iodide crystal arising from the increased energy supplied to the crystal did bring about thermal strains that broadened the iodine resonance in the region that was otherwise almost completely free of strains. The broadening was not because of the increased ultrasonic power as such since we permitted the temperature to come to equilibrium, whereas, measurements made at 80 v before the crystal had time to increase its temperature gave ultrasonic line widths for iodine that were essentially the same as those we obtained at 50 v applied to the quartz.

The ultrasonic line width is larger than the line width measured by the Pound-Watkins marginal oscillator by a factor of about three. Part of this broadening may be attributed to the quadrupole broadening of the satellite lines,[3] but it is also possible that part of the broadening at low levels of ultrasonic radiation is due to the band width of the ultrasonic radiation which, though introduced at the monochromatic frequency of 10 Mc/sec, decays to other neighboring modes by phonon-phonon collision. Measurements made on iodine nuclei in potassium iodide at low ultrasonic intensities give an ultrasonic line width of 3 kc/sec. This is somewhat less than the ultrasonic line width of iodine nuclei in sodium iodide.

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Electron Interaction in Solids. The Nature of the Elementary Excitations

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Possible elementary excitations in solids are studied with the aid of the general theoretical approach developed in the preceding papers of this series. Particular attention is paid to the basic theoretical justification for the individual-particle-like elementary excitations ("effective" electrons). It is concluded that good qualitative arguments may now be given for the existence of effective electrons in solids, but that a detailed quantitative deduction has yet to be made. The presence of an energy gap is shown to be a necessary condition for the existence of strong spatial correlations between minority carriers in solids (excitons, conduction electron plasmons in semiconductors, etc.) and the nature of such correlated minority electron excitations is discussed. The plasmon spectrum of various solids is discussed and compared with experiment.

1. INTRODUCTION

IN the preceding papers of this series[1] we have considered in some detail the influence on electronic motion of the long-range correlations introduced by the Coulomb interaction between the electrons. We have seen that these correlations, in most solids, give rise to a collective excitation of the electron system as a whole, the plasmon. We have developed a technique for isolating the plasmon excitations by introducing a set of extra variables and carrying out a series of canonical transformations on the system Hamiltonian. We have postponed until now any inquiry into the nature of the remaining elementary excitations in solids.

Most of the problems of solid-state physics are treated within the framework of a one-electron approximation. Considering how crude such an approximation is, its impressive success is very puzzling, as has been emphasized anew recently by Mott.[2] Detailed effects, such as the de Haas-van Alphen effect in metals or cyclotron resonance in semiconductors, appear understandable only within the framework of the concept of a Fermi surface and of independent electron excitations. There is, consequently, little question that certain elementary excitations in solids bear a close formal resemblance to those postulated in a one-electron model. In this paper, we consider the present theoretical basis for the one-electron approximation. Our arguments are somewhat qualitative in character; we propose lines along which one may hope to make them quantitative.

The justification of the one-electron model in the free electron gas has been considered recently by Landau[3] and by Gell-Mann.[4] Both assume that as one switches on the charge of the electrons, the energy levels vary continuously from their free-electron values. With this assumption, one may establish a one-to-one correspondence between the energy levels of the systems of interacting and noninteracting electrons. It is then possible to justify a one-particle approximation in the limit of low-energy excitations.

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[1] P. Nozières and D. Pines, Phys. Rev. **109**, 741, 762 (1958); hereafter referred to as NP I and NP II.

[2] N. F. Mott, Nature **178**, 1205 (1956).

[3] L. D. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **30**, 1058 (1956) [translation: Soviet Phys. JETP **3**, 920 (1957)].

[4] M. Gell-Mann, Phys. Rev. **106**, 369 (1957).

The approach of Landau and Gell-Mann obviously misses the existence of bound states, such as excitons, impurity levels in semiconductors, and the like. A more serious shortcoming, in our view, is their neglect of possible spatial correlations between the electrons brought about by the long-range Coulomb interactions. These correlations may play a role in the following manner. We know that the Coulomb interaction introduces spatial correlations which correspond to plasmons. Further, the ground state of the electron system corresponds to a state in which there is no plasmon excitation. This, in turn, implies a definite spatial correlation between the electrons *in the ground state*, or in the low-lying excited states. Whether such correlations are consistent with the notion of independent-particle excitations will form one of the topics of this paper.

Kohn[5] has considered the applicability of an independent-electron model in a somewhat more restricted problem, that of a single electron moving in an otherwise empty band in a semiconductor or insulator. He has shown that the interaction between the conduction electron and the valence electrons may be described, in the limit of low frequencies and long wavelengths, by an effective mass and a dielectric constant. We shall discuss the extent to which his conclusions are applicable to the case of actual semiconductors and insulators.

We begin this paper by assuming that we may neglect completely the long-range part of the Coulomb interaction between electrons. One may then apply with confidence the arguments of Landau and Gell-Mann, and show that there exists a set of elementary excitations whose structure at low energy is the same as that of a gas of independent "effective particles." Such an approach is sketched in Sec. 2.

We next introduce the long-range part of the Coulomb interaction. From NP I, we know that, after isolation of the plasmons, this interaction is screened, and must be used together with a set of subsidiary conditions on the wave function of the system. In Sec. 3, we present a set of qualitative arguments which tend to justify the neglect of these new complications. We conclude that the effective electrons of Sec. 2 should be meaningful in the actual problem. In Sec. 4, we try to make the conclusions of the preceding section more quantitative by isolating a group of minority carriers near the Fermi surface (as was done in NP II). We show that if we neglect the short-range Coulomb interactions, we can justify the concept of effective electrons at low energy. We are, however, unable to treat simultaneously the long-range and short-range particle interaction, although we strongly believe that a treatment which takes both into account simultaneously will yield essentially similar results.

In Sec. 5, we look for possible correlated motions of a set of minority carriers. We show that such correlated motions are possible only if the excitation spectrum of the remaining majority carriers possesses an energy gap. We then discuss the possibility of bound states (excitons, impurity states, etc.) and of collective states (plasmons of conduction electrons in semiconductors, etc.). In Sec. 6 we compare the results of NP I, NP II, and the present paper with experiment for various kinds of solids, and in Sec. 7 we present our conclusions on the nature of the elementary excitation spectrum in solids.

2. EFFECTIVE ELECTRONS

Let us first suppose that we may neglect entirely the long-range interaction between electrons. We therefore study the structure of the eigenstate spectrum of (H_0+H_{sr}) where the screening radius, k_c^{-1}, is sufficiently short that no collective excitations exist in the system. We then may follow the approach suggested by Gell-Mann[4] and Landau,[3] Consider first the eigenstates of H_0 alone: they are Slater determinants Φ_n built with "one-electron" wave functions $\varphi_{\kappa,\nu}$. In what follows, we shall find it convenient to use an extended zone scheme, and to label the $\varphi_{\kappa,\nu}$ by a single index κ which runs over the entire wave-vector space. In the ground state Φ_0, all levels inside a certain surface S of the reciprocal space are filled, all those outside S are empty: S is the Fermi surface. An excited state Φ_n is described by p electrons outside S (momenta $\mathbf{K}_1, \cdots \mathbf{K}_p$) and p holes inside S (momenta $\mathbf{K}_1', \cdots \mathbf{K}_p'$). The energy E_n is additive:

$$E_n-E_0=\sum_{i=1}^{p} E(K_i)-\sum_{i=1}^{p} E(K_i'). \tag{2.1}$$

Let us now switch on the short-range Coulomb interaction H_{sr}, letting the electronic charge e increase progressively from 0 to its actual value. Let $\Phi_n(e)$ represent the eigenstates of the system for a given value of e. Under what conditions is it possible to establish a one-to-one continuous correspondence between $\Phi_n(e)$ and $\Phi_n(0)$? Given a state $\Phi_n(0)$, we can always derive a formal perturbation expansion in powers of e^2 which satisfies term by term the differential equation for $\Phi_n(e)$. If this series converges uniformly, its sum yields an eigenstate $\Phi_n(e)$ which may be followed continuously from $\Phi_n(0)$. Under these circumstances, we may establish a continuous mapping of the perturbed states, $\Phi_n(e)$ on the unperturbed one $\Phi_n(0)$. We may then label the $\Phi_n(e)$ by the same indices $\mathbf{K}_i$ and $\mathbf{K}_i'$ used for the independent particles. At this stage the $\mathbf{K}_i$ and $\mathbf{K}_i'$ are parameters with no direct physical meaning.

It must be emphasized that the convergence of the perturbation series yielding $\Phi_n(e)$ is a completely unsolved mathematical problem. One must assume that all goes well for the actual value of e. The calculation of the correlation energy by Brueckner and Gell-Mann[6]

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[5] W. Kohn, Phys. Rev. **105**, 509 (1957).

[6] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

which gives a finite result tends to support this view. The above procedure then gives perturbed eigenstates, but does not give all of them, since it misses all the bound states (excitons, impurity states, positronium, etc.). Such states do not appear when $e=0$, and have to be dealt with separately. We shall consider them in Sec. 5.

Knowing the spectrum of $\Phi_n(e)$, we can find by inspection the state $\Phi_0(e)$ which gives rise to the lowest energy. This state will correspond to an unperturbed state $\Phi_0(0)$ where all levels inside a certain surface S' of K space are filled, while those outside S' are empty. S' plays the role of the Fermi surface of the perturbed system. Note that generally S' does not need to be the same as the unperturbed Fermi surface S. The two surfaces only have to enclose the same volume, corresponding to N states. For an isotropic solid, however, S and S' are identical spheres, for obvious symmetry reasons. An excited state $\Phi_n(e)$ is deduced from an unperturbed state $\Phi_n(0)$ with p holes inside and p electrons outside S'. Although the physical interpretation is no longer simple, we still can describe the perturbed excited states in terms of "effective holes" and "effective electrons."

Thus far we have considered the $\mathbf{K}_i$ and $\mathbf{K}_i'$ as parameters without physical meaning for the perturbed states. This is not quite true, for the total momentum of the system, $\mathbf{K}_{\text{tot}}=\sum_i \mathbf{K}_i$, is still a constant of the motion. In the ground state $\Phi_0(e)$, $\mathbf{K}_{\text{tot}}$ has to be zero, by symmetry. Consider, for example, a new state made by adding one electron $\mathbf{K}_i$ to the ground state. The only parameter is $\mathbf{K}_i$, which is consequently the total momentum of the system. This is just the case studied by Kohn,[5] who uses precisely this interpretation of $\mathbf{K}_i$.

Let us now turn to the energy of the excited states. Consider first a very simple case: what is the energy $E_{K_iK_i'}$ of the state $\Phi_n(e)$ with one excited electron $\mathbf{K}_i$ and one hole $\mathbf{K}_i'$? Let $E_{K_i'}$ be the energy of the system with a hole at $\mathbf{K}_i$, but no excited electron. We may write

$$E_{K_iK_i'}-E_0=(E_{K_iK_i'}-E_{K_i'})+(E_{K_i'}-E_0). \quad (2.2)$$

The second term of (2.2) describes the energy needed to create the hole $\mathbf{K}_i'$. The first term describes the energy needed to create the electron $\mathbf{K}_i$ *in presence* of the hole $\mathbf{K}_i'$. Now, does this first term really depend on the presence of the hole? Such a dependence can arise only from the Coulomb interaction of the hole and the electron. Assume that both of them are spread throughout the solid without any correlation; for a given position of the electron, the hole is uniformly distributed over all the solid. In such a case, the Coulomb interaction of the hole and the electron is of order $1/N$ smaller than the interaction of each of them with the remaining electrons, and is certainly negligible. Then, (2.2) may be written as

$$E_{K_iK_i'}-E_0=E(K_i)+E(K_i'), \quad (2.3)$$

where $E(K_i)$ and $E(K_i')$ are the energies of the "effective particles," which are now independent.

Equation (2.3) is no longer true if the hole and the electron undergo strong spatial correlations, forming, for instance, some kind of bound state corresponding to an exciton. This case will be discussed in more detail in Sec. 5. It is difficult to give a precise mathematical statement of what we mean by "correlation" of the hole and the electron. We are dealing with many-body wave functions, which do not yield the spatial distribution of any given particle. In $\Phi_{K_iK_i'}(e)$, we cannot tell which part of the charge density corresponds to the hole, and which part corresponds to the electron. *A fortiori*, we cannot define their correlation. The physical picture is, however, clear, and, in our mind, justifies a distinction between "correlated" and "uncorrelated" states.

If we were considering the actual long-range Coulomb interaction between the electrons, at this stage we should consider the possibility of another kind of spatial correlation between the excited particles. Such correlations are indirect in the sense that they occur through the interaction of excited particles with those remaining in the ground state. Thus, if there are collective effects, the excitation of one particle may modify that part of the excitation energy of another particle which arises from the interaction of the latter with the particles in the ground state. Just such an effect may occur through the correlations imposed by the condition that there be no plasmons in the ground state. These effects are neglected in the approach of Landau and Gell-Mann, and it is difficult to see how their relative importance may be considered within that framework.

Obviously, (2.3), where it is valid, may be generalized to an arbitrary number of electrons and holes, provided their total number is small compared to the number of particles in the ground state. In other words, the excited holes and electrons must constitute a minority group, spread at random throughout the solid. (Their average distance is then much larger than k_c^{-1}, which further reduces their interaction energy.) Under these conditions, the energy of the various excited states may be written in the form (2.1). The elementary excitations may then be described in terms of independent effective holes and electrons, and the Fermi surface may be defined unambiguously.

In most problems of solid-state physics, one is dealing with excitation energies of order kT, much smaller than the Fermi energy E_0. It is obvious from continuity arguments that, at such energies, the number of excited particles has to be very small. The above considerations then apply and justify the use of a one-electron model, provided one is justified in neglecting the effects of the long-range interaction. The knowledge of the function $E(K)$ allows one to determine trivially the density of states at low energy, and hence the specific heat, the paramagnetic spin susceptibility, transport properties, and the like.

We may formulate these conclusions in somewhat more mathematical form. The $\Phi_n(0)$ constitute a complete orthonormal set. We can always make the set of $\Phi_n(e)$ orthonormal, but it is complete only if there is no bound state. Let us write

$$\Phi_n(e)=\sum_m T_n{}^m\Phi_m(0). \tag{2.4}$$

This change of basis amounts to a transformation of the state vector Ψ into $T\Psi$. T^*T is always equal to 1, but TT^* is 1 only if there is no bound state. We can describe the states $\Phi_n(0)$ in terms of creation and destruction operators $C_K{}^*$ and C_K for free electrons outside S', free holes inside S'. It is then straightforward to prove that

$$\Gamma_K{}^*=TC_K{}^*T^*,\quad \Gamma_K=TC_KT^* \tag{2.5}$$

represent creation and destruction operators for the effective holes and electrons. The Hamiltonian THT^* is now diagonal, and has the following form:

$$\begin{aligned}H=&\sum_{K_1}E(K_1)\Gamma_{K_1}{}^*\Gamma_{K_1}\\&+\sum_{K_1,K_2}E(K_1,K_2)\Gamma_{K_1}{}^*\Gamma_{K_1}\Gamma_{K_2}{}^*\Gamma_{K_2}\cdots\\&+\sum_{K_1\cdots K_n}E(K_1\cdots K_n)\Gamma_{K_1}{}^*\Gamma_{K_1}\cdots\\&\qquad\times\Gamma_{K_n}{}^*\Gamma_{K_n}+\cdots.\end{aligned} \tag{2.6}$$

In this "cluster expansion," $E(K_1)$ represents the energy of the K_1 excitation, $E(K_1,K_2)$ the interaction of the K_1 and K_2 excitations, $E(K_1,K_2,K_3)$ the change in the pair interaction energy brought in by clusters of three particles, and so on.

If the free electrons and holes are acted upon by an external potential V, the effective particles feel the potential TVT^*, which may be appreciably different from V if H_{sr} has a large influence on the particle motion. This change of potential corresponds to a complicated screening due to the short-range forces.

3. EFFECTIVE ELECTRONS IN SOLIDS

We now consider the extent to which the concept of effective electrons is applicable in actual solids. The actual interaction between electrons is a Coulomb interaction. As we have mentioned before, one might expect that the long range of the Coulomb interaction could cause essential complications, since it might introduce strong spatial correlations between a large number of electrons in such a way that the requirements of the preceding section for effective electrons cannot be satisfied. Of course, just this effect occurs; the strong spatial correlations give rise to a collective electron excitation, the plasmon. However, plasmon excitation will not occur at the low temperatures in which we are presently interested, so that we might accordingly hope that effective electrons may be given a sensible interpretation at low temperatures. To see whether this is true, let us now turn to the detailed theory we have developed in the preceding papers.

Our basic Hamiltonian may be taken from (5.16) of NP I; it is

$$H=H_0+H_{\mathrm{sr}}+H_{\mathrm{pl}}+H_{\mathrm{rp}}. \tag{3.1}$$

H_0 is the usual one-electron Hamiltonian for electrons moving independently in the periodic field of the ion cores,

$$H_0=\sum_i[p_i{}^2/2m+V(\mathbf{r}_i)]. \tag{3.2}$$

H_{sr} is the screened short-range interaction between the electrons,

$$H_{\mathrm{sr}}=\sum_{i\neq j}\sum_{k>k_c}\tfrac{1}{2}M_k{}^2\exp\{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)\}. \tag{3.3}$$

H_{pl} and H_{rp} are defined (in the general case) in the representation in which (H_0+H_{sr}) is diagonal; they represent the plasmon-field Hamiltonian and the remaining long-range interactions between the electrons. We have

$$H_{\mathrm{pl}}=\tfrac{1}{2}\sum_{k<k_c}\{P_kP_k+\omega^2Q_kQ_k\}, \tag{3.4}$$

where ω^2 is defined by

$$1=\frac{4\pi e^2}{m}\sum_n\frac{f_{0n}}{\omega^2-\omega_{n0}{}^2}, \tag{3.5}$$

and

$$\begin{aligned}(H_{\mathrm{rp}})_{mn,\,pq}=&\sum_{k<k_c}\tfrac{1}{4}M_k{}^2(\rho_k)_{mn}(\rho_{-k})_{pq}\\&\times\omega_{mn}\omega_{pq}\left\{\frac{1}{\omega^2-\omega_{mn}{}^2}+\frac{1}{\omega^2-\omega_{pq}{}^2}\right\}.\end{aligned} \tag{3.6}$$

We should like to emphasize that the basic representation we use for the collective approach is just the electron system discussed in the preceding section, so that the energy levels and oscillator strengths defined thereby may be regarded as belonging to our system of effective electrons.

The remaining complications in our justification of the notion of effective electrons reside in H_{rp}, and in the subsidiary conditions imposed on our system wave function,

$$(\rho_k+\tfrac{1}{2}B_k)\Psi=0,\quad (B_k)_{mn}=\frac{\omega_{mn}{}^2}{\omega^2-\omega_{mn}{}^2}(\rho_k)_{mn}. \tag{3.7}$$

These complications represent our inheritance from the Coulomb interaction; they correspond to the effective Hamiltonian after plasmons have been removed, and the inhibition on the degrees of freedom of the system imposed by our introduction of collective modes. As we have remarked earlier, H_{rp} gives rise to just such long-range correlations in electron motions as are required to enable the electrons to satisfy the subsidiary conditions.

There are perhaps three major difficulties introduced by the attempt to work with wave functions which take into account explicitly the presence of H_{rp} and the subsidiary conditions, (3.8).[7] The first is one of normalization. For instance, consider the original form of the subsidiary conditions, which was $P_k\Psi=0$. Since Ψ must be a delta function in the P_k representation, we must normalize it with some care, using, for instance, a finite representation for the delta function, and proceeding to the limit with due caution.[8] Similar difficulties arise after the series of canonical transformations are carried out. A second difficulty is that H_{rp}, when treated by ordinary second-order perturbation theory, yields a result comparable to that calculated in lowest order.* Both contributions to the energy are quite small, so that one is not in difficulty with the over-all system energy. The small net shift in the energy coming from H_{rp} represents the energy required to rearrange the ρ_k's (and hence the electronic configurations) in such a way that the subsidiary conditions are satisfied. Such correlations undoubtedly involve many electrons, so that the nonconvergence of a perturbation-theoretic treatment is scarcely surprising.* Thus, it is not evident at present exactly how H_{rp} produces wave functions which satisfy the subsidiary conditions. The third difficulty is that the subsidiary conditions reduce the total number of electronic degrees of freedom. However, this difficulty need not concern us as long as we consider only low-energy excitations. As pointed out in BHP, the reduction occurs only for electronic excitations with an energy comparable to, or larger than, the plasmon energy.

Since the plasmon at long wavelengths is an excitation in which many electrons take part,[9] we might accordingly expect that the subsidiary conditions should influence only many-electron states. Thus, even at high energies ($\gtrsim\hbar\omega_p$) the long-wavelength individual electronic excitations are still unaffected, but many-electron excitations must satisfy the subsidiary conditions. For what the subsidiary conditions tell us is that we cannot describe the plasmons twice. Once we have isolated and, indeed, named the plasmon excitations, we cannot allow the remaining "electrons" to carry out a plasma oscillation. In other words, the subsidiary conditions guarantee that there be no plasmons among the excitation modes of our "dressed" electrons.[10] This conclusion tends to justify the argument that only electron excitations of $\sim\hbar\omega_p$ are influenced by the subsidiary conditions, since a plasmon involves a kinetic energy of order $\hbar\omega_p$ (distributed, to be sure, between many electrons).

The preceding statements begin to break down when $k\lesssim k_c$ because the number of electrons taking part in a plasma oscillation approaches unity. Under these circumstances, the "plasmon" states knocked out by the subsidiary conditions are closer and closer to individual electronic excitations. Hence the high-energy electronic excitations at such wavelengths may be modified appreciably by the subsidiary conditions.

4. ISOLATION OF A MINORITY ELECTRON GROUP

We have seen in the preceding section that the notion of a low-energy elementary excitation which has the properties of an "effective" electron is at least a plausible one. We should now like to investigate the extent to which we can make a more precise statement along these lines by regarding the effective electrons as minority carriers in the sense of NP II. For a semiconductor or an insulator, the low-energy elementary excitations will be those appropriate to the comparatively small number of electrons in the conduction band. For a metal with strongly overlapping bands, we need consider only those few electrons lying within a region ΔE of the Fermi surface, where

$$kT\lesssim\Delta E\ll E_0.$$

Thus, in both cases we are interested in the behavior of a small group of electrons, $\tilde{N}$ in number, where $\tilde{N}\ll N$, and we may attempt to apply the techniques of Sec. VI of NP II.

Let us begin by neglecting the short-range interaction between the electrons, a model directly opposed to that of the preceding section. For the moment, let us also neglect the indistinguishability of the electrons, an approximation equivalent to neglecting the exchange effects in the interactions between the electrons. We may then introduce plasmons for the majority carriers alone, as in Sec. VI of NP II, and so take as our basic Hamiltonian (6.4) of NP II,

$$\begin{aligned}H_{\mathrm{ext}}=H_0+\sum_k\tfrac{1}{2}(P_kP_{-k}+\omega_p{}^2Q_kQ_{-k})+H_{\mathrm{int}}+U+\tilde{H}_0\\+\sum_{k<k_c}\{M_k(\tilde{\rho}_k-\tilde{\rho}_k{}^s)P_{-k}+M_k{}^2\tilde{\rho}_k{}^s\rho_{-k}\\+\tfrac{1}{2}M_k{}^2\tilde{\rho}_k\tilde{\rho}_{-k}\},\quad(4.1)\end{aligned}$$

where

$$(\tilde{\rho}_k{}^s)_{\mu\nu}=\frac{(\tilde{\rho}_k)_{\mu\nu}}{\epsilon(k,\omega_{\mu\nu})},\qquad(4.2)$$

and the tilde, as before, refers to the minority electrons.

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[7] For a more detailed discussion of these points, we refer the reader to Bohm, Huang, and Pines, Phys. Rev. **107**, 71 (1957), hereafter referred to as BHP.

[8] Otherwise one encounters all sorts of simple paradoxes; e.g., $\langle\Psi|[P_k,Q_k]|\Psi\rangle=0$ as well as $-i\hbar$.

* *Note added in proof.*—The perturbation series expansion of H_{rp} has now been summed, within the random phase approximation, for the free electron gas. The result, which is exact in the high density limit, is a contribution to the system energy from the second, and all higher, order terms which is one-third the expectation of H_{rp}.

[9] The number of electrons taking part in a plasmon is evaluated by R. A. Ferrell, Phys. Rev. **107**, 450 (1957).

[10] See, for instance, BP III, where it was shown that what corresponds to a plasmon mode is an oscillation of

$$\sum_i\frac{\omega^2}{\omega^2-(\mathbf{k}\cdot\mathbf{p}_i-hk^2/2m)^2}\exp(-i\mathbf{k}\cdot\mathbf{x}_i)$$

(for the free-electron gas). Hence, the subsidiary conditions in the transformed coordinate system guarantee that no plasmons exist in the field. Brueckner, Fukuda, and Sawada (private communication) have reached a similar conclusion from a somewhat different point of view.

At this point, we could first decouple the plasmons from the electrons by using a suitable canonical transformation to eliminate the term H_{int} from (4.1). We might then eliminate the plasmon-minority electron interaction by the methods used in Sec. IV of NP II. [See Eq. (4.12) of NP II.] We would obtain

$$H=H_0+H_{\text{sr}}+H_{\text{rp}}+\tilde{H}_0+\sum_{k<k_c} M_k\tilde{\rho}_{-k}(B_k+\tfrac{1}{2}\tilde{B}_k), \quad (4.3)$$

where

$$(\tilde{B}_k)_{\mu\nu}=\frac{\omega_{\mu\nu}{}^2}{\omega_{\mu\nu}{}^2-\omega^2}M_k(\tilde{\rho}_k)_{\mu\nu}. \quad (4.4)$$

The procedure followed to obtain (4.3) and (4.4) is identical with that we used in Sec. IV of NP II to obtain the collective contribution to the dielectric constant. We note that the minority electrons do not appear in the subsidiary conditions, but that there remains in (4.3) a long-range interaction between the minority electrons and the majority electrons. In cases where this interaction may lead to an effective dielectric constant in the minority-minority electron interaction, we could then carry out a further canonical transformation to obtain this effective interaction. However, even where this cannot be done, we may find it useful to work with a set of minority electrons which are not bound by the subsidiary conditions.

Where the concept of an effective dielectric constant is meaningful, it is more convenient to obtain the final result by a single transformation which simultaneously eliminates the interaction of the minority electrons with both the plasmons and the majority electrons. The transformation is just that generated by (6.6) of NP II. The resultant long-range interaction between the electrons is

$$H_{\text{coul}}=\sum_{k<k_c}\tfrac{1}{2}M_k{}^2\tilde{\rho}_{-k}\tilde{\rho}_k{}^s. \quad (4.5)$$

The "effective" minority electrons appearing in (4.5) *are not subject to the subsidiary conditions.* They represent "dressed" electrons, each surrounded by a cloud of virtual plasmons and majority electron excitations, in such a way that their effective interaction is characterized by the dielectric constant of the solid. Thus the combined effect of the subsidiary conditions and H_{rp} on the minority electrons is expressed in the cloud of virtual excitations about each minority electron, which leads to the simple law of interaction between them expressed by (4.5).

One further consequence of (4.5) is of interest. According to (4.2), $(\tilde{\rho}_k{}^s)_{\mu\nu}=(\tilde{\rho}_k)_{\mu\nu}/\epsilon(k,\omega_{\mu\nu})$. For long wavelengths and low frequencies, $\epsilon(k,\omega_{\mu\nu})$ is just ϵ_0, the static dielectric constant. To the extent, therefore, that we can neglect the dispersion in ϵ_0, there will be no corrections to the effective mass of the electrons arising from their long-range interaction with the majority electrons. The electronic effective mass will then be just that arising from the periodic crystalline field. Such lack of dispersion in the dielectric constant reflects the fact that the majority electrons are able to follow the minority electrons perfectly, giving rise to no inertial effects. It is therefore obvious that the crystalline-field effective-mass approximation will break down because of electron-electron interaction for sufficiently short wavelengths or for high-frequency electronic motion.

What is the validity of (4.5)? First, in obtaining it we have neglected the influence of the screened long-range density fluctuations of the majority electrons on the minority electrons, an excellent approximation for sufficiently small k, and one which appears adequate for $k\lesssim k_c$. Second, we neglected the indistinguishability of the electrons, an approximation which again is fine for small k, and should prove adequate for $k\lesssim k_c$. (The effects of exchange appear only through the screened long-range minority-majority interaction, which is weak because of the screening. Physically, one does not expect exchange effects to be important for distances larger than the electron de Broglie wavelength, which is of order k_c^{-1}.)

The most important approximation is our neglect of H_{sr}, which will give rise to both exchange and correlation effects. The short-range majority-majority interaction,

$$\tfrac{1}{2}\sum_{k>k_c} M_k{}^2\rho_k\rho_{-k},$$

may be treated along the lines of the preceding section. There remains the short-range minority-minority interaction,

$$\sum_{k>k_c}\left(\frac{2\pi e^2}{k^2}\right)\tilde{\rho}_k\tilde{\rho}_{-k},$$

and the minority-majority interaction,

$$\sum_{k>k_c}\frac{4\pi e^2}{k^2}\rho_k\tilde{\rho}_{-k}.$$

The former interaction is exceedingly small for small $\tilde{N}$ (again neglecting the possibility of strong spatial correlations between the minority electrons). The major effect of the minority-majority interaction is the modification of the energy spectrum of the individual minority electrons. Thus, since $k_c^{-1}\ll\tilde{r}_s$, the short-range interactions should not be expected to alter the effective interaction between the minority carriers, apart from their indirect influence through the shift they produce in the excitation frequencies, $\omega_{\mu\nu}$, and perhaps also in the matrix elements, $(\tilde{\rho}_k)_{\mu\nu}$.

The principal difficulty we face, therefore, is that of accounting for the shift in the energy levels of the electrons at the top of the Fermi distribution due to H_{sr}. For a metal in which the minority electrons lie in the same band with the majority electrons, the problem is particularly pressing. We do not see at present how to manage a formal treatment of the problem in which the fairly large shifts in the position of the Fermi level due to H_{sr} may be included *after* we have treated the long-range part of the interaction. (It does not appear feasible to take into account H_{sr} *first* and then treat the long-range part of the interaction because the procedure outlined in Sec. 2 has not been reduced to Hamiltonian form.)

The difficulties introduced by H_{sr} appear more malleable in the case of the conduction electrons in an insulator or semiconductor, because the band gap markedly reduces the exchange contribution to the electronic energy levels, and may be expected to reduce somewhat the correlation terms as well. In this case we expect that a perturbation-theoretic or slighly better treatment of the interaction between the minority and majority electrons will go through with no essential difficulties. We have a natural scheme for defining our minority electrons, and there are no difficulties in principle in calculating the properties of the effective electrons. A similar situation should arise from the semimetals.

It is interesting to compare our approach and results with those of Kohn.[5] Kohn considered the problem of a single extra electron in an insulator and proved that its interaction with a very weak external charge may be characterized by an effective mass and the static dielectric constant. Our approach is more general than that of Kohn, since we may consider a large number of conduction electrons. On the other hand, our results are not so rigorous, since we have not established in detail the validity of all the approximations described above. We believe that our approach furnishes a good framework within which Kohn's results may be generalized; what we have done in this section is to outline how that generalization is to be carried out.

For instance, Kohn has conjectured that the response of a single extra electron in an insulating crystal to an external electromagnetic field which varies slowly in space compared to a lattice spacing, and in time compared to $\hbar/\Delta E$ (ΔE being the energy gap), may be characterized by an effective mass, the static dielectric constant, and the static magnetic susceptibility. We believe this conjecture may be generalized to a number of electrons in the conduction band ($\tilde{N}\ll N$), and that it may be proved along the following lines. Consider first only long-range interactions. Then the derivation leading to (4.5) may be utilized, where the external field is regarded as one of the "minority carriers," as in Sec. VII and Sec. VIII of NP II. How will the short-range interactions alter this situation? They, of course shift the energy levels of the minority electrons, but that shift should not be influenced by the external field as long as its time and space variation are sufficiently slow, from which the generalization follows.

5. CORRELATED ELECTRON MOTION

In Sec. 2, we systematically neglected the interaction between excited effective particles, on the grounds that they were not spatially correlated. In Sec. 4, we made an equivalent approximation, neglecting the interaction between the electrons near the Fermi surface. In this section, we consider cases in which this interaction gives rise to new elementary excitations. We begin our study with the isolated set of minority carriers of the preceding section.

For wavelengths longer than the screening radius, the effective interaction between the minority carriers is given by (4.5). As we have emphasized in NP II, this interaction may be used for treating exchange and scattering effects, but one must be very careful in applying it to correlation effects (which appear in bound or collective states of the minority carriers). We first wish to consider the conditions under which (4.5) may be used to describe correlated motion of the minority carriers. (We remark that for wavelengths smaller than the interelectron spacing, $r_s\sim k_c{}^{-1}$, the minority-minority interaction is very slightly perturbed by the majority electrons. If two electrons are separated by a distance R smaller than r_s, we can treat their relative motion without including the response of the majority electrons. Such cases occur infrequently in practice.)

A given minority carrier is subject to the screened field of the other minority carriers [given by (4.5)], and to the screened fluctuating field of all the majority carriers. The latter may be obtained from the screened interaction between majority and minority carriers given in (4.3):

$$\sum_{k<k_c} M_k\rho_k B_{-k}, \tag{5.1}$$

where B_k is defined by (4.4). We may compare the relative influence of the majority and minority carriers on a given minority carrier by comparing the mean-square fluctuations of $\tilde{\rho}_k{}^s$ and B_k/M_k. If the latter are negligible, we will be justified in using (4.3) to treat correlations between minority carriers.

For a nondegenerate minority electron gas, $(\tilde{\rho}_k{}^s\tilde{\rho}_{-k}{}^s)_{00}$ is approximately equal to $\tilde{N}/\epsilon^2$, while for a degenerate gas it is roughly given by

$$(\tilde{N}/\epsilon^2)(k/\tilde{k}_0).$$

(Since the minority processes always involve low energies, we have replaced $\epsilon(k,\omega_{\mu\nu})$ by the static dielectric constant ϵ.) The expectation value of $B_kB_{-k}/M_k{}^2$ is equal to

$$\sum_n |(\rho_k)_{0n}|^2\frac{\omega_{0n}{}^4}{(\omega^2-\omega_{0n}{}^2)^2}. \tag{5.2}$$

In (5.2), each term of the sum corresponds to a fluctuation at a frequency ω_{n0}. The interband part therefore involves very rapid fluctuations. Unless its amplitude is very much larger than $(\tilde{\rho}_k{}^s\tilde{\rho}_{-k}{}^s)_{00}$, it cannot alter much slow motion of the minority carriers, because of the large frequency mismatch. (Neglecting these terms amounts to an adiabatic approximation.) The really crucial part of (5.2) is therefore the intraband part (if it exists), which involves very low frequencies ω_{n0}.

Let us consider first a metal. We then have intraband transitions, which give a contribution to (5.2) of order $N(k/k_0)(k^4/k_c^4)$. In such a case, the dielectric constant is, for low k, entirely determined by the intraband effects, and is of order k_c^2/k^2. Furthermore, because the minority carriers lie in the same band with the majority electrons, they must be regarded as forming a degenerate electron gas. The minority-minority interaction is then measured by $\tilde{N}(k/\tilde{k}_0)(k^4/k_c^4)$, which is far smaller than the intraband part of the fluctuation of the majority carriers. Therefore, there cannot be any coherent long-range correlations between minority carriers in a metal. We may also remark that the interband part of (5.2) is proportional to k^2. For low k, its amplitude becomes very large compared to the intraband terms, and its size may in fact overcome the frequency mismatch.

Consider now the opposite case, in which the majority carriers fill a band completely, as is the case with valence electrons in a semiconductor. We then need only consider the interband part of (5.2) which is of order

$$Nk^2\frac{\hbar}{2m}\frac{\langle\omega_{0n}{}^3\rangle_{\mathrm{Av}}}{\omega^4}.$$

Furthermore the dielectric constant ϵ is of order

$$\omega^2/\langle\omega_{0n}{}^2\rangle.$$

The minority-minority interaction is then measured by $\tilde{N}(\langle\omega_{n0}{}^4\rangle/\omega^4)$ (with an extra factor $k/\tilde{k}_0$ if the minority gas is degenerate). The amplitude of the majority fluctuations becomes negligible when $k^2 < (\tilde{N}/N)(2m\langle\omega_{n0}\rangle/\hbar)$. Furthermore, we may expect the effect of the majority fluctuations to be reduced markedly because of their high frequency. Therefore, we may safely use (4.5) to treat the minority-minority correlations down to wavelengths of the order of the minority-carrier spacing. To conclude, in order for a selected group of minority carriers to undergo correlated motion with small wave vector and frequency, there must be an energy gap in the excitation spectrum of the majority carriers.

Let us now consider what kind of correlated elementary excitations may occur for the minority carriers. First, we may obtain bound states between several minority carriers. Remark that such states are precisely those which we miss when we make a perturbation treatment of the Coulomb interaction, since they have no equivalent in the independent-particle model. The simplest case which we can imagine is the one of a hole and an electron bound together in an insulator, an exciton. In NaCl, for instance, the radius of the exciton is fairly small, and we do not know too well how to take into account the screening due to valence electrons. On the other hand, in a semiconductor, the exciton wave function is very spread out, and the screening just appears through the dielectric constant.

The same kind of problem is encountered when a conduction electron forms a bound state with a defect in the solid, as for impurity states in semiconductors,[5] or for bound states around an atom ionized by x-ray absorption.[11] The preceding remarks still hold. An interesting case is the formation of positronium.[12] There, the radius of the bound state is very small ($<r_s$), and we are in the simple case mentioned at the beginning of this section; there is little screening, and positronium may perhaps exist in metals as well as in insulators. In the intermediate case (radius of the bound state of the order of r_s), we simply do not know what happens. There may, or may not, exist bound states, and the distinction between metals and insulators is irrelevant.

In addition to bound states, the correlations between minority carriers may give rise to collective effects, i.e., to minority plasmons, and to a screening of the minority-carrier interactions by one another. This is precisely what happens for conduction electrons in semiconductors. (Such a situation might also occur for s electrons in transition metals, although in this case the fluctuations of d electrons and the damping by individual transitions tend strongly to destroy any organized motion of the s electrons alone.) In Ge, for instance, the conduction plasmons will be in the microwave range,[13] and must not be confused with the valence plasmons which lie in the far ultraviolet. We may calculate the frequency, ω_c, of the conduction-electron plasmons, from the effective interaction, (4.5).

Since conduction-electron density fluctuations $\tilde{\rho}_k$, oscillate at a frequency ω_c, we may simply replace $\epsilon(\omega_{\mu\nu})$ by $\epsilon(\omega_c)$. We then apply the general treatment of NP I to conduction electrons alone, replacing $M_k{}^2$ by $M_k{}^2/\epsilon_{\mathrm{val}}(k,\omega_c)$. The dispersion relation for the conduction plasmon frequency ω_c is easily found to be

$$\frac{4\pi e^2}{m\epsilon_{\mathrm{val}}(k,\omega_c)}\sum_\nu\frac{f_{0\nu}(k)}{\omega_c{}^2-\omega_{0\nu}{}^2}=1, \tag{5.3}$$

where the index ν refers to excited states of conduction electrons alone. If now we replace $\epsilon_{\mathrm{val}}(k,\omega_c)$ by the expression obtained in NP II, (5.3) becomes

$$\frac{4\pi e^2}{m}\left\{\sum_n\frac{f_{0n}(k)}{\omega_c{}^2-\omega_{0n}{}^2}+\sum_\nu\frac{f_{0\nu}(k)}{\omega_c{}^2-\omega_{0\nu}{}^2}\right\}=1, \tag{5.4}$$

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[11] J. Friedel, Phil. Mag. **43**, 153 (1952).

[12] See the review particle by R. Ferrell, Revs. Modern Phys. **28**, 308 (1956).

[13] These conduction plasmons are precisely those considered by Dresselhaus, Kip, and Kittel in their study of magnetoplasma effect (coupling between plasma and cyclotron resonances) [Phys. Rev. **100**, 618 (1955)].

where the index n refers to excited states of valence electrons. Equation (5.4) is just the equation determining the frequency ω of the (valence+conduction) plasmons. Therefore, there is only one dispersion relation which has two roots; a high-frequency root in the ultraviolet range, and a low-frequency root in the microwave range. The existence of a *single* dispersion relation is a consequence of the fact that it follows simply from a study of the equations of motion for the most general longitudinal wave propagated by the electrons.[14]

In practice, we may simplify (5.4) considerably. In most cases, $\hbar\omega_c$ will be smaller than 1/10 ev, much smaller than any excitation frequencies of valence electrons (which are certainly larger than the energy gap). We may therefore replace $\epsilon_{\text{val}}(k,\omega_c)$ by the static dielectric constant ϵ_{val}. Furthermore, only intraband transitions will contribute to the plasmons. Therefore, (5.4) reduces to

$$\omega_c^2=4\pi N_c e^2/(m^*\epsilon_{\text{val}}),\qquad(5.5)$$

where N_c is the number of conduction electrons, and m^* their effective mass.

As a counterpart of the minority plasmons, there exists a mutual screening of the minority carriers. If $\langle\tilde{v}^2\rangle$ denotes the average square velocity of the conduction electrons, the corresponding screening wavelength $\tilde{k}_c$ is given by

$$\tilde{k}_c^2\sim\omega_c^2/\langle\tilde{v}^2\rangle.\qquad(5.6)$$

For a very low density of minority carriers, k_c is very small, and the screening is only of importance for long-range electrostatic phenomena, such as the scattering of free carriers by ionized impurities in a semiconductor.[15] When the density of carriers increases, k_c increases also, and it may happen that the screening radius becomes smaller than the radius of some bound state (exciton, impurity states, etc.). In such a case, the collective effects destroy the bound state.[16] In some sense, the bound states (as excitons), and the collective excitations at comparable wavelengths, are complementary. Either may exist, but not both.[17]

A majority plasmon corresponds to minority and majority charges oscillating in phase. On the contrary, in a minority plasmon, the two kinds of charges oscillate out of phase, the majority carriers screening the restoring field of the minority ones. One may then imagine a more complicated case, in which there are two kinds of minority carriers such as electrons and holes in a semiconductor or a semimetal. In a minority plasmon, these two carriers oscillate out of phase. One may inquire whether there is an additional longitudinal mode in which they oscillate in phase. This problem is entirely similar to the problem of optical and acoustic phonons in an ionic crystal: by analogy, we may call these new modes "acoustic plasmons." We have considered the possible existence of acoustic plasmons in a gas containing two types of free carriers.[18] Here we summarize the physical content of our results.

Acoustic plasmons represent an excitation in which one kind of carrier (the "heavy" one) is followed, and hence screened, by the other (the "light" particle). A condition for their existence is that the "light" particles be sufficiently numerous and mobile to follow closely and in phase the motion of the "heavy" particles. This condition is equivalent to the applicability of the adiabatic approximation. Consider the case of equal numbers, $\tilde{N}$, of light and heavy particles, both of which form a degenerate electron gas. The above condition implies that their masses, $\tilde{m}$ and $\tilde{M}$, are very different ($\tilde{m}\ll\tilde{M}$). Their original interaction is screened by the dielectric constant ϵ of the majority carriers. Furthermore, the screening of the heavy minority carriers by the light ones may be described by the dielectric constant of the latter, $\tilde{\epsilon}$, which is easily shown to be

$$\tilde{\epsilon}\cong\frac{3\omega_c^2}{k^2\tilde{v}_0^2}=\frac{12\pi\tilde{N}e^2}{k^2\tilde{v}_0^2\epsilon\tilde{m}},\qquad(5.7)$$

where ω_c denotes the frequency of the minority "optical" plasmons, and $\tilde{v}_0$ the Fermi velocity of the light particles. The effective interaction between heavy particles is then

$$\sum_k \frac{M_k^2}{2\epsilon\tilde{\epsilon}}\tilde{\rho}_k{}^{\text{heavy}}\tilde{\rho}_{-k}{}^{\text{heavy}}.\qquad(5.8)$$

In the adiabatic approximation, we may use (5.8) to treat the correlations of heavy particles among themselves. Equation (5.8) then gives rise to acoustic plasmons whose frequency Ω is given by

$$\Omega^2=\frac{\tilde{N}}{\tilde{M}}k^2\frac{M_k^2}{\epsilon\tilde{\epsilon}}=\frac{1}{3}\frac{\tilde{m}}{\tilde{M}}\tilde{v}_0^2k^2.\qquad(5.9)$$

The acoustic plasmons therefore propagate at a constant velocity,

$$s=(\tilde{m}/3\tilde{M})^{\frac{1}{2}}\tilde{v}_0.$$

The requirement for the validity of an adiabatic treatment turns out to be that the velocity s be much faster than the average heavy-particle velocity, and

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[14] An outline of such a treatment is given in the appendix of NP I.

[15] The use of a Debye screening wavelength in this problem leads to the Brooks-Herring formula. See for instance, P. R. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).

[16] This probably explains why excitons are so difficult to observe in a semiconductor. One needs a minimum number of free carriers to have a reasonable number of excitons, so that one then encounters rapidly the limit set up by collective effects. This problem has been studied by P. Morel, Diplôme d'Etudes Supérieures, Université de Paris, France, 1955 (unpublished).

[17] A similar conclusion has been reached by N. F. Mott [Proc. Phys. Soc. (London) **A62**, 416 (1949)].

[18] A brief preliminary account of our results may be found in D. Pines, Can. J. Phys. **34**, 1379 (1956). The detailed Hamiltonian treatment of the problem will be the subject of a forthcoming paper.

much slower than the light-particle velocity. This is realized if $\tilde{m}/\tilde{M}$ is small enough.[19] We remark that if one expresses ϵ and $\bar{\epsilon}$ in terms of the $f_{0n}(k)$ and ω_{n0}, one obtains for the acoustic plasmons the same dispersion equation which we encountered for the other two kinds of plasma waves.

It must be recognized that the above treatment is somewhat idealized. In fact, one very rarely encounters solids where there exist two groups of degenerate carriers with very different masses. Such a situation may occur in semimetals, or as a transient effect in semiconductors. It is tempting to apply the concept of "acoustic plasmons" to electrons and holes in a metal, but we do not believe it is truly applicable. First, the fluctuations of majority carriers destroy any long-range order at such low frequency. Furthermore, it was pointed out to us by Feynman[20] that in a metal there occurs a very fast recombination of holes and electrons, which would completely damp out the acoustic plasmons. At the present stage of the game, these new "elementary excitations" are, therefore, of a somewhat odd and tentative character. They may nevertheless prove to be useful in explaining odd effects.

6. PLASMONS IN SOLIDS

In this section we should like to consider anew the effects of Coulomb interaction and particularly the plasmon spectrum of solids, in the light of what we have learned in this paper and the preceding papers of this series. Our general point of view is that outlined in NP I and NP II, that the relative importance of the Coulomb interactions is determined by the competition at a given wavelength between ω_p, the free-electron plasma frequency, and $\bar{\omega}_{n0}$, the average one-electron excitation frequency.

Let us first consider the extreme case, $\bar{\omega}_{n0} \gg \omega_p$. Such a case is rather exceptional. It might occur for molecular crystals, in which the valence electron density is small (ω_p small), and the excitation frequency ω_{n0} is large, e.g., the solid rare gases. The effect of the Coulomb interaction is then small, and is well treated by a perturbation technique. There are no plasma oscillations, and the electrons display entirely individual particle behavior. The polarizability is small, leading to a refractive index in the visible range which is almost 1.

The opposite extreme corresponds to all ω_{n0} of the valence electrons being much smaller than ω_p. That is precisely what occurs at long wavelengths for free electrons, as is discussed in BP III. For actual solids, this implies that only interband transitions such that $\omega_{n0} < \omega_p$ have an appreciable oscillator strength. This is in fact quite possible: $\hbar\omega_p$ is generally between 10 and 20 ev. This is a fairly large energy range within which we may have several bands which collect most of the f_{0n}. Such appears to be the situation in most of the "well-behaved" metals, e.g., alkali metals, the alkaline earths, Al. It is also the case for the usual "valence" semiconductors, like Si and Ge. These have an energy gap of order 1 ev, much smaller than ω_p, which does not matter at all as far as collective behavior is concerned.

TABLE I. A comparison between $\hbar\omega_p$ and $\hbar\omega_{\text{el}}$ in solids for which the valence electrons are weakly bound ($\bar{\omega}_{n0} \ll \omega$). The quantity ω_p is calculated under the assumption that all valence electrons are free (2 per atom for Mg, 3 for B, 4 for C, $\cdots$); ϵ is obtained from static measurements for Si and Ge, from the index of refraction in the visible range for B and C; ω_{el} is taken from the review article of Pines.[a]

Element	Be	Mg	Al	B	C	Si	Ge
$\hbar\omega_p$(ev)	19	11	16	24	25	17	16
$\hbar\omega_{\text{el}}$(ev)	19	10	15	19	22	17	17
ϵ				6.2	5.7	12	16

[a] See reference 22.

For such solids, the collective treatment is essential. We expect them to show plasma oscillations, at a frequency very close to the free electron ω_p. Their electronic polarizability is usually very high, an indication of very strong screening. In some cases, it may happen that the core shells have a non-negligible polarizability (for instance for the heavy alkali metals, K, Rb, Cs). From NP I, we know that the plasma frequency must then be corrected for the dielectric constant of the core.

Let us compare these conclusions with experiment. In a subsequent paper[21] we shall see that there are two ways of obtaining the plasma frequency experimentally. One is the measurement of the energy loss of fast electrons passing through thin solid foils.[22] We shall denote the corresponding observed value of ω by ω_{el}. This determination is not always reliable, but it has been carried out for a wide variety of solids. The other method of obtaining ω involves the optical properties. As shown, for instance, in NP II, when the frequency of an electromagnetic wave reaches the plasma frequency, the solid passes from a reflecting region to a transmitting region. This is a very accurate measurement of ω. Unhappily, the corresponding frequency lies in the far ultraviolet, and the experiment has been carried out only for the alkali metals. We shall denote by ω_{opt} the corresponding results for the plasma frequency.

In Table I, we give the calculated ω_p and experimental ω_{el} for three metals, two semiconductors and two insulators. For the insulators and semiconductors, we furthermore give their dielectric constant ϵ. We calculate ω_p assuming all valence electrons free (4 per atom for C, as an example). For the three metals, the

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[19] In a metal, one may consider the valence electrons as light particles, and the ions as heavy ones. The above treatment then applies. The acoustic plasmons are just the usual sound waves, and (5.8) yields the sound velocity. This problem has been treated by Staver [T. Staver, thesis, Princeton University, 1952 (unpublished); D. Bohm and T. Staver, Phys. Rev. **84**, 836 (1952)].

[20] R. P. Feynman (private communication).

[21] P. Nozières and D. Pines (to be published), NP IV.

[22] For a detailed discussion of this method and its results, see D. Pines, Revs. Modern Phys. **28**, 184 (1956).

TABLE II. A comparison between theoretical and experimental results for alkali metals. ω_p = free-electron plasma frequency; ω = the same corrected for core polarizability; ω_{opt} = value measured in optical experiment; ω_{el} = value measured in energy-loss experiment. (Data taken from reference 22.)

Element	Li	Na	K	Rb	Cs
$\hbar\omega_p$(ev)	8.1	6.0	4.4	4.0	3.6
$\hbar\omega$(ev)	8.0	5.7	3.9	3.4	2.9
$\hbar\omega_{\mathrm{opt}}$(ev)	8.02	5.91	3.94	3.65	3.27
$\hbar\omega_{\mathrm{el}}$(ev)	9.5	5.4	3.8		

agreement is excellent, as is the case for Si and Ge, which have a very high polarizability. For all these elements, the ω_{n0} are therefore much smaller than ω_p. We expect narrow undamped plasmon lines, which are, in fact, observed. On the other hand, B and C have polarizabilities which, although large, are definitely smaller than those of Si and Ge. For these elements, many ω_{n0} are of the order of ω_p. This explains the shift of the line from the free electron value. It also explains the observed fact that the plasma line in B and C is much broader than that in Si and Ge. This conclusion is consistent with the known fact that the band gap of C is much larger than that in Si.

In Table II, we give an example of the corrections due to the core polarizability. We obtain the polarizabilities from values given by Van Vleck.[23] We denote by ω the corrected theoretical plasma frequency. We see that ω may differ appreciably from ω_p. The agreement between theoretical values and the optical data is good. The energy-loss data do not fit very well. The discrepancy is perhaps not surprising in view of the severe experimental difficulties arising from oxidation.

The case of all solids of Tables I and II is comparatively clean cut: the valence electrons are weakly bound ($\omega_{n0} \ll \omega$), giving narrow plasma lines, while the core electrons are strongly bound ($\omega_{n0} \gg \omega$), and influence the collective motion only slightly. Such is no longer the situation when we consider the transition elements, or the metals which follow them in the periodic table. We shall here consider two series of such elements.

In Table III, we give the observed quantum of energy loss, and the theoretical ω_p for the elements from Ti to Zn. The quantity ω_p is calculated assuming all s and d electrons to be free (4 per atom for Ti, 12 for Zn). Such a value does not agree with experiment, since the d electrons have excitation frequencies ω_{n0} which are of order of ω_p. As the atomic number of the element increases, the inner d electrons become more and more bound. We therefore expect the average ω_{n0} to increase from Ti to Zn. A simple inspection of the dispersion relation shows that the theoretical frequency ω is at first larger than ω_p, and finally much smaller. The accidental crossover occurs when as many states lie above and below ω. This seems to be observed experimentally. The accidental agreement occurs for Cr, and is also found for other elements with 6 electrons per atom, such as Mo, W, Se.[22] One may argue qualitatively that the width of the plasma line will be largest when the average ω_{n0} is just equal to ω, i.e., when the accidental agreement between ω and ω_p occurs. This seems to be observed experimentally, the Cr line being broadest, although its experimental verification is by no means completely well-established.[22]

TABLE III. Comparison between theory and experiment for transition metals. ω_p is calculated for a gas of free s and d electrons. (Data taken from reference 22.)

Element	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn
$\hbar\omega_p$(ev)	17	24	28	31	34	35	36	32
$\hbar\omega_{\mathrm{el}}$(ev)	22	24	22	21	21	23	20	23

The constancy of the observed ω_{el} throughout the transition element series is quite striking. This strongly suggests that only a limited number of d electrons may take part in the plasma, that is that only the crust of the d shell is free enough to sustain a collective oscillation. Thus the low-lying extra d electrons are so tightly bound to the ion cores that they may be regarded as frozen compared to the outer d carriers.

TABLE IV. Comparison between theory and experiment for metals following the transition series. ω_p is calculated for a plasma of free s and p electrons. (Data taken from reference 22.)

Element	Ag	Cd	In	Sn	Sb	Te
$\hbar\omega_p$(ev)	9	11	11	12	14	15
$\hbar\omega_{\mathrm{el}}$(ev)	23	20	12	12	15	18

Let us now turn to the case of Cu and Zn. The free-electron plasma frequency calculated for s electrons alone is 11 ev for Cu and 13 ev for Zn, while for the s and d electrons it is respectively 36 and 32 ev. The average excitation energy of a d electron is of order 4 ev for Cu, 10 ev for Zn. We are therefore exactly in the intermediate range. We may include s and d electrons in the plasmons; there is then a large d electron-plasmon coupling which depresses the plasma frequency ω from its free-electron value $\omega_p(s,d)$, since the d electrons are not truly free. Alternately, we may consider only a plasma of s electrons. The large polarizability of the d shell then markedly modifies the electrostatic behavior; since the d electrons are not truly bound. Therefore, neither approach is satisfactory. However, the average value of ω_{n0} is somewhat smaller than ω. Therefore, we believe the collective approach with an s-d plasma is somewhat more suitable than that with an s-plasma alone. In particular, it leads much more naturally to a discussion of the line width (which is large). Let us remark that the dilemma does not concern the existence of collective modes: the plasmons exist. Our choice is rather one involving the formulation of the interaction of the plasmons with the d shell.

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[23] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), p. 225.

Let us now consider another series, from Ag to Te. In Table IV, we give experimental and theoretical results, ω_p being calculated for s and p electrons alone. For Ag and Cd, we can draw the same conclusions as for Cu and Zn; the d shell is so polarizable that an approach which includes the d electrons in the plasmons is better. The discrepancy between ω_p and ω_{el} is therefore not surprising. For In and Sn, the electric charge of the ion increases, and the polarizability of the d shell decreases (ϵ_{core} is roughly 1.3 for In and 1.2 for Sn). It is no longer necessary to include d electrons in the plasmons. However, ϵ_{core} is still appreciably different from 1, and the agreement between ω_p and ω_{el} is almost too good. The core polarization is perhaps compensated by an interband effect of the s and p electrons. Such an effect is also suggested by the width of the line, which is definitely larger than for Be and Al. For Sb, the situation is at its best: the d shell is no longer polarizable, while the s and p electrons are still sufficiently free. For Te, on the contrary, the s electrons begin to be tightly bound, and this pushes up the plasma frequency, in accordance with our dispersion relation. (The situation is there quite analogous to that in Ti.) For this series, the line is definitely broader than that for Al, which indicates a larger spread in ω_{n0}.

TABLE V. Comparison of the experimental and theoretical plasma frequencies for various compounds. ϵ is the dielectric constant of the solid in the visible range. (Data taken from reference 22.)

Compound	ZnS	PbS	BeO	MgO	Al_2O_3	SiO_2	SnO_2	KBr	KCl	NaCl
$\hbar\omega_p$(ev)	17	16	29	25	27	25	26	13	14	16
$\hbar\omega_{el}$(ev)	17	15	29	25	23	25	20	13	13	16
ϵ	5.6	15	3.0	3.0	3.1	2.2	4	2.4	2.2	2.4

Let us now consider the situation in compounds. In Table V we compare experimental and theoretical values of the characteristic energy loss for a group of compounds. We also give the dielectric constant derived from the index of refraction in the visible range. The quantity ω_p is obtained by including all the valence electrons outside the last closed shell (4 electrons/atom for Pb, 6 to O, 7 for Cl, etc.). Clearly such an approximation, although it be the most natural one in the spirit of our general approach, cannot always be successful. Thus in Cl, even though the plasma frequency is 20 ev, the low-lying electrons should not be regarded as free to take part in a plasma oscillation.

For the sulfides, the polarizability is rather large, the electrons are rather weakly bound, and the excellent agreement of ω_{el} and ω_p is not surprising. This suggests that the 6 valence electrons of S are not very tightly bound, which is supported by the existence of hexavalent sulfur compounds. For the oxides, on the contrary, ϵ is smaller; and the observed agreement is a bit puzzling. The s and p electrons in O are rather tightly bound (there are only divalent compounds of oxygen). The agreement for MgO and SiO_2 might be due to a compensation of the type observed for Cr. Finally, the excellent agreement observed for the halides is definitely surprising. The polarizability is small, and the plasmon frequency should be considerably shifted with respect to ω_p: in this case, we believe the agreement to be fortuitous. The results are certainly striking, and we believe they deserve further investigation.

7. CONCLUSION

We here summarize our views on the present theoretical understanding of the nature of the elementary excitations in solids. The situation with respect to plasmons is relatively straightforward. For long wavelengths we expect them to constitute well-defined elementary excitations in nearly all solids. When k is of the order of k_c, the damping of the plasmons by the individual electrons becomes sufficiently strong that it is no longer appropriate to regard the plasmon as an elementary excitation. Where, however, plasmons exist, we may carry out a satisfactory theoretical treatment of their behavior and this treatment formed the basis for NP I.

The situation with regard to individual electron-like elementary excitations is not quite so satisfactory. After separating out the plasmons, we are left with a set of interacting electrons plus a set of subsidiary conditions (equal in number to the plasmon degrees of freedom) on the electronic wave functions. If we neglect the long-range part of the interactions and the subsidiary conditions, the approach of Landau and Gell-Mann may be used to show that the low-energy part of the excitation spectrum has essentially an individual-particle character, provided the number of excited effective electrons is small. Similarly, if we neglect the short-range part of the Coulomb interaction, we may show that the long-range interactions and the subsidiary conditions do not alter the individual-particle character of the low-lying excitations. For a small group of minority electrons, their joint effect is to "dress" each electron with a cloud of majority electrons. The effective interaction between the "dressed" electrons is given by Eq. (4.5).

It seems, therefore, likely that since we get individual-particle-like elementary excitations by taking into account, in turn, both the long-range and the short-range part of the electron interaction, the excitations should not change their character when both are taken into account. However, an explicit proof that this is the case does not yet appear possible. We have seen in Sec. 3 that there is good reason to believe that the subsidiary conditions, which guarantee that no plasmons exist in the "dressed" electron excitation spectrum, do not alter for long wavelengths the conclusions reached by using the approach of Gell-Mann and Landau. For wavelengths of the order of k_c^{-1}, the excitation spectrum is probably not at all simple, since one is just in the transition region between independent-particle and collective effects. Again, the inclusion of H_{sr} should not materially influence the conclusions reached in Sec. 4 concerning the effective interaction between the dressed electrons, but a definite proof has not been carried through.

We may next consider the possible existence of other elementary excitations in solids. These correspond to excitations in which a few minority carriers undergo correlated motion. Such correlated motion is only possible if the direct correlations between minority carriers are stronger than the fluctuating correlations with the much more numerous majority carriers. This occurs only when the majority carriers fill a band completely, as in semiconductors or semimetals. The effective interaction between minority carriers is then given by (4.5). One may imagine two kinds of such correlated motion. First, two minority carriers may be found together, forming an exciton. Second, for long enough wavelengths, the minority carriers may undergo a collective motion, such as the conduction-electron plasmon in semiconductors. As we have mentioned, excitons and minority plasmons should be regarded as "complementary" excitations. When the density of minority carriers increases, the cutoff k_c increases. When k_c^{-1} reaches the size of an exciton, the latter is destroyed, and replaced by plasmon degrees of freedom.

If there exist two kinds of minority carriers with very different masses, there is the possibility of yet another collective degree of freedom, which we have called "acoustic plasmon." Such a mode corresponds to an electronic sound wave in which the heavy carriers are screened by the light ones, as the ions are screened by the electrons in the usual sound waves in metals. In fact, the conditions for the existence of such an excitation are probably encountered only infrequently in actual solids.

We should like to point out that our approach is, to our knowledge, the only one which enables one to describe the minority plasmons from first principles. In the scheme of Landau and Gell-Mann, the interaction between excited particles is neglected at the outset. Kohn's treatment is very close to ours, but is limited to the case of a single electron, and, therefore, cannot be used to describe collective effects in the conduction band.

To summarize, we expect plasmons in nearly all solids, with the exception of molecular crystals. "Effective electron" excitations are also present in all solids. Correlated minority excitations, such as excitons or minority plasmons, can only appear in solids with almost empty bands, i.e., in semimetals, semiconductors, or insulators.

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Quantum Efficiency of Photoconductive Lead Sulfide Films*

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By using photoconductivity measurements it is shown that the quantum efficiency of lead sulfide films is almost unity. Mobilities calculated from photoconductivity data agree with mobilities obtained from noise and Hall measurements. It is concluded that noise at room temperature is not photon noise.

RECENTLY two independent methods have been used to calculate the quantum efficiency of photoconductive lead sulfide films. From signal-to-noise ratio measurements Wolfe[1] concluded that 0.25% of the photons are effective. From Hall constant and photoconductivity measurements Petritz[2] concluded that 62% are effective. Since both values are for lead sulfide films manufactured by the Eastman Kodak Company, it is worth while estimating the quantum efficiency for similar films by using a third independent method involving only photoconductivity measurements. The method previously used by Rose[3] is employed.

Figure 1 shows the usual circuit for measuring photoconductivity in lead sulfide films.

When the conductance of the lead sulfide G_c equals the conductance of the load resistor G_r, it can be shown that the photovoltage ΔV developed across G_r, is

$$\Delta V=\tfrac{1}{4}E\Delta G_c/G_c, \tag{1}$$

where E is the bias voltage.

The number of electronic charges which flow through G_r per electron-hole pair liberated photoelectrically is $\Delta VG_r/Fe$, where e is the electronic charge and F is the number of excitations per second. This equals the ratio of the lifetime of the majority carriers τ (assumed

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