

## The Independent Particle Approximation

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### 15-1 Spin waves

In Chapter 13 we worked out the theory for the propagation of an electron or of some other “particle,” such as an atomic excitation, through a crystal lattice. In the last chapter we applied the theory to semiconductors. But when we talked about situations in which there are many electrons we disregarded any interactions between them. To do this is of course only an approximation. In this chapter we will discuss further the idea that you can disregard the interaction between the electrons. We will also use the opportunity to show you some more applications of the theory of the propagation of particles. Since we will generally continue to disregard the interactions between particles, there is very little really new in this chapter except for the new applications. The first example to be considered is, however, one in which it is possible to write down quite exactly the correct equations when there is more than one “particle” present. From them we will be able to see how the approximation of disregarding the interactions is made. We will not, though, analyze the problem very carefully.

As our first example we will consider a “spin wave” in a ferromagnetic crystal. We have discussed the theory of ferromagnetism in Chapter 36 of Volume II. At zero temperature all the electron spins that contribute to the magnetism in the body of a ferromagnetic crystal are parallel. There is an interaction energy between the spins, which is lowest when all the spins are down. At any nonzero temperature, however, there is some chance that some of the spins are turned over. We calculated the probability in an approximate manner in Chapter 36. This time we will describe the quantum mechanical theory—so you will see what you would have to do if you wanted to solve the problem more exactly. (We will still make some idealizations by assuming that the electrons are localized at the atoms and that the spins interact only with neighboring spins.)

We consider a model in which the electrons at each atom are all paired except one, so that all of the magnetic effects come from one spin- $\frac{1}{2}$  electron per atom. Further, we imagine that these electrons are localized at the atomic sites in the lattice. The model corresponds roughly to metallic nickel.

We also assume that there is an interaction between any two adjacent spinning electrons which gives a term in the energy of the system

$$E = - \sum_{i, j} K \sigma_i \cdot \sigma_j, \quad (15.1)$$

where  $\sigma$ 's represent the spins and the summation is over all adjacent pairs of electrons. We have already discussed this kind of interaction energy when we considered the hyperfine splitting of hydrogen due to the interaction of the magnetic moments of the electron and proton in a hydrogen atom. We expressed it then as  $A \sigma_e \cdot \sigma_p$ . Now, for a given pair, say the electrons at atom 4 and at atom 5, the Hamiltonian would be  $-K \sigma_4 \cdot \sigma_5$ . We have a term for each such pair, and the Hamiltonian is (as you would expect for classical energies) the sum of these terms for each interacting pair. The energy is written with the factor  $-K$  so that a positive  $K$  will correspond to ferromagnetism—that is, the lowest energy results when adjacent spins are parallel. In a real crystal, there may be other terms which are the interactions of *next* nearest neighbors, and so on, but we don't need to consider such complications at this stage.

With the Hamiltonian of Eq. (15.1) we have a complete description of the ferromagnet—within our approximation—and the properties of the magnetization

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should come out. We should also be able to calculate the thermodynamic properties due to the magnetization. If we can find all the energy levels, the properties of the crystal at a temperature  $T$  can be found from the principle that the probability that a system will be found in a given state of energy  $E$  is proportional to  $e^{-E/kT}$ . This problem has never been completely solved.

We will show some of the problems by taking a simple example in which all the atoms are in a line—a one-dimensional lattice. You can easily extend the ideas to three dimensions. At each atomic location there is an electron which has two possible states, either spin up or spin down, and the whole system is described by telling how all of the spins are arranged. We take the Hamiltonian of the system to be the operator of the interaction energy. Interpreting the spin vectors of Eq. (15.1) as the sigma-operators—or the sigma-matrices—we write for the linear lattice

$$\hat{H} = \sum_n -\frac{A}{2} \hat{\sigma}_n \cdot \hat{\sigma}_{n+1}. \quad (15.2)$$

In this equation we have written the constant as  $A/2$  for convenience (so that some of the later equations will be exactly the same as the ones in Chapter 13).

Now what is the lowest state of this system? The state of lowest energy is the one in which all the spins are parallel—let's say, all up.† We can write this state as  $|\cdots + + + \cdots\rangle$ , or  $|\text{gnd}\rangle$  for the “ground,” or lowest, state. It's easy to figure out the energy for this state. One way is to write out all the vector sigmas in terms of  $\hat{\sigma}_x$ ,  $\hat{\sigma}_y$ , and  $\hat{\sigma}_z$ , and work through carefully what each term of the Hamiltonian does to the ground state, and then add the results. We can, however, also use a good short cut. We saw in Section 12-2, that  $\hat{\sigma}_i \cdot \hat{\sigma}_j$  could be written in terms of the Pauli spin exchange operator like this:

$$\hat{\sigma}_i \cdot \hat{\sigma}_j = (2\hat{P}_{ij}^{\text{spin ex}} - 1), \quad (15.3)$$

where the operator  $\hat{P}_{ij}^{\text{spin ex}}$  interchanges the spins of the  $i$ th and  $j$ th electrons. With this substitution the Hamiltonian becomes

$$\hat{H} = -A \sum_n (\hat{P}_{n, n+1}^{\text{spin ex}} - \frac{1}{2}). \quad (15.4)$$

It is now easy to work out what happens to different states. For instance if  $i$  and  $j$  are both up, then exchanging the spins leaves everything unchanged, so  $\hat{P}_{ij}$  acting on the state just gives the same state back, and is equivalent to multiplying by  $+1$ . The expression  $(\hat{P}_{ij} - \frac{1}{2})$  is just equal to one-half. (From now on we will leave off the descriptive superscript on the  $P$ .)

For the ground state all spins are up; so if you exchange a particular pair of spins, you get back the original state. The ground state is a stationary state. If you operate on it with the Hamiltonian you get the same state again multiplied by a sum of terms,  $-(A/2)$  for each pair of spins. That is, the energy of the system in the ground state is  $-A/2$  per atom

Next we would like to look at the energies of some of the excited states. It will be convenient to measure the energies with respect to the ground state—that is, to choose the ground state as our zero of energy. We can do that by adding the energy  $A/2$  to each term in the Hamiltonian. That just changes the “ $\frac{1}{2}$ ” in Eq. (15.4) to “1.” Our new Hamiltonian is

$$\hat{H} = -A \sum_n (\hat{P}_{n, n+1} - 1). \quad (15.5)$$

With this Hamiltonian the energy of the lowest state is zero; the spin exchange operator is equivalent to multiplying by unity (for the ground state) which is cancelled by the “1” in each term.

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† The ground state here is really “degenerate”; there are other states with the same energy—for example, all spins down, or all in any other direction. The slightest external field in the  $z$ -direction will give a different energy to all these states, and the one we have chosen will be the true ground state.

For describing states other than the ground state we will need a suitable set of base states. One convenient approach is to group the states according to whether one electron has spin down, or two electrons have spin down, and so on. There are, of course, many states with one spin down. The down spin could be at atom "4," or at atom "5," or at atom "6," . . . We can, in fact, choose just such states for our base states. We could write them this way:  $|4\rangle$ ,  $|5\rangle$ ,  $|6\rangle$ , . . . It will, however, be more convenient later if we label the "odd atom"—the one with the down-spinning electron—by its coordinate  $x$ . That is, we'll define the state  $|x_5\rangle$  to be one with all the electrons spinning up except for the one on the atom at  $x_5$ , which has a down-spinning electron (see Fig. 15-1). In general,  $|x_n\rangle$  is the state with one down spin that is located at the coordinate  $x_n$  of the  $n$ th atom.

What is the action of the Hamiltonian (15.5) on the state  $|x_5\rangle$ ? One term of the Hamiltonian is say  $-A(\hat{P}_{7,8} - 1)$ . The operator  $\hat{P}_{7,8}$  exchanges the two spins of the adjacent atoms 7, 8. But in the state  $|x_5\rangle$  these are both up, and nothing happens;  $\hat{P}_{7,8}$  is equivalent to multiplying by 1:

$$\hat{P}_{7,8} |x_5\rangle = |x_5\rangle.$$

It follows that

$$(\hat{P}_{7,8} - 1) |x_5\rangle = 0.$$

Thus all the terms of the Hamiltonian give zero—except those involving atom 5, of course. On the state  $|x_5\rangle$ , the operation  $\hat{P}_{4,5}$  exchanges the spin of atom 4 (up) and atom 5 (down). The result is the state with all spins up except the atom at 4. That is

$$\hat{P}_{4,5} |x_5\rangle = |x_4\rangle.$$

In the same way

$$\hat{P}_{5,6} |x_5\rangle = |x_6\rangle.$$

Hence, the only terms of the Hamiltonian which survive are  $-A(\hat{P}_{4,5} - 1)$  and  $-A(\hat{P}_{5,6} - 1)$ . Acting on  $|x_5\rangle$  they produce  $-A|x_4\rangle + A|x_5\rangle$  and  $-A|x_6\rangle + A|x_5\rangle$ , respectively. The result is

$$\hat{H} |x_5\rangle = -A \sum_n (\hat{P}_{n,n+1} - 1) |x_5\rangle = -A\{|x_6\rangle + |x_4\rangle - 2|x_5\rangle\}. \quad (15.6)$$

When the Hamiltonian acts on state  $|x_5\rangle$  it gives rise to some amplitude to be in states  $|x_4\rangle$  and  $|x_6\rangle$ . That just means that there is a certain amplitude to have the down spin jump over to the next atom. So because of the interaction between the spins, if we begin with one spin down, then there is some probability that at a later time another one will be down instead. Operating on the general state  $|x_n\rangle$ , the Hamiltonian gives

$$\hat{H} |x_n\rangle = -A\{|x_{n+1}\rangle + |x_{n-1}\rangle - 2|x_n\rangle\}. \quad (15.7)$$

Notice particularly that if we take a complete set of states with only one spin down, they will only be mixed among themselves. The Hamiltonian will never mix these states with others that have more spins down. So long as you only exchange spins you never change the total number of down spins.

It will be convenient to use the matrix notation for the Hamiltonian, say  $H_{n,m} \equiv \langle x_n | \hat{H} | x_m \rangle$ ; Eq. (15.7) is equivalent to

$$\begin{aligned} H_{n,n} &= A; \\ H_{n,n+1} &= H_{n,n-1} = -A; \\ H_{n,m} &= 0, \quad \text{for } |n - m| > 1. \end{aligned} \quad (15.8)$$

Now what are the energy levels for states with one spin down? As usual we let  $C_n$  be the amplitude that some state  $|\psi\rangle$  is in the state  $|x_n\rangle$ . If  $|\psi\rangle$  is to be a definite energy state, all the  $C_n$ 's must vary with time in the same way, namely,

$$C_n = a_n e^{-iEt/\hbar}. \quad (15.9)$$

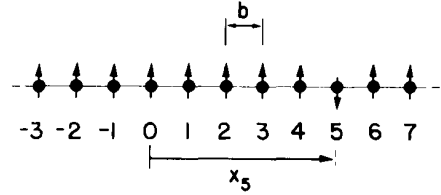


Fig. 15-1. The base state  $|x_5\rangle$  of a linear array of spins. All the spins are up except the one at  $x_5$ , which is down.

We can put this trial solution into our usual Hamiltonian equation

$$i\hbar \frac{dC_n}{dt} = \sum_m H_{nm} C_m, \quad (15.10)$$

using Eq (15.8) for the matrix elements. Of course we get an infinite number of equations, but they can all be written as

$$Ea_n = 2Aa_n - Aa_{n-1} - Aa_{n+1} \quad (15.11)$$

We have again exactly the same problem we worked out in Chapter 13, except that where we had  $E_0$  we now have  $2A$ . The solutions correspond to amplitudes  $C_n$  (the down-spin amplitude) which propagate along the lattice with a propagation constant  $k$  and an energy

$$E = 2A(1 - \cos kb), \quad (15.12)$$

where  $b$  is the lattice constant.

The definite energy solutions correspond to “waves” of down spin—called “spin waves.” And for each wavelength there is a corresponding energy. For large wavelengths (small  $k$ ) this energy varies as

$$E = Ab^2k^2. \quad (15.13)$$

Just as before, we can consider a localized wave packet (containing, however, only long wavelengths) which corresponds to a spin-down electron in one part of the lattice. This down spin will behave like a “particle.” Because its energy is related to  $k$  by (15.13) the “particle” will have an effective mass:

$$m_{\text{eff}} = \frac{\hbar^2}{2Ab^2}. \quad (15.14)$$

These “particles” are sometimes called “magnons.”

### 15-2 Two spin waves

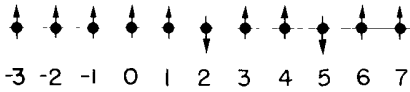


Fig. 15-2. A state with two down spins.

Now we would like to discuss what happens if there are *two* down spins. Again we pick a set of base states. We'll choose states in which there are down spins at two atomic locations, such as the state shown in Fig. 15-2. We can label such a state by the  $x$ -coordinates of the two sites with down spins. The one shown can be called  $|x_2, x_5\rangle$ . In general the base states are  $|x_n, x_m\rangle$ —a doubly infinite set! In this system of description, the state  $|x_4, x_9\rangle$  and the state  $|x_9, x_4\rangle$  are exactly the same state, because each simply says that there is a down spin at 4 and one at 9; there is no meaning to the order. Furthermore, the state  $|x_4, x_4\rangle$  has no meaning, there isn't such a thing. We can describe any state  $|\psi\rangle$  by giving the amplitudes to be in each of the base states. Thus  $C_{m,n} = \langle x_m, x_n | \psi \rangle$  now means the amplitude for a system in the state  $|\psi\rangle$  to be in a state in which both the  $m$ th and  $n$ th atoms have a down spin. The complications which now arise are not complications of ideas—they are merely complexities in bookkeeping. (One of the complexities of quantum mechanics is just the bookkeeping. With more and more down spins, the notation becomes more and more elaborate with lots of indices and the equations always look very horrifying, but the ideas are not necessarily more complicated than in the simplest case.)

The equations of motion of the spin system are the differential equations for the  $C_{n,m}$ . They are

$$i\hbar \frac{dC_{n,m}}{dt} = \sum_{i,j} (H_{nm,ij}) C_{ij}. \quad (15.15)$$

Suppose we want to find the stationary states. As usual, the derivatives with respect to time become  $E$  times the amplitudes and the  $C_{m,n}$  can be replaced by the

coefficients  $a_{m,n}$ . Next we have to work out carefully the effect of  $H$  on a state with spins  $m$  and  $n$  down. It is not hard to figure out. Suppose for a moment that  $m$  and  $n$  are far enough apart so that we don't have to worry about the obvious trouble. The operation of exchange at the location  $x_n$  will move the down spin either to the  $(n + 1)$  or  $(n - 1)$  atom, and so there's an amplitude that the present state has come from the state  $|x_m, x_{n+1}\rangle$  and also an amplitude that it has come from the state  $|x_m, x_{n-1}\rangle$ . Or it may have been the other spin that moved; so there's a certain amplitude that  $C_{m,n}$  is fed from  $C_{m+1,n}$  or from  $C_{m-1,n}$ . These effects should all be equal. The final result for the Hamiltonian equation on  $C_{m,n}$  is

$$Ea_{m,n} = -A(a_{m+1,n} + a_{m-1,n} + a_{m,n+1} + a_{m,n-1}) + 4Aa_{m,n}. \quad (15.16)$$

This equation is correct except in two situations. If  $m = n$  there is no equation at all, and if  $m = n \pm 1$ , then two of the terms in Eq. (15.16) should be missing. *We are going to disregard these exceptions.* We simply ignore the fact that some few of these equations are slightly altered. After all, the crystal is supposed to be infinite, and we have an infinite number of terms; neglecting a few might not matter much. So for a first rough approximation let's forget about the altered equations. In other words, we assume that Eq. (15.16) is true for all  $m$  and  $n$ , even for  $m$  and  $n$  next to each other. *This is the essential part of our approximation.*

Then the solution is not hard to find. We get immediately

$$C_{m,n} = a_{m,n}e^{-iEt/\hbar}, \quad (15.17)$$

with

$$a_{m,n} = (\text{const.}) e^{ik_1x_m}e^{ik_2x_n}, \quad (15.18)$$

where

$$E = 4A - 2A \cos k_1b - 2A \cos k_2b. \quad (15.19)$$

Think for a moment what would happen if we had two *independent, single* spin waves (as in the previous section) corresponding to  $k = k_1$  and  $k = k_2$ ; they would have energies, from Eq. (15.12), of

$$\epsilon_1 = (2A - 2A \cos k_1b)$$

and

$$\epsilon_2 = (2A - 2A \cos k_2b).$$

Notice that the energy  $E$  in Eq. (15.19) is just their sum,

$$E = \epsilon(k_1) + \epsilon(k_2). \quad (15.20)$$

In other words we can think of our solution in this way. There are two particles—that is, two spin waves. One of them has a momentum described by  $k_1$ , the other by  $k_2$ , and the energy of the system is the sum of the energies of the two objects. The two particles act completely independently. That's all there is to it.

Of course we have made some approximations, but we do not wish to discuss the precision of our answer at this point. However, you might guess that in a reasonable size crystal with billions of atoms—and, therefore, billions of terms in the Hamiltonian—leaving out a few terms wouldn't make much of an error. If we had so many down spins that there was an appreciable density, then we would certainly have to worry about the corrections.

[Interestingly enough, an exact solution can be written down if there are just the *two* down spins. The result is not particularly important. But it is interesting that the equations can be solved exactly for this case. The solution is:

$$a_{m,n} = \exp^{[ik_c(x_m+x_n)]} \sin k |x_m - x_n|, \quad (15.21)$$

with the energy

$$E = 4A - 2A \cos k_1b - 2A \cos k_2b,$$

and with the wave numbers  $k_c$  and  $k$  related to  $k_1$  and  $k_2$  by

$$k_1 = k_c - k, \quad k_2 = k_c + k. \quad (15.22)$$

This solution includes the “interaction” of the two spins. It describes the fact that when the spins come together there is a certain chance of scattering. The spins act very much like particles with an interaction. But the detailed theory of their scattering goes beyond what we want to talk about here.]

### 15-3 Independent particles

In the last section we wrote down a Hamiltonian, Eq. (15.15), for a two-particle system. Then using an approximation which is equivalent to neglecting any “interaction” of the two particles, we found the stationary states described by Eqs. (15.17) and (15.18). This state is just the product of two single-particle states. The solution we have given for  $a_{m,n}$  in Eq. (15.18) is, however, really not satisfactory. We have very carefully pointed out earlier that the state  $|x_9, x_4\rangle$  is *not* a different state from  $|x_4, x_9\rangle$ —the *order* of  $x_m$  and  $x_n$  has no significance. In general, the algebraic expression for the amplitude  $C_{m,n}$  must be unchanged if we interchange the values of  $x_m$  and  $x_n$ , since that doesn’t change the state. Either way, it should represent the amplitude to find a down spin at  $x_m$  and a down spin at  $x_n$ . But notice that (15.18) is *not* symmetric in  $x_m$  and  $x_n$ —since  $k_1$  and  $k_2$  can in general be different.

The trouble is that we have not forced our solution of Eq. (15.15) to satisfy this additional condition. Fortunately it is easy to fix things up. Notice first that a solution of the Hamiltonian equation just as good as (15.18) is

$$a_{m,n} = K e^{ik_2 x_m} e^{ik_1 x_n}. \quad (15.23)$$

It even has the same energy we got for (15.18). Any linear combination of (15.15) and (15.23) is also a good solution, and has an energy still given by Eq. (15.19). The solution we should have chosen—because of our symmetry requirement—is just the sum of (15.15) and (15.23):

$$a_{m,n} = K [e^{ik_1 x_m} e^{ik_2 x_n} + e^{ik_2 x_m} e^{ik_1 x_n}]. \quad (15.24)$$

Now, given any  $k_1$  and  $k_2$  the amplitude  $C_{m,n}$  is independent of which way we put  $x_m$  and  $x_n$ —if we should happen to define  $x_m$  and  $x_n$  reversed we get the same amplitude. Our interpretation of Eq. (15.24) in terms of “magnons” must also be different. We can no longer say that the equation represents *one* particle with wave number  $k_1$  and a *second* particle with wave number  $k_2$ . The amplitude (15.24) represents *one* state with two particles (magnons). The *state* is characterized by the two wave numbers  $k_1$  and  $k_2$ . Our solution looks like a compound state of one particle with the momentum  $p_1 = \hbar/k_1$  and another particle with the momentum  $p_2 = \hbar/k_2$ , but in our state we can’t say which particle is which.

By now, this discussion should remind you of Chapter 4 and our story of identical particles. We have just been showing that the particles of the spin waves—the magnons—behave like identical Bose particles. All amplitudes must be symmetric in the coordinates of the two particles—which is the same as saying that if we “interchange the two particles,” we get back the same amplitude and with the same sign. But, you may be thinking, why did we choose to *add* the two terms in making Eq. (15.24). Why not subtract? With a minus sign, interchanging  $x_m$  and  $x_n$  would just change the sign of  $a_{m,n}$  which doesn’t matter. But interchanging  $x_m$  and  $x_n$  *doesn’t change anything*—all the electrons of the crystal are exactly where they were before, so there is no reason for even the sign of the amplitude to change. The magnons will behave like Bose particles.†

† In general, the quasi particles of the kind we are discussing may act like either Bose particles or Fermi particles, and as for free particles, the particles with integral spin are bosons and those with half-integral spins are fermions. The “magnon” stands for a spin-up electron turned over. The *change* in spin is *one*. The magnon has an integral spin, and is a boson.

The main points of this discussion have been twofold: First, to show you something about spin waves, and, second, to demonstrate a state whose amplitude is a *product* of two amplitudes, and whose energy is the *sum* of the energies corresponding to the two amplitudes. For *independent particles* the amplitude is the product and the energy is the sum. You can easily see why the energy is the sum. The energy is the coefficient of  $t$  in an imaginary exponential—it is proportional to the frequency. If two objects are doing something, one of them with the amplitude  $e^{-iE_1 t/\hbar}$  and the other with the amplitude  $e^{-iE_2 t/\hbar}$ , and if the amplitude for the two things to happen together is the product of the amplitudes for each, then there is a single frequency in the product which is the sum of the two frequencies. The energy corresponding to the amplitude product is the sum of the two energies.

We have gone through a rather long-winded argument to tell you a simple thing. When you don't take into account any interaction between particles, you can think of each particle independently. They can individually exist in the various different states they would have alone, and they will each contribute the energy they would have had if they were alone. However, you must remember that if they are identical particles, they may behave either as Bose or as Fermi particles depending upon the problem. Two extra electrons added to a crystal, for instance, would have to behave like Fermi particles. When the positions of two electrons are interchanged, the amplitude must reverse sign. In the equation corresponding to Eq. (15.24) there would have to be a minus sign between the two terms on the right. As a consequence, two Fermi particles cannot be in exactly the same condition—with equal spins and equal  $k$ 's. The amplitude for this state is zero.

#### 15-4 The benzene molecule

Although quantum mechanics provides the basic laws that determine the structures of molecules, these laws can be applied exactly only to the most simple compounds. The chemists have, therefore, worked out various approximate methods for calculating some of the properties of complicated molecules. We would now like to show you how the independent particle approximation is used by the organic chemists. We begin with the benzene molecule.

We discussed the benzene molecule from another point of view in Chapter 10. There we took an approximate picture of the molecule as a two-state system, with the two base states shown in Fig. 15-3. There is a ring of six carbons with a hydrogen bonded to the carbon at each location. With the conventional picture of valence bonds it is necessary to assume double bonds between half of the carbon atoms, and in the lowest energy condition there are the two possibilities shown in the figure. There are also other, higher-energy states. When we discussed benzene in Chapter 10, we just took the two states and forgot all the rest. We found that the ground-state energy of the molecule was not the energy of one of the states in the figure, but was lower than that by an amount proportional to the amplitude to flip from one of these states to the other.

Now we're going to look at the same molecule from a completely different point of view—using a different kind of approximation. The two points of view will give us different answers, but if we improve either approximation it should lead to the truth, a valid description of benzene. However, if we don't bother to improve them, which is of course the usual situation, then you should not be surprised if the two descriptions do not agree exactly. We shall at least show that also with the new point-of-view the lowest energy of the benzene molecule is lower than either of the three-bond structures of Fig. 15-3.

Now we want to use the following picture. Suppose we imagine the six carbon atoms of a benzene molecule connected only by single bonds as in Fig. 15-4. We have removed six electrons—since a bond stands for a pair of electrons—so we have a six-times ionized benzene molecule. Now we will consider what happens when we put back the six electrons one at a time, imagining that each one can run freely around the ring. We assume also that all the bonds shown in Fig. 15-4 are satisfied, and don't need to be considered further.

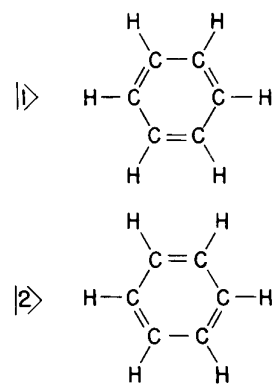


Fig. 15-3. The two base states for the benzene molecule used in Chapter 10.

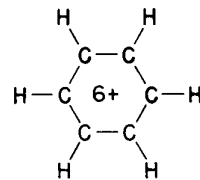


Fig. 15-4. A benzene ring with six electrons removed.

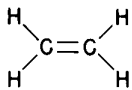


Fig. 15-5. The ethylene molecule.

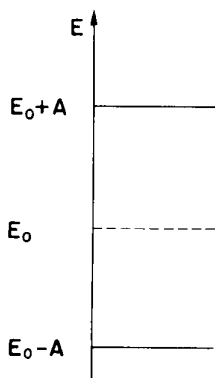


Fig. 15-6. The possible energy levels for the "extra" electrons in the ethylene molecule.

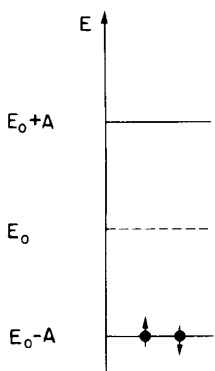


Fig. 15-7. In the extra bond of the ethylene molecule two electrons (one spin up, one spin down) can occupy the lowest energy level.

What happens when we put one electron back into the molecular ion? It might, of course, be located in any one of the six positions around the ring—corresponding to six base states. It would also have a certain amplitude, say  $A$ , to go from one position to the next. If we analyze the stationary states, there would be certain possible energy levels. That's only for one electron.

Next put a second electron in. And now we make the most ridiculous approximation that you can think of—that *what one electron does is not affected by what the other is doing*. Of course they really will interact; they repel each other through the Coulomb force, and furthermore when they are both at the same site, they must have considerably different energy than twice the energy for one being there. Certainly the approximation of independent particles is not legitimate when there are only six sites—particularly when we want to put in *six* electrons. Nevertheless the organic chemists have been able to learn a lot by making this kind of an approximation.

Before we work out the benzene molecule in detail, let's consider a simpler example—the ethylene molecule which contains just two carbon atoms with two hydrogen atoms on either side as shown in Fig. 15-5. This molecule has one "extra" bond involving two electrons between the two carbon atoms. Now remove one of these electrons; what do we have? We can look at it as a two-state system—the remaining electron can be at one carbon or the other. We can analyze it as a two-state system. The possible energies for the single electron are either  $(E_0 - A)$  or  $(E_0 + A)$ , as shown in Fig. 15-6.

Now add the second electron. Good, if we have two electrons, we can put the first one in the lower state and the second one in the upper. Not quite; we forgot something. Each one of the states is really double. When we say there's a possible state with the energy  $(E_0 - A)$ , there are really two. Two electrons can go into the same state if one has its spin up and the other, its spin down. (No more can be put in because of the exclusion principle.) So there really are two possible states of energy  $(E_0 - A)$ . We can draw a diagram, as in Fig. 15-7, which indicates both the energy levels and their occupancy. In the condition of lowest energy both electrons will be in the lowest state with their spins opposite. The energy of the extra bond in the ethylene molecule therefore is  $2(E_0 - A)$  if we neglect the interaction between the two electrons.

Let's go back to the benzene. Each of the two states of Fig. 15-3 has three double bonds. Each of these is just like the bond in ethylene, and contributes  $2(E_0 - A)$  to the energy if  $E_0$  is now the energy to put an electron on a site in benzene and  $A$  is the amplitude to flip to the next site. So the energy should be roughly  $6(E_0 - A)$ . But when we studied benzene before, we got that the energy was lower than the energy of the structure with three extra bonds. Let's see if the energy for benzene comes out lower than three bonds from our new point of view.

We start with the six-times ionized benzene ring and add one electron. Now we have a six-state system. We haven't solved such a system yet, but we know what to do. We can write six equations in the six amplitudes, and so on. But let's save some work—by noticing that we've already solved the problem, when we worked out the problem of an electron on an infinite line of atoms. Of course, the benzene is not an infinite line, it has 6 atomic sites in a circle. But imagine that we open out the circle to a line, and number the atoms along the line from 1 to 6. In an infinite line the next location would be 7, but if we insist that this location be identical with number 1 and so on, the situation will be just like the benzene ring. In other words we can take the solution for an infinite line *with an added requirement* that the solution must be periodic with a cycle six atoms long. From Chapter 13 the electron on a line has states of definite energy when the amplitude at each site is  $e^{ikx_n} = e^{ikbn}$ . For each  $k$  the energy is

$$E = E_0 - 2A \cos kb. \quad (15.25)$$

We want to use now only those solutions which repeat every 6 atoms. Let's do first the general case for a ring of  $N$  atoms. If the solution is to have a period



of  $N$  atomic spacing,  $e^{ikbN}$  must be unity; or  $kbN$  must be a multiple of  $2\pi$ . Taking  $s$  to represent any integer, our condition is that

$$kbN = 2\pi s. \quad (15.26)$$

We have seen before that there is no meaning to taking  $k$ 's outside the range  $\pm\pi/b$ . This means that we get all possible states by taking values of  $s$  in the range  $\pm N/2$ .

We find then that for an  $N$ -atom ring there are  $N$  definite energy states† and they have wave numbers  $k_s$  given by

$$k_s = \frac{2\pi}{Nb} s. \quad (15.27)$$

Each state has the energy (15.25). We have a line spectrum of possible energy levels. The spectrum for benzene ( $N = 6$ ) is shown in Fig. 15-8(b). (The numbers in parentheses indicate the number of *different* states with the same energy.)

There's a nice way to visualize the six energy levels, as we have shown in part (a) of the figure. Imagine a circle centered on a level with  $E_0$ , and with a radius of  $2A$ . If we start at the bottom and mark off six equal arcs (at angles from the bottom point of  $k_s b = 2\pi s/N$ , or  $2\pi s/6$  for benzene), then the vertical heights of the points on the circle are the solutions of Eq. (15.25). The six points represent the six possible states. The lowest energy level is at  $(E_0 - 2A)$ ; there are two states with the same energy ( $E_0 - A$ ), and so on.‡ These are possible states for one electron. If we have more than one electron, two—with opposite spins—can go into each state.

For the benzene molecule we have to put in six electrons. For the ground state they will go into the lowest possible energy states—two at  $s = 0$ , two at  $s = +1$ , and two at  $s = -1$ . According to the independent particle approximation the energy of the ground state is

$$\begin{aligned} E_{\text{ground}} &= 2(E_0 - 2A) + 4(E_0 - A) \\ &= 6E_0 - 8A. \end{aligned} \quad (15.28)$$

The energy is indeed less than that of three separate double bonds—by the amount  $2A$ .

By comparing the energy of benzene to the energy of ethylene it is possible to determine  $A$ . It comes out to be 0.8 electron volt, or, in the units the chemists like, 18 kilocalories per mole.

We can use this description to calculate or understand other properties of benzene. For example, using Fig. 15-8 we can discuss the excitation of benzene by light. What would happen if we tried to excite one of the electrons? It could move up to one of the empty higher states. The lowest energy of excitation would be a transition from the highest filled level to the lowest empty level. That takes the energy  $2A$ . Benzene will absorb light of frequency  $\nu$  when  $h\nu = 2A$ . There will also be absorption of photons with the energies  $3A$  and  $4A$ . Needless to say, the absorption spectrum of benzene has been measured and the pattern of spectral lines is more or less correct except that the lowest transition occurs in the ultraviolet; and to fit the data one would have to choose a value of  $A$  between 1.4 and 2.4 electron volts. That is, the numerical value of  $A$  is two or three times larger than is predicted from the chemical binding energy.

What the chemist does in situations like this is to analyze many molecules of a similar kind and get some empirical rules. He learns, for example: For calculating binding energy use such and such a value of  $A$ , but for getting the absorption spectrum approximately right use another value of  $A$ . You may feel

† You might think that for  $N$  an even number there are  $N + 1$  states. That is not so because  $s = \pm N/2$  give the same state.

‡ When there are two states (which will have different amplitude distributions) with the same energy, we say that the two states are "degenerate." Notice that *four* electrons can have the energy  $E_0 - A$ .

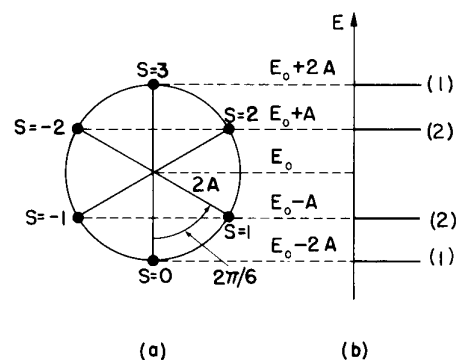


Fig. 15-8. The energy levels in a ring with six electron locations (for example, a benzene ring).

that this sounds a little absurd. It is not very satisfactory from the point of view of a physicist who is trying to understand nature from first principles. But the problem of the chemist is different. He must try to guess ahead of time what is going to happen with molecules that haven't been made yet, or which aren't understood completely. What he needs is a series of empirical rules; it doesn't make much difference where they come from. So he uses the theory in quite a different way than the physicist. He takes equations that have some shadow of the truth in them, but then he must alter the constants in them—making empirical corrections.

In the case of benzene, the principal reason for the inconsistency is our assumption that the electrons are independent—the theory we started with is really not legitimate. Nevertheless, it has some shadow of the truth because its results seem to be going in the right direction. With such equations plus some empirical rules—including various exceptions—the organic chemist makes his way through the morass of complicated things he chooses to study. (Don't forget that the reason a physicist can really calculate from first principles is that he chooses only simple problems. He never solves a problem with 42 or even 6 electrons in it. So far, he has been able to calculate reasonably accurately only the hydrogen atom and the helium atom.)

### 15-5 More organic chemistry

Let's see how the same ideas can be used to study other molecules. Consider a molecule like butadiene (1, 3)—it is drawn in Fig. 15-9 according to the usual valence bond picture.

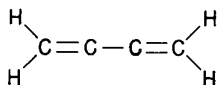


Fig. 15-9. The valence bond representation of the molecule butadiene (1, 3).

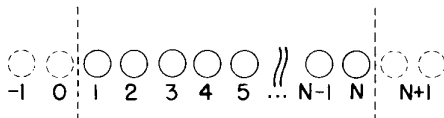


Fig. 15-10. A line of  $N$  molecules.

We can play the same game with the extra four electrons corresponding to the two double bonds. If we remove four electrons, we have four carbon atoms in a line. You already know how to solve a line. You say, "Oh no, I only know how to solve an *infinite* line." But the solutions for the infinite line also include the ones for a finite line. Watch. Let  $N$  be the number of atoms on the line and number them from 1 to  $N$  as shown in Fig. 15-10. In writing the equations for the amplitude at position 1 you would not have a term feeding from position 0. Similarly, the equation for position  $N$  would differ from the one that we used for an infinite line because there would be nothing feeding from position  $N + 1$ . But suppose that we can obtain a solution for the infinite line which has the following property: the amplitude to be at atom 0 is zero and the amplitude to be at atom  $(N + 1)$  is also zero. Then the set of equations for all the locations from 1 to  $N$  on the finite line are also satisfied. You might think no such solution exists for the infinite line because our solutions all looked like  $e^{ikx_n}$  which has the same absolute value of the amplitude everywhere. But you will remember that the energy depends only on the absolute value of  $k$ , so that another solution, which is equally legitimate for the same energy, would be  $e^{-ikx_n}$ . And the same is true of any superposition of these two solutions. By subtracting them we can get the solution  $\sin kx_n$ , which satisfies the requirement that the amplitude be zero at  $x = 0$ . It still corresponds to the energy  $(E_0 - 2A \cos kb)$ . Now by a suitable choice for the value of  $k$  we can also make the amplitude zero at  $x_{N+1}$ . This requires that  $(N + 1)kb$  be a multiple of  $\pi$ , or that

$$kb = \frac{\pi}{(N + 1)} s, \quad (15.29)$$

where  $s$  is an integer from 1 to  $N$ . (We take only positive  $k$ 's because each solution contains  $+k$  and  $-k$ ; changing the sign of  $k$  gives the same state all over again.) For the butadiene molecule,  $N = 4$ , so there are four states with

$$kb = \pi/5, \quad 2\pi/5, \quad 3\pi/5, \quad \text{and} \quad 4\pi/5. \quad (15.30)$$

We can represent the energy levels using a circle diagram similar to the one for benzene. This time we use a semicircle divided into five equal parts as shown in Fig. 15-11. The point at the bottom corresponds to  $s = 0$ , which gives no

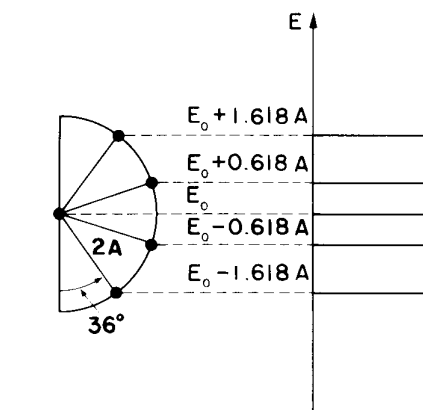


Fig. 15-11. The energy levels of butadiene.

state at all. The same is true of the point at the top, which corresponds to  $s = N + 1$ . The remaining 4 points give us four allowed energies. There are four stationary states, which is what we expect having started with four base states. In the circle diagram, the angular intervals are  $\pi/5$  or 36 degrees. The lowest energy comes out ( $E_0 - 1.618A$ ). (Ah, what wonders mathematics holds; the golden mean of the Greeks† gives us the lowest energy state of the butadiene molecule according to this theory!)

Now we can calculate the energy of the butadiene molecule when we put in four electrons. With four electrons, we fill up the lowest two levels, each with two electrons of opposite spin. The total energy is

$$E = 2(E_0 - 1.618A) + 2(E_0 - 0.618A) = 4(E_0 - A) - 0.477A. \quad (15.31)$$

This result seems reasonable. The energy is a little lower than for two simple double bonds, but the binding is not so strong as in benzene. Anyway this is the way the chemist analyzes some organic molecules.

The chemist can use not only the energies but the probability amplitudes as well. Knowing the amplitudes for each state, and which states are occupied, he can tell the probability of finding an electron anywhere in the molecule. Those places where the electrons are more likely to be are apt to be reactive in chemical substitutions which require that an electron be shared with some other group of atoms. The other sites are more likely to be reactive in those substitutions which have a tendency to yield an extra electron to the system.

The same ideas we have been using can give us some understanding of a molecule even as complicated as chlorophyll, one version of which is shown in Fig. 15-12. Notice that the double and single bonds we have drawn with heavy lines form a long closed ring with twenty intervals. The extra electrons of the double bonds can run around this ring. Using the independent particle method we can get a whole set of energy levels. There are strong absorption lines from transitions between these levels which lie in the visible part of the spectrum, and give this molecule its strong color. Similar complicated molecules such as the xanthophylls, which make leaves turn red, can be studied in the same way.

There is one more idea which emerges from the application of this kind of theory in organic chemistry. It is probably the most successful or, at least in a certain sense, the most accurate. This idea has to do with the question: In what situations does one get a particularly strong chemical binding? The answer is very interesting. Take the example, first, of benzene, and imagine the sequence of events that occurs as we start with the six-times ionized molecule and add more and more electrons. We would then be thinking of various benzene ions—negative or positive. Suppose we plot the energy of the ion (or neutral molecule) as a function of the number of electrons. If we take  $E_0 = 0$  (since we don't know what it is), we get the curve shown in Fig. 15-13. For the first two electrons the slope of the function is a straight line. For each successive group the slope increases, and there is a discontinuity in slope between the groups of electrons. The slope changes when one has just finished filling a set of levels which all have the same energy and must move up to the next higher set of levels for the next electron.

The actual energy of the benzene ion is really quite different from the curve of Fig. 15-13 because of the interactions of the electrons and because of electrostatic energies we have been neglecting. These corrections will, however, vary with  $n$  in a rather smooth way. Even if we were to make all these corrections, the resulting energy curve would still have kinks at those values of  $n$  which just fill up a particular energy level.

Now consider a very smooth curve that fits the points on the average like the one drawn in Fig. 15-14. We can say that the points *above* this curve have "higher-than-normal" energies, and the points *below* the curve have "lower-than-normal"

† The ratio of the sides of a rectangle which can be divided into a square and a similar rectangle.

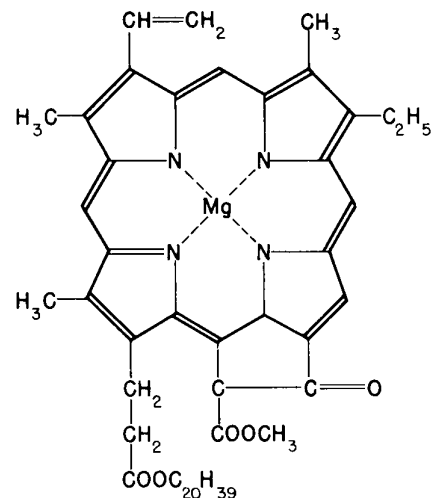


Fig. 15-12. A chlorophyll molecule.

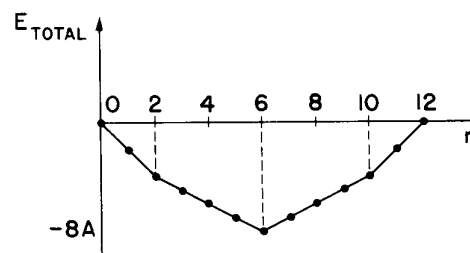


Fig. 15-13. The sum of all the electron energies when the lowest states in Fig. 15-8 are occupied by  $n$  electrons if we take that  $E_0 = 0$ .

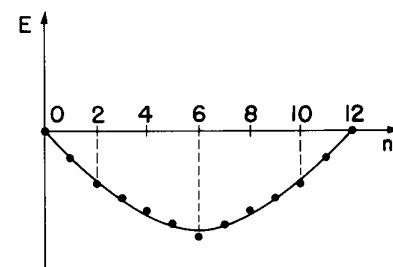


Fig. 15-14. The points of Fig. 15-12 with a smooth curve. Molecules with  $n = 2, 6, 10$  are more stable than the others.

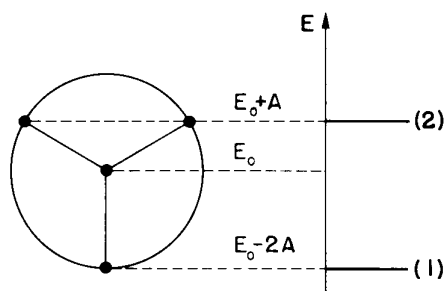


Fig. 15-15. Energy diagram for a ring of three.

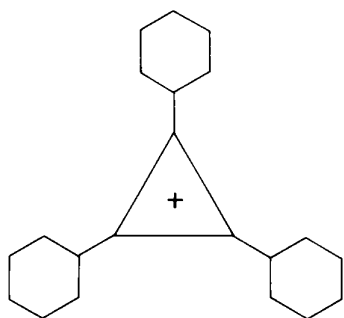


Fig. 15-16. The triphenyl cyclopropanyl cation.

energies. We would, in general, expect that those configurations with a lower-than-normal energy would have an above average stability—chemically speaking. Notice that the configurations farther below the curve always occur at the end of one of the straight line segments—namely when there are enough electrons to fill up an “energy shell,” as it is called. This is the very accurate prediction of the theory. Molecules—or ions—are particularly stable (in comparison with other similar configurations) when the available electrons just fill up an energy shell.

This theory has explained and predicted some very peculiar chemical facts. To take a very simple example, consider a ring of three. It’s almost unbelievable that the chemist can make a ring of three and have it stable, but it has been done. The energy circle for three electrons is shown in Fig. 15-15. Now if you put two electrons in the lower state, you have only two of the three electrons that you require. The third electron must be put in at a much higher level. By our argument this molecule should not be particularly stable, whereas the two-electron structure should be stable. It does turn out, in fact, that the neutral molecule of triphenyl cyclopropanyl is very hard to make, but that the positive ion shown in Fig. 15-16 is relatively easy to make. The ring of three is never really easy because there is always a large stress when the bonds in an organic molecule make an equilateral triangle. To make a stable compound at all, the structure must be stabilized in some way. Anyway if you add three benzene rings on the corners, the positive ion can be made. (The reason for this requirement of added benzene rings is not really understood.)

In a similar way the five-sided ring can also be analyzed. If you draw the energy diagram, you can see in a qualitative way that the six-electron structure should be an especially stable structure, so that such a molecule should be most stable as a negative ion. Now the five-ring is well known and easy to make and always acts as a negative ion. Similarly, you can easily verify that a ring of 4 or 8 is not very interesting, but that a ring of 14 or 10—like a ring of 6—should be especially stable as a neutral object.

### 15-6 Other uses of the approximation

There are two other similar situations which we will describe only briefly. In considering the structure of an atom, we can consider that the electrons fill successive shells. The Schrödinger theory of electron motion can be worked out easily only for a *single* electron moving in a “central” field—one which varies only with the distance from a point. How can we then understand what goes on in an atom which has 22 electrons?! One way is to use a kind of independent particle approximation. First you calculate what happens with one electron. You get a number of energy levels. You put an electron into the lowest energy state. You can, for a rough model, continue to ignore the electron interactions and go on filling successive shells, but there is a way to get better answers by taking into account—in an approximate way at least—the effect of the electric charge carried by the electron. Each time you add an electron you compute its amplitude to be at various places, and then use this amplitude to estimate a kind of spherically symmetric charge distribution. You use the field of this distribution—together with the field of the positive nucleus and all the previous electrons—to calculate the states available for the next electron. In this way you can get reasonably correct estimates for the energies for the neutral atom and for various ionized states. You find that there are energy shells, just as we saw for the electrons in a ring molecule. With a partially filled shell, the atom will show a preference for taking on one or more extra electrons, or for losing some electrons so as to get into the most stable state of a filled shell.

This theory explains the machinery behind the fundamental chemical properties which show up in the periodic table of the elements. The inert gases are those elements in which a shell has just been completed, and it is especially difficult to make them react. (Some of them do react of course—with fluorine and oxygen, for example; but such compounds are very weakly bound; the so-called inert gases are nearly inert.) An atom which has one electron more or one electron less

than an inert gas will easily lose or gain an electron to get into the especially stable (low-energy) condition which comes from having a completely filled shell—they are the very active chemical elements of valence  $+1$  or  $-1$ .

The other situation is found in nuclear physics. In atomic nuclei the protons and neutrons interact with each other quite strongly. Even so, the independent particle model can again be used to analyze nuclear structure. It was first discovered experimentally that nuclei were especially stable if they contained certain particular numbers of neutrons—namely 2, 8, 20, 28, 50, 82. Nuclei containing protons in these numbers are also especially stable. Since there was initially no explanation for these numbers they were called the “magic numbers” of nuclear physics. It is well known that neutrons and protons interact strongly with each other; people were, therefore, quite surprised when it was discovered that an independent particle model predicted a shell structure which came out with the first few magic numbers. The model assumed that each nucleon (proton or neutron) moved in a central potential which was created by the average effects of all the other nucleons. This model failed, however, to give the correct values for the higher magic numbers. Then it was discovered by Maria Mayer, and independently by Jensen and his collaborators, that by taking the independent particle model and adding only a correction for what is called the “spin-orbit interaction,” one could make an improved model which gave all of the magic numbers. (The spin-orbit interaction causes the energy of a nucleon to be lower if its spin has the same direction as its orbital angular momentum from motion in the nucleus.) The theory gives even more—its picture of the so-called “shell structure” of the nuclei enables us to predict certain characteristics of nuclei and of nuclear reactions.

The independent particle approximation has been found useful in a wide range of subjects—from solid-state physics, to chemistry, to biology, to nuclear physics. It is often only a crude approximation, but is able to give an understanding of why there are especially stable conditions—in shells. Since it omits all of the complexity of the interactions between the individual particles, we should not be surprised that it often fails completely to give correctly many important details.