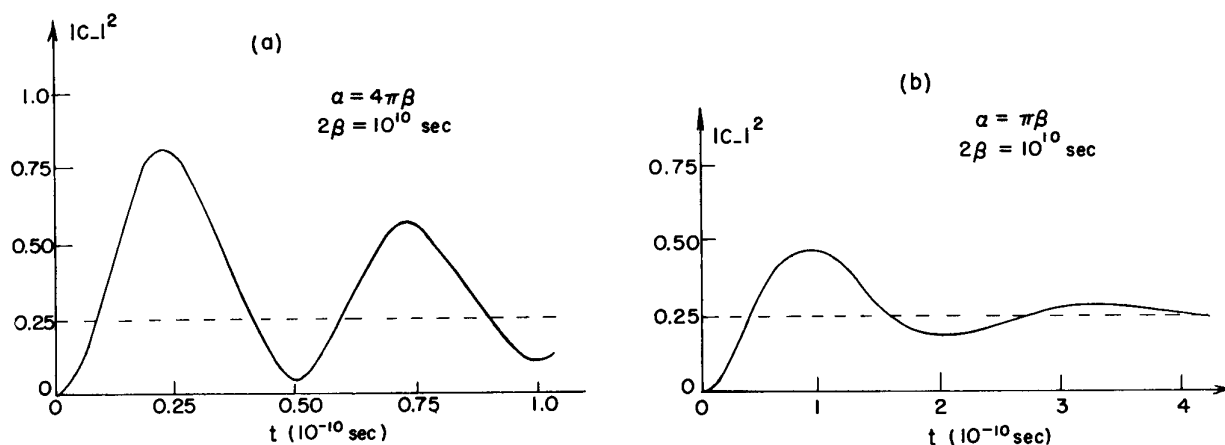


Fig. 11-6. The function of Eq. (11-56): (a) for $\alpha = \pi\beta$, (b) for $\alpha = 4\pi\beta$ (with $2\beta = 10^{10}$ sec).

If there is any place where we have a chance to test the main principles of quantum mechanics in the purest way—does the superposition of amplitudes work or doesn't it?—this is it. In spite of the fact that this effect has been predicted now for several years, there is no experimental determination that is very clear. There are some rough results which indicate that the α is not zero, and that the effect really occurs—they indicate that α is between 2β and 4β . That's all there is, experimentally. It would be very beautiful to check out the curve exactly to see if the principle of superposition really still works in such a mysterious world as that of the strange particles—with unknown reasons for the decays, and unknown reasons for the strangeness.

The analysis we have just described is very characteristic of the way quantum mechanics is being used today in the search for an understanding of the strange particles. All the complicated theories that you may hear about are no more and no less than this kind of elementary hocus-pocus using the principles of superposition and other principles of quantum mechanics of that level. Some people claim that they have theories by which it is possible to calculate the β and α , or at least the α given the β , but these theories are completely useless. For instance, the theory that predicts the value of α , given the β , tells us that the value of α should be infinite. The set of equations with which they originally start involves two π -mesons and then goes from the two π 's back to a K^0 , and so on. When it's all worked out, it does indeed produce a pair of equations like the ones we have here; but because there are an infinite number of states of two π 's, depending on their momenta, integrating over all the possibilities gives an α which is infinite. But nature's α is *not* infinite. So the dynamical theories are wrong. It is really quite remarkable that the phenomena which can be predicted *at all* in the world of the strange particles come from the principles of quantum mechanics at the level at which you are learning them now.

11-6 Generalization to N -state systems

We have finished with all the two-state systems we wanted to talk about. In the following chapters we will go on to study systems with more states. The extension to N -state systems of the ideas we have worked out for two states is pretty straightforward. It goes like this.

If a system has N distinct states, we can represent any state $|\psi(t)\rangle$ as a linear combination of any set of base states $|i\rangle$, where $i = 1, 2, 3, \dots, N$;

$$|\psi(t)\rangle = \sum_{\text{all } i} |i\rangle C_i(t). \quad (11.57)$$

The coefficients $C_i(t)$ are the amplitudes $\langle i | \psi(t) \rangle$. The behavior of the amplitudes C_i with time is governed by the equations

$$i\hbar \frac{dC_i(t)}{dt} = \sum_j H_{ij} C_j, \quad (11.58)$$

where the energy matrix H_{ij} describes the physics of the problem. It looks the same as for two states. Only now, both i and j must range over all N base states, and the energy matrix H_{ij} —or, if you prefer, the Hamiltonian—is an N by N matrix with N^2 numbers. As before, $H_{ij}^* = H_{ji}$ —so long as particles are conserved—and the diagonal elements H_{ii} are real numbers.

We have found a general solution for the C 's of a two-state system when the energy matrix is constant (doesn't depend on t). It is also not difficult to solve Eq. (11.58) for an N -state system when H is not time dependent. Again, we begin by looking for a possible solution in which the amplitudes all have the *same* time dependence. We try

$$C_i = a_i e^{-(i/\hbar)Et}. \quad (11.59)$$

When these C_i 's are substituted into (11.58), the derivatives $dC_i(t)/dt$ become just $(-i/\hbar)EC_i$. Canceling the common exponential factor from all terms, we get

$$Ea_i = \sum_j H_{ij} a_j. \quad (11.60)$$

This is a set of N linear algebraic equations for the N unknowns a_1, a_2, \dots, a_n , and there is a solution only if you are lucky—only if the determinant of the coefficients of all the a 's is zero. But it's not necessary to be that sophisticated; you can just start to solve the equations any way you want, and you will find that they can be solved only for certain values of E . (Remember that E is the only adjustable thing we have in the equations.)

If you want to be formal, however, you can write Eq. (11.60) as

$$\sum_j (H_{ij} - \delta_{ij}E) a_j = 0. \quad (11.61)$$

Then you can use the rule—if you know it—that these equations will have a solution only for those values of E for which

$$\text{Det}(H_{ij} - \delta_{ij}E) = 0. \quad (11.62)$$

Each term of the determinant is just H_{ij} , except that E is subtracted from every diagonal element. That is, (11.62) means just

$$\text{Det} \begin{pmatrix} H_{11} - E & H_{12} & H_{13} & \dots \\ H_{21} & H_{22} - E & H_{23} & \dots \\ H_{31} & H_{32} & H_{33} - E & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} = 0. \quad (11.63)$$

This is, of course, just a special way of writing an algebraic equation for E which is the sum of a bunch of products of all the terms taken a certain way. These products will give all the powers of E up to E^N .

So we have an N th order polynomial equal to zero, and there are, in general, N roots. (We must remember, however, that some of them may be multiple roots—meaning that two or more roots are equal.) Let's call the N roots

$$E_I, E_{II}, E_{III}, \dots, E_n, \dots, E_N. \quad (11.64)$$

(We will use n to represent the n th Roman numeral, so that n takes on the values I, II, \dots , N.) It may be that some of these energies are equal—say $E_{II} = E_{III}$ —but we will still choose to call them by different names.

The equations (11.60)—or (11.61)—have one solution for each value of E . If you put any one of the E 's—say E_n —into (11.60) and solve for the a_i , you get a set which belongs to the energy E_n . We will call this set $a_i(n)$.

Using these $a_i(n)$ in Eq. (11.59), we have the amplitudes $C_i(n)$ that the definite energy states are in the base state $|i\rangle$. Letting $|n\rangle$ stand for the state vector of the definite energy state at $t = 0$, we can write

$$C_i(n) = \langle i | n \rangle e^{(i/\hbar) E_n t},$$

with

$$\langle i | n \rangle = a_i(n). \quad (11.65)$$

The complete definite energy state $|\psi_n(t)\rangle$ can then be written as

$$|\psi_n(t)\rangle = \sum_i |i\rangle a_i(n) e^{-(i/\hbar) E_n t},$$

or

$$|\psi_n(t)\rangle = |n\rangle e^{(i/\hbar) E_n t}. \quad (11.66)$$

The state vectors $|n\rangle$ describe the configuration of the definite energy states, but have the time dependence factored out. Then they are constant vectors which can be used as a new base set if we wish.

Each of the states $|n\rangle$ has the property—as you can easily show—that when operated on by the Hamiltonian operator \hat{H} it gives just E_n times the same state:

$$\hat{H} |n\rangle = E_n |n\rangle. \quad (11.67)$$

The energy E_n is, then, a number which is a characteristic of the Hamiltonian operator \hat{H} . As we have seen, a Hamiltonian will, in general, have several characteristic energies. In the mathematician's world these would be called the “characteristic values” of the matrix H_{ij} . Physicists usually call them the “eigenvalues” of \hat{H} . (“Eigen” is the German word for “characteristic” or “proper.”) With each eigenvalue of \hat{H} —in other words, for each energy—there is the state of definite energy, which we have called the “stationary state.” Physicists usually call the states $|n\rangle$ “the eigenstates of \hat{H} .” Each eigenstate corresponds to a particular eigenvalue E_n .

Now, generally, the states $|n\rangle$ —of which there are N —can also be used as a base set. For this to be true, all of the states must be orthogonal, meaning that for any two of them, say $|n\rangle$ and $|m\rangle$,

$$\langle n | m \rangle = 0. \quad (11.68)$$

This will be true automatically if all the energies are different. Also, we can multiply all the $a_i(n)$ by a suitable factor so that all the states are normalized—by which we mean that

$$\langle n | n \rangle = 1 \quad (11.69)$$

for all n .

When it happens that Eq. (11.63) accidentally has two (or more) roots with the same energy, there are some minor complications. First, there are still two different sets of a_i 's which go with the two equal energies, but the states they give

may *not* be orthogonal. Suppose you go through the normal procedure and find two stationary states with equal energies—let's call them $|\mu\rangle$ and $|\nu\rangle$. Then it will not necessarily be so that they are orthogonal—if you are unlucky,

$$\langle\mu|\nu\rangle \neq 0.$$

It is, however, always true that you can cook up two new states, which we will call $|\mu'\rangle$ and $|\nu'\rangle$, that have the same energies and are also orthogonal, so that

$$\langle\mu'|\nu'\rangle = 0. \quad (11.70)$$

You can do this by making $|\mu'\rangle$ and $|\nu'\rangle$ a suitable linear combination of $|\mu\rangle$ and $|\nu\rangle$, with the coefficients chosen to make it come out so that Eq. (11.70) is true. It is always convenient to do this. We will generally assume that this has been done so that we can always assume that our proper energy states $|\mathbf{n}\rangle$ are all orthogonal.

We would like, for fun, to prove that when two of the stationary states have different energies they are indeed orthogonal. For the state $|\mathbf{n}\rangle$ with the energy $E_{\mathbf{n}}$, we have that

$$\hat{H}|\mathbf{n}\rangle = E_{\mathbf{n}}|\mathbf{n}\rangle. \quad (11.71)$$

This operator equation really means that there is an equation between numbers. Filling the missing parts, it means the same as

$$\sum_j \langle i|\hat{H}|j\rangle\langle j|\mathbf{n}\rangle = E_{\mathbf{n}}\langle i|\mathbf{n}\rangle. \quad (11.72)$$

If we take the complex conjugate of this equation, we get

$$\sum_j \langle i|\hat{H}|j\rangle^*\langle j|\mathbf{n}\rangle^* = E_{\mathbf{n}}^*\langle i|\mathbf{n}\rangle^*. \quad (11.73)$$

Remember now that the complex conjugate of an amplitude is the reverse amplitude, so (11.73) can be rewritten as

$$\sum_j \langle \mathbf{n}|j\rangle\langle j|\hat{H}|i\rangle = E_{\mathbf{n}}^*\langle \mathbf{n}|i\rangle. \quad (11.74)$$

Since this equation is valid for *any* i , its “short form” is

$$\langle \mathbf{n}|\hat{H} = E_{\mathbf{n}}^*\langle \mathbf{n}|, \quad (11.75)$$

which is called the *adjoint* to Eq. (11.71).

Now we can easily prove that $E_{\mathbf{n}}$ is a real number. We multiply Eq. (11.71) by $\langle \mathbf{n}|$ to get

$$\langle \mathbf{n}|\hat{H}|\mathbf{n}\rangle = E_{\mathbf{n}}, \quad (11.76)$$

since $\langle \mathbf{n}|\mathbf{n}\rangle = 1$. Then we multiply Eq. (11.75) on the left by $|\mathbf{n}\rangle$ to get

$$\langle \mathbf{n}|\hat{H}|\mathbf{n}\rangle = E_{\mathbf{n}}^*. \quad (11.77)$$

Comparing (11.76) with (11.77) it is clear that

$$E_{\mathbf{n}} = E_{\mathbf{n}}^*, \quad (11.78)$$

which means that $E_{\mathbf{n}}$ is real. We can erase the star on $E_{\mathbf{n}}$ in Eq. (11.75).

Finally we are ready to show that the different energy states are orthogonal. Let $|\mathbf{n}\rangle$ and $|\mathbf{m}\rangle$ be any two of the definite energy base states. Using Eq. (11.75) for the state \mathbf{m} , and multiplying it by $|\mathbf{n}\rangle$, we get that

$$\langle \mathbf{m}|\hat{H}|\mathbf{n}\rangle = E_{\mathbf{m}}\langle \mathbf{m}|\mathbf{n}\rangle.$$

But if we multiply (11.71) by $\langle \mathbf{m} |$, we get

$$\langle \mathbf{m} | \hat{H} | \mathbf{n} \rangle = E_{\mathbf{n}} \langle \mathbf{m} | \mathbf{n} \rangle.$$

Since the left sides of these two equations are equal, the right sides are, also:

$$E_{\mathbf{m}} \langle \mathbf{m} | \mathbf{n} \rangle = E_{\mathbf{n}} \langle \mathbf{m} | \mathbf{n} \rangle. \quad (11.79)$$

If $E_{\mathbf{m}} = E_{\mathbf{n}}$ the equation does not tell us anything. But if the energies of the two states $|\mathbf{m}\rangle$ and $|\mathbf{n}\rangle$ are *different* ($E_{\mathbf{m}} \neq E_{\mathbf{n}}$), Eq. (11.79) says that $\langle \mathbf{m} | \mathbf{n} \rangle$ must be zero, as we wanted to prove. The two states are necessarily orthogonal so long as $E_{\mathbf{n}}$ and $E_{\mathbf{m}}$ are numerically different.