

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

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

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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:

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

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.†

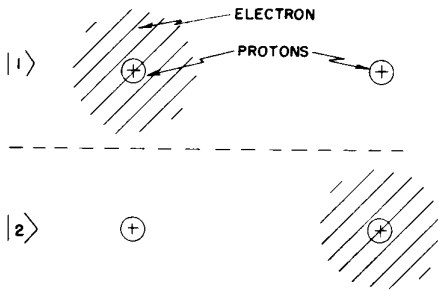


Fig. 10-1. A set of base states for two protons and an electron.

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.

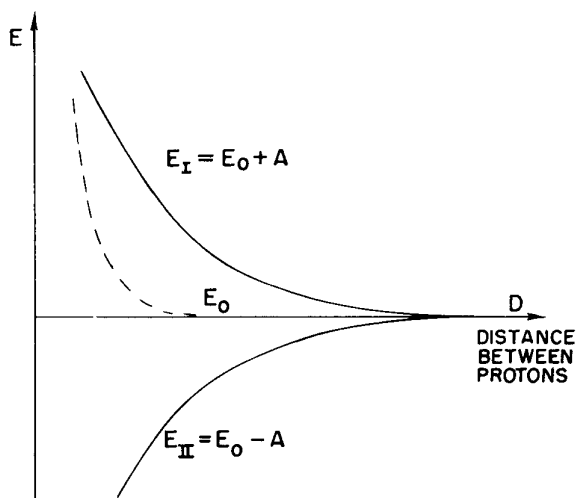


Fig. 10-2. The energies of the two stationary states of the H_2^+ ion as a function of the distance between the two protons.

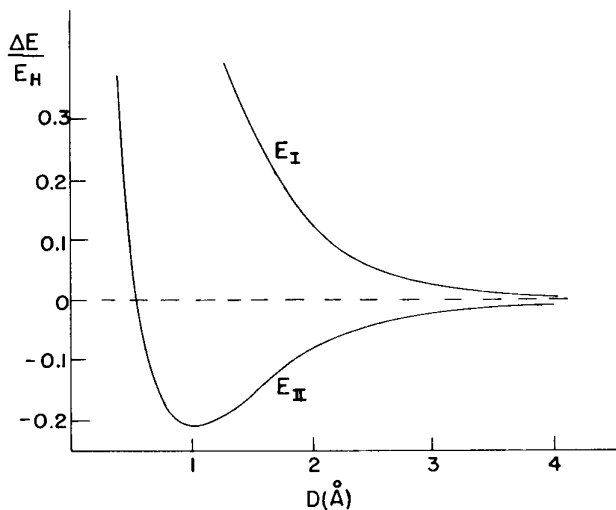


Fig. 10-3. The energy levels of the H_2^+ ion as a function of the interproton distance D . ($E_h = 13.6$ ev.)

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 $|1\rangle$ and $|2\rangle$. Because of the symmetry of $|1\rangle$ 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

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

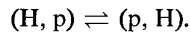
They are now very nearly just the energies H_{11} and H_{22} of the isolated atoms, pushed apart only slightly by the flip-flop amplitude A .

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



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:



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.

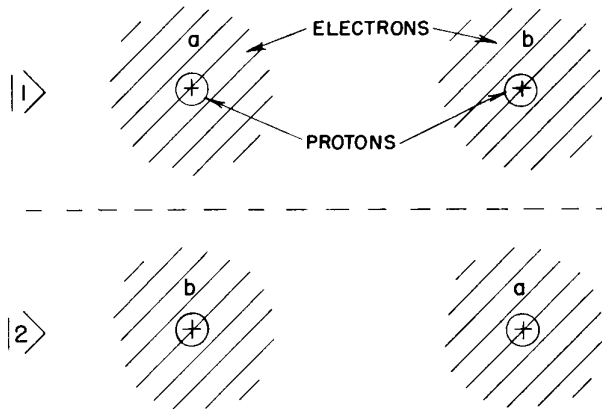


Fig. 10-4. A set of base states for the H_2 molecule.

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

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

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

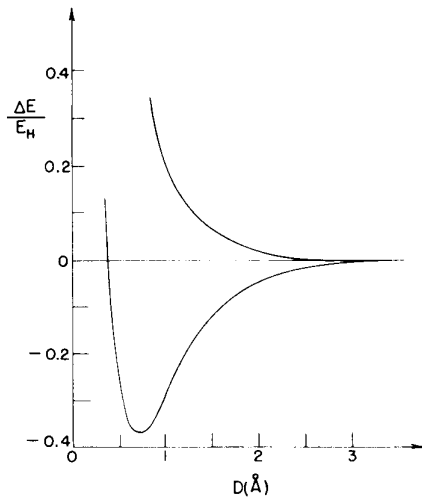


Fig. 10-5. The energy levels of the H_2 molecule for different interproton distances D . ($E_h = 13.6$ ev.)

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 $t = 0$)

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

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

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

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

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

For this state, an interchange of the two electrons gives

$$(|2\rangle - |1\rangle),$$

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.

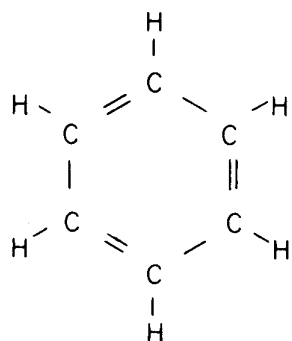


Fig. 10-6. The benzene molecule, C_6H_6 .

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

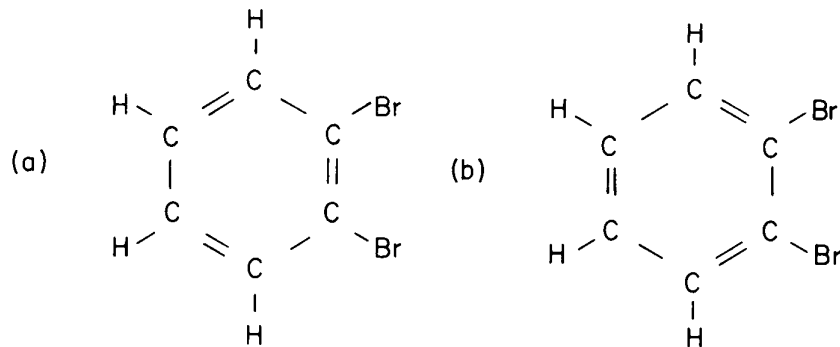


Fig. 10-7. Two possibilities of orthodibromobenzene. The two bromines could be separated by a single bond or by a double bond.

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 $\omega = (E_I - E_{II})/h$. 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

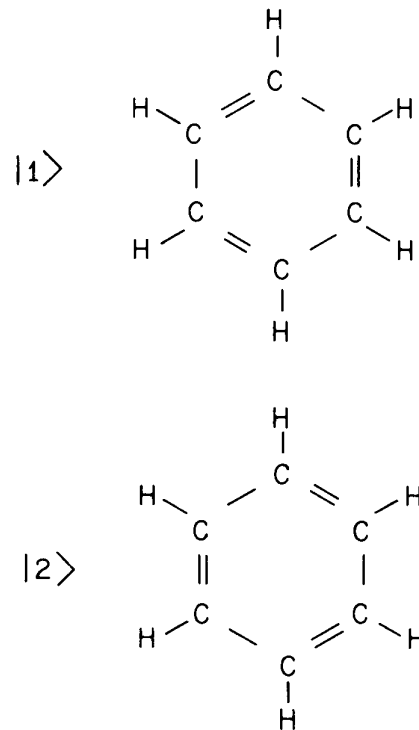


Fig. 10-8. A set of base states for the benzene molecule.

† 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!

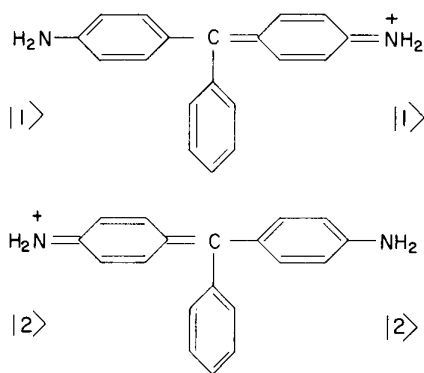


Fig. 10-9. Two base states for the molecule of the dye magenta.

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:

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

For this special case, the Hamiltonian is

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

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,

$$E_I = -\mu\sqrt{B_x^2 + B_y^2 + B_z^2}\tag{10.19}$$

and

$$E_{II} = +\mu\sqrt{B_x^2 + B_y^2 + B_z^2}.$$

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_0c^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

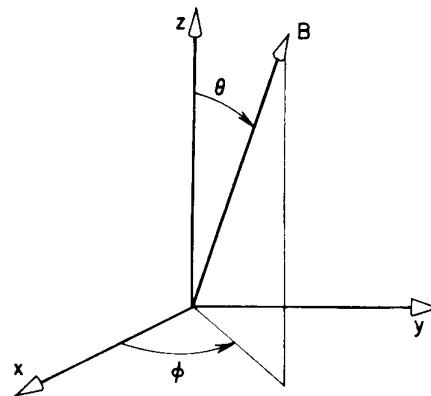


Fig. 10-10. The direction of \mathbf{B} is defined by the polar angle θ and the azimuthal angle ϕ .

$1 - \cos \theta = 2 \sin^2(\theta/2)$, 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 lets 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

$$C_1(t) = C_1(0)e^{-iE_1 t/\hbar} = C_1(0)e^{+i\mu B t/\hbar},$$

and

$$C_2(t) = C_2(0)e^{-iE_2 t/\hbar} = C_2(0)e^{-i\mu B t/\hbar}.$$

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.

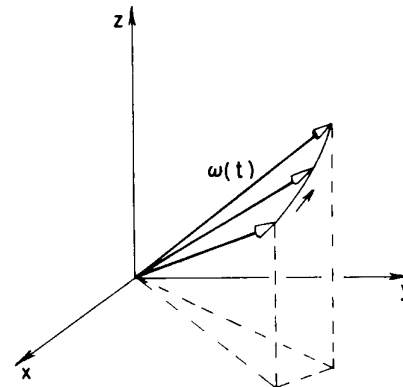


Fig. 10-11. The spin direction of an electron in a varying magnetic field $\mathbf{B}(t)$ precesses at the frequency $\omega(t)$ about an axis parallel to \mathbf{B} .