

Introductory Remarks on Solid-State Physics

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The purpose of these introductory lectures will be to give a brief review of some of the typical situations encountered in solid-state theory and to identify those which are difficult to solve and therefore call for the techniques of many-body theory which will form the subject of the later discussions.

By far the simplest case is that of the electronic ground state of a nonconducting solid. We may picture this as an assembly of atoms, molecules, or ions with closed-shell configurations, such as a solid noble gas, or an ionic crystal like NaCl. Each separate atom or ion is in a unique quantum state (neglecting nuclear spin) separated from the next higher level by an energy gap of several electronvolts. We can therefore be sure that the electron system in the crystal is still in a single, nondegenerate quantum state, and there is still an appreciable energy gap to the next excited state. (However, the first excited electron state will, in general, form the beginning of a continuum, as we shall see.)

The wave function and energy of the electron state depend on the position of the nuclei, but they may be determined as if the nuclei were fixed, since the motion of the nuclei is slow. We are here relying on the familiar adiabatic approximation, which is valid provided the nuclear displacement d , which causes a substantial change in the electronic wave function divided by the nuclear velocity v , is large compared to the electronic period. In other words,

$$\frac{d}{v} \gg \frac{\hbar}{\Delta E}$$

where ΔE is the lowest excitation energy.

It should be stressed that we do not claim that the electronic state of each atom can be approximately described by that of a free atom; in a realistic crystal the mutual disturbance of the atoms is substantial. We use only the fact that this disturbance is not large enough to diminish the energy gap in order of magnitude, or to invert the sequence of energy levels. It is possible that even starting from atoms with a degenerate ground state the degeneracy may be removed in the solid, so that there is a substantial energy gap, and the crystal is an insulator as, for example, in the case of diamond

For a nonconducting crystal in the electronic ground state, we may therefore treat the nuclei as moving in a static potential, which is just the electronic energy as function of the position of the nuclei. The position is quite similar to the problem of a diatomic molecule, for which the adiabatic approximation is usually set up, except that instead of one coordinate, the internuclear distance, we are dealing with a large number of variables.

The potential energy which is thus defined reaches its lowest value for a configuration which forms a perfect lattice, and for small oscillations around this equilibrium configuration we may expand the potential energy in powers of the displacements; symbolically:

$$U = U_0 + \sum A_{n,n'} u_n u_{n'} + \dots$$

where u_n is the displacement of the n th atom, both n and n' being vectors. The linear term is absent since $u_n \equiv 0$ is an equilibrium configuration.

The series may be expected to converge rapidly if the displacements are small compared to the interatomic spacing: $u \ll a$. (Strictly speaking, we require only that $|u_n - u_m| \ll a$, where n and m are two atoms with a substantial interaction between them, since a uniform displacement of the crystal does not affect the potential energy.) For most crystals this condition is well satisfied even near the melting point, but for some exceptional cases, notably in solid He, even the zero-point motion has an amplitude comparable with a . These cases are very hard to analyze.

Otherwise, a good approximation is obtained by neglecting all terms higher than the second in the series for U , and the result is coupled harmonic motion (which in a well-known way can be solved by the use of normal coordinates) whose quanta of oscillation lead to the concept of phonons.

In this sense even the simple case of the nonconducting crystal represents a many-body problem, but it is of a specially simple kind, since in the harmonic approximation the different normal modes (or the different phonons) are independent. The situation is similar to that of the perfect gas, which is really an assembly of one-particle problems. As in the case of the nearly perfect gas, one is forced to consider collisions even if they are small, because they produce qualitatively new effects. In the harmonic crystal, as in the perfect gas, the transport coefficients, such as the thermal conductivity, are infinite, and a realistic approach relies on anharmonic terms, which cause changes in the phonon distributions, just as collisions in the gas cause changes in the velocities of the molecules.

The exact treatment of "phonon collisions" due to anharmonic terms in the potential is rather difficult, but it represents a problem in statistical mechanics rather than a typical many-body problem. Some features of the phonon collisions can be studied very directly in experiments on neutron scattering. If the neutron wavelength is too long for Bragg scattering to occur, each scattering must involve the creation or annihilation of at least one phonon. By observing the energy and momentum change of the neutron, one therefore expects to see the energy-momentum relation for phonons. Multiphonon processes give a broad background, the one-phonon effect represents a peak which would be a sharp line in the harmonic limit. Its width is a measure of the phonon lifetime; its relation to the imaginary part of the energy of a one-phonon state, as defined by a one-phonon Green function, is an interesting subject for study.

There is apparently some indication that for this phonon decay processes in which two phonons are absorbed and two created, are as important as those in which two go into one or vice versa, although the former are due only to the quartic terms in the potential energy, or come from the operation of the cubic terms twice through a virtual intermediate stage. This may be due to the fact that the three-phonon processes can happen only in special circumstances which are rather sensitive to the energy-momentum relation for phonons, and thus represent a rather small amount of phase space.

Cubic and quartic terms are also responsible for thermal expansion. In the presence of thermal expansion one might be doubtful about the

validity of the Taylor series for the potential energy, since the distance of two atoms at opposite ends of the crystal is now $N(a + \delta a)$ instead of Na , so that either or both must have moved an amount $N\delta a$ from the equilibrium position. It was stressed earlier that we require only the relative displacement of interacting atoms to be small, and this will always be the case, so that there is no reason to be doubtful about the validity of the series.

However, the convergence can be improved by expanding about the equilibrium configuration at the given temperature. The fact that the meaning of the variables then depends on the temperature causes no fundamental difficulty, though it requires some care in dealing with fluctuation problems.

The next problem in increasing order of complexity is that of a semiconductor, which we can regard as an insulating crystal with a few additional electrons (or a few electrons removed). As long as the number of carriers is small, we may treat them as independent, and therefore the basic problem is that of one additional electron (or one hole). In a perfect crystal, treating the nuclei for the moment as being fixed, the translational symmetry requires that the electronic wave function changes only by a phase factor upon a displacement of the whole system by one lattice constant. Calling this factor $\exp(ika)$, one defines a wave number k in each direction, and thus a wave vector \mathbf{k} .

By imagining this state built up adiabatically from separated atoms, or from noninteracting electrons we are led to expect that the lowest energy for any given \mathbf{k} will be discrete, so that there exists a function $E(\mathbf{k})$, as in the case of a single electron moving in a periodic potential.

In reality, this is not the energy of a single electron, but a state of a many-electron system, since the last electron interacts with all the electrons in the closed-shell atoms. In the language of many-body theory $E(\mathbf{k})$ is the energy of a "quasi-particle." However, it would be pedantic to insist on this usage. Indeed in the physics of elementary particles we invariably deal with particles which interact strongly with fields in which they are embedded, and if we were pedantic we should always talk about quasi-protons, quasi-mesons, etc.

If we start from an insulator with a small energy gap, thermal excitation will produce electron-hole pairs ("intrinsic" semiconductor) the electron and the hole may separate and can then be treated as inde-

pendent. They may, however, also remain bound to each other by their coulomb interaction. This is called an "exciton." The motion of the exciton as a whole is again characterized by a single wave vector \mathbf{k} , with the energy being a function of \mathbf{k} . However, there are also internal degrees of freedom. For a state in which the mean distance of the electron and the hole is large compared to the lattice spacing a , these can be described by a continuum theory, resembling the theory of positronium, except that the effective mass of electron and hole, and the dielectric constant of the crystal, alter the scale factors. There is some doubt, however, whether this description is applicable to the low-lying levels of the system, in which there is an appreciable probability of the electron and hole being in the same atom, so that the atomic structure of the crystal is clearly vital.

Another type of exciton may be pictured as an excitation of an atom in the crystal without an appreciable probability of an electron leaving the atom. A typical example of this is provided by the optical excitation of rare-earth atoms in crystals, in which the excitation is in one of the inner, shielded shells so that it is affected only slightly by the neighboring atoms. In this type of exciton one also finds a continuous energy spectrum, characterized by a single function $E(\mathbf{k})$ of a wave vector, which determines the propagation of the excitation through the crystal.

Dr. Pines has pointed out in this discussion the existence of a plasmon mode also in an insulating crystal. This can be visualized as a collective state made up of a coherent superposition of all possible particle-hole pairs, including not only all possible relative momenta of particle and hole, but also all possible particle and hole bands. The energy of this mode lies fairly high and its description requires more specific model assumptions or approximations than the low-lying states enumerated above, whose nature follows directly from conservation laws, together with considerations of adiabatic changes from simpler systems.

In a real crystal all these modes are coupled with the lattice vibrations, so that there is an electron-phonon, hole-phonon, exciton-phonon, or plasmon-phonon interaction. This alters (renormalizes) the energy of the excited mode and also leads to real scattering and thus to a finite lifetime and finite transport coefficients for these modes.

An especially interesting example is the additional electron in a polar

crystal. Because of the long range of electric interactions, the coupling with optical phonons is here particularly strong, and also particularly simple since its major part can be treated in a continuum approximation. Since a substantial lattice distortion accompanies the moving electron the renormalization of its inertial mass may be appreciable.

The situation becomes more complex when we consider a metal, for two reasons: (a) The definition of the effective forces between the nuclei, and hence of the lattice vibrations does not apply any more, (b) the electronic excitation spectrum not only has no threshold, but has many states with the same wave vector.

As regards the first point we notice that the usual justification of the adiabatic approximation, which we have used to define the lattice potential for the insulating crystal, clearly fails when there is a continuous spectrum, since the condition for its validity contains the energy gap. Even if one tried hopefully to ignore this condition and to calculate the energy of the electron system as a function of the nuclear coordinates it would be hard to make this unique since it is then not clear what is meant by specifying a given electronic state for different such configurations. (This could be done if one restricted oneself always to the lowest electronic state, but in the continuum this would be quite unrealistic.) One way of overcoming this difficulty is to start with the effect of electrons in closed shells only, and replacing the conduction electrons by a uniform static charge distribution, to avoid unphysical space charge effects. This part of the problem is like that of an insulating crystal. The answer it gives for the lattice vibrations is unrealistic, since it does not allow properly for the effects due to the conduction electrons, in particular for the screening of longitudinal vibrations, and this has then to be corrected; the corrections appear formally as electron-phonon interactions, but treated in this way they are appreciable and have to be handled better than low-order perturbation theory.

On the second difficulty it is evident that for a system of noninteracting electrons in a static potential there are many excited states of the same momentum q . If $\varepsilon(p)$ is the energy of one electron, transfer of one electron gives an energy change, $\varepsilon(p + q) - \varepsilon(p)$, p being an occupied state and $p + q$ empty which is least for p and q parallel and $p + q$ just outside the Fermi surface. From this minimum the excitation spectrum extends upward. Lower states of the same momentum can be produced by excit-

ing more particles. The absolute minimum is obtained by sharing the momentum equally by all particles, when the energy increase is negligibly small.

A powerful approach to the problem, due to Landau, is to consider a state with one electron added to the system. For noninteracting electrons this will have a definite energy $\varepsilon(q)$ if all the other electrons remain in their previous states. In the presence of interactions this is no longer a definite stationary state, but it is plausible that there should be a long-lived state with an energy which is a definite function of momentum, and with a finite life time, i.e., a finite width. For very low excitation energy (i.e., electrons close to the Fermi surface) the width is small compared to the energy and therefore the concept of such one-particle states (or quasi-particles) is useful. For very high excitations it is still possible to define a decaying state, but its properties then become dependent on the precise details of its definition.

Similarly one can define a quasi-hole by considering the states formed by removing one electron from the system. The excitations of the system can then be built up by putting in an equal number of particles and holes. As long as that number is small, the states can be described as those of single quasi-particles and holes, with interactions between them. At the same time one must of course include the interactions with phonons. That these complications are not academic is made evident by the existence of superconductivity. The possibility of this arises from the fact that the large number of coupled degrees of freedom opens up the possibility of strong correlations which make the dynamics of the system quite different from the uncoupled one.

It is normal to ignore most of these complications in the nonsuperconducting metals and even in the normal state of a superconductor above the transition point. There is indeed no experimental evidence that anything special happens in a superconductor slightly above the transition temperature (as opposed to the case of a ferromagnet above the Curie point) and this point of view may well be justified.

In that case one obtains the usual description in terms of electrons, phonons, and their collisions, in which the energy of each is again assumed to contain all the interactions, except those that give rise to real collisions.

Even in this simple framework there are nontrivial questions. One

of them concerns the matrix element of the electron-phonon interaction, which is usually written in first-order perturbation theory, based on a Taylor expansion of the potential energy of an electron in terms of the nuclear displacements. Since, however, the potential in the interior of an atom is very strong, this is hardly justified, and a much better approach is to treat this interaction in terms of a "pseudopotential" which is designed to give the correct scattering by one atom when treated in first-order Born approximation. Since the definition of a pseudo-potential depends on the medium in which the scattering takes place, the use of such a concept in the case of a solid requires considerable care.

Among the challenging simple problems is that of an electron system without a lattice, containing only a uniform positive charge distribution for neutralization. This is a problem with a single parameter, namely, the density. At high densities the electrons are not very strongly correlated and a perturbation treatment is relatively easy. F. Bloch conjectured many years ago that for low density this system would become ferromagnetic. If all electron spins are made parallel this increases the kinetic energy, since the Pauli principle then requires a Fermi surface of greater volume, but the mutual electrostatic interaction is reduced since the antisymmetrization of the orbital wave function keeps the electrons apart in space. Low density favors the second factors as compared with this first, but a quantitative treatment of this problem is difficult. The simple perturbation theory used by Bloch is certainly invalid when it predicts ferromagnetism. At very low density the electrons almost certainly form a lattice, and in the extreme case, in which the zero-point amplitude is much less than the spacing, there is no opportunity for ferromagnetism. Its occurrence at somewhat higher densities is not settled but seems unlikely.

Another interesting problem in solid-state theory is that of ferromagnetism. Here it is usual to idealize the situation by assuming that the number of electrons in each atom is fixed. This appears to contradict the picture of conduction electrons in metals which we have used so far, but one must remember that magnetic electrons in the ferromagnetic metals always are inner d -electrons which belong to a narrow band, and therefore their tendency to run about independently of each other is probably not too strong. Another complication usually disregarded is the fact that d -electrons have orbital moments. For free atoms the

orientation of the orbital angular momenta would represent important degrees of freedom. In the crystal these are in some way locked to each other so that they are in a definite nondegenerate state, but the resultant anisotropy of each atom should complicate the problem of the interaction of the spins.

Apart from these complications one is then dealing with a problem in which the total number of states for the whole crystal is $N^{(2S+1)}$ where S is the spin of one atom, this is a large, but finite number, and the spectrum of magnetic energies covers a finite energy interval. The structure of this energy spectrum is again a typical many-body problem.

Its Hamiltonian is usually obtained from the Heitler-London approximation, although recently some doubt has arisen about justification of the Heitler-London procedure for finding the relation position of different spin states.