

band and moves a short distance through the lattice before being retrapped as Br_2^- .

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Excitons and Plasmons in Superconductors*

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The Anderson-Rickayzen equations of motion for a superconductor derived within the random-phase approximation (RPA) are used to investigate the collective excitations of superconductors. A spherical harmonic expansion is made of the two-body interaction potential $V(\mathbf{k}, \mathbf{k}')$ and a spectrum of excitations whose energies lie within the energy gap 2Δ is obtained. These excitations may be characterized by the quantum numbers L and M involved in the potential expansion. For an L -state exciton to exist, the L -wave part of the potential must be attractive at the Fermi surface. Odd- L excitons have unit spin and may be considered as spin waves. For s -state pairing in the superconducting ground state, the plasmon mode corresponds to the $L=0$ exciton whose energy is strongly modified by the long-range Coulomb interaction. For a general potential several bound states may exist for given L and M . If the L -wave potential is stronger than the s -wave part of the potential, the system is unstable with respect to formation of L -state excitons. In this case, the ground state is formed with L -state pairing, special cases of which are the p -state pairing considered by Fisher and the d -state pairing proposed recently by several authors for the ground state of He^3 and nuclear matter. Corrections to the Anderson-Rickayzen equations are discussed which lead to a new set of exciton states if the L -wave potential is repulsive. These excitons are interpreted as bound electron-hole pairs, as opposed to the particle-particle excitons present with an attractive L -wave potential.

I. INTRODUCTION

IN the original theory of Bardeen, Cooper, and Schrieffer¹ an approximation to the ground-state wave function of a superconductor was obtained by a variational calculation. Basic to the theory is Cooper's result² that if a net attraction exists between the particles, the Fermi sea is unstable with respect to the formation of bound pairs. The BCS ground-state wave function is formed from a linear combination of normal state-like configurations in which particles are excited to states of low energy above the Fermi surface. In all of these normal configurations, the single-particle states are occupied in pairs ($\mathbf{k}\uparrow, -\mathbf{k}\downarrow$), so that interactions other than those between pairs of electrons of zero net momentum and spin are neglected. The theory leads to the single quasi-particle excitation spectrum given by $E_{\mathbf{k}} = (\epsilon_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}^2)^{1/2}$, where $\epsilon_{\mathbf{k}}$ is the Bloch energy measured with respect to the Fermi level and $\Delta_{\mathbf{k}}$ is the energy gap; that is, $2\Delta_{\mathbf{k}}$ represents the minimum energy required to

excite a pair of quasi-particles from the ground state. The quasi-particle excitations are fermions and no boson excitations appear other than the phonons.

This independent quasi-particle approximation has been surprisingly successful in explaining the thermodynamic properties as well as the acoustic and electromagnetic absorption, the nuclear spin relaxation, and the Meissner effect observed in the superconducting state. The derivation of the last has been criticized because it is not strictly gauge-invariant. This is primarily due to the neglect of residual interactions between particles in states $-\mathbf{k}$ and $\mathbf{k}' \neq \mathbf{k}$. These interactions give rise to a set of collective excitations (bosons) and lead to a gauge-invariant description of the Meissner effect.

For the investigation of these collective excitations, Anderson³ and Bogoliubov, Tolmachev, and Shirkov⁴ have used a generalized time-dependent self-consistent field or random-phase approximation (RPA). Their work shows that in the superconducting state, the plasmon frequency and the plasmon coordinate in the

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¹ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

² L. N. Cooper, *Phys. Rev.* **104**, 1189 (1956).

³ P. W. Anderson, *Phys. Rev.* **112**, 1900 (1958).

⁴ N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *A New Method in the Theory of Superconductivity* (Consultants Bureau, Inc., New York, 1959).

long-wavelength limit are essentially the same as in the normal state. They have also suggested the existence of the exciton modes lying within the energy gap which we investigate in the main body of this paper. A thorough discussion of the generalized RPA has been given by Rickayzen,⁵ who used it to derive the complex dielectric constant of a superconductor and the Meissner effect in a gauge-invariant manner. The BCS quasi-particle states $|\alpha\rangle$ and $|\beta\rangle$ do not satisfy the continuity equation; that is, $\langle\alpha|\nabla\cdot\mathbf{j}+\rho|\beta\rangle\neq 0$. When collective modes are included, the current and charge density operators \mathbf{j} and ρ are decomposed into a sum of individual-particle operators and collective operators. A virtual cloud of plasmons surrounds each quasi-particle, producing a back-flow current which leads to over-all charge conservation of the excitation. Therefore, the continuity equation is satisfied within the generalized RPA. This condition is sufficient to guarantee a gauge-invariant form of the electromagnetic response kernel. Tsuneto⁶ has applied Rickayzen's analysis to the problem of the surface impedance at finite frequency. While he finds that a precursor absorption exists for frequencies below that of the gap, his results, when applied to lead and mercury, predict an absorption which results from exciton states in the gap which is an order of magnitude smaller than that observed by Ginsberg, Richards, and Tinkham⁷ in these materials. The origin of the observed peak is uncertain at present.

In this paper we interpret the exciton mode in the superconductor as a bound pair of quasi-particles whose center-of-mass $[(\mathbf{r}_1+\mathbf{r}_2)/2]$ propagates with momentum $\hbar\mathbf{q}$. The exciton spectrum is investigated through the generalized RPA equations of motion proposed by Anderson in the form introduced by Rickayzen involving the quasi-particle operators $\gamma_{\mathbf{k}}$ of Bogoliubov⁸ and Valatin⁹ rather than $c_{\mathbf{k}}$, the usual electron operators. In these equations we make an expansion of the interaction potential $V(\mathbf{k},\mathbf{k}')$ in terms of spherical harmonics. It is found that excitons may be characterized by the approximate quantum numbers L and M describing the symmetry of the states with respect to the relative coordinate $\mathbf{r}_1-\mathbf{r}_2$. The existence of an L -state exciton (corresponding to the p, d, f, \dots excitons) is dependent on V_L being negative, where V_L is the L -wave part of $V(\mathbf{k},\mathbf{k}')$. The plasmon state corresponds to an s -state exciton whose energy is greatly increased by the long-range Coulomb interaction.

To obtain solutions to the Anderson-Rickayzen equations, we take matrix elements of the equations between a state with one collective excitation and the ground state which has been renormalized so as to include the zero-point motion of the collective modes. The results give two sets of solutions $\Lambda_{LM}(\mathbf{q})$ and

$\Gamma_{LM}(\mathbf{q})$ which correspond to what Anderson has termed odd and even solutions. We show that the $\Lambda_{LM}(\mathbf{q})$ modes are unphysical and that the $\Gamma_{LM}(\mathbf{q})$ modes correspond to the exciton states. The quantum numbers L and M are found to be exact in the limit of zero center-of-mass momentum $\hbar q$. For larger q , states of different L are mixed, although the mixing is small for $q\xi_0\ll 1$, where ξ_0 is the coherence length. The magnetic quantum number M , however, remains a good quantum number for all q if the potential has no crystalline anisotropy. The exciton energy for the $q=0$ case is plotted as a function of the L -wave coupling constant g_L defined by $g_L=-N(0)V_L/4\pi$, where $N(0)$ is the density of states in the normal phase at the Fermi surface. For $g_L>g_0$, the excitation energy proves to be imaginary and the implications of this with respect to the original BCS ground state are discussed. The $M\neq 0$ exciton may be considered as transverse collective excitations since they do not couple with a longitudinal field. In the general case if the ground state is formed from L_0, M_0 pairs, the L_0, M_0 exciton becomes the plasma oscillation.

In Sec. II we discuss the generalized RPA from a diagrammatic point of view. Solutions for the collective excitations are obtained in Sec. III. In Sec. IV we consider corrections to the Anderson-Rickayzen equations which lead to a new type of exciton state closely related to exciton states occurring in insulators.

II. EQUATIONS OF MOTION

We consider a system of electrons interacting via an effective two-body potential V , whose matrix elements in the Bloch state representation are given by

$$\langle\mathbf{k}_1',\mathbf{k}_2'|V|\mathbf{k}_1,\mathbf{k}_2\rangle=\frac{1}{2}\{V(\mathbf{k}_1,\mathbf{k}_1')+V(\mathbf{k}_2,\mathbf{k}_2')\} \\ \times\delta_{\mathbf{k}_1+\mathbf{k}_2,\mathbf{k}_1'+\mathbf{k}_2'}. \quad (2.1)$$

This potential arises from both Coulomb and phonon interactions between electrons and will be discussed in detail below. The Hamiltonian is expressed in the Heisenberg representation in terms of the operators $c_{\mathbf{k}\sigma}^\dagger$ and $c_{\mathbf{k}\sigma}$ which create and annihilate electrons in Bloch states of momentum \mathbf{k} and spin σ . They satisfy the usual Fermi anticommutation relations. The single-particle Bloch energies $\epsilon_{\mathbf{k}}$, measured relative to the Fermi energy E_F , are assumed to be of the form $(\hbar^2k^2/2m)-E_F$. The Hamiltonian of the system is given by

$$H=\sum_{\mathbf{k},\sigma}\epsilon_{\mathbf{k}}c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}+\frac{1}{2}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q},\sigma,\sigma'}V(\mathbf{k},\mathbf{k}+\mathbf{q}) \\ \times c_{\mathbf{k}+\mathbf{q},\sigma}^\dagger c_{\mathbf{k}'-\mathbf{q},\sigma'}^\dagger c_{\mathbf{k}',\sigma'} c_{\mathbf{k},\sigma}. \quad (2.2)$$

In the generalized RPA one studies the time evolution of bilinear operators of the form

$$b_{\mathbf{k}}^\dagger(\mathbf{q})=c_{\mathbf{k}+\mathbf{q}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger, \quad (2.3a)$$

$$b_{\mathbf{k}+\mathbf{q}}(-\mathbf{q})=c_{-\mathbf{k}-\mathbf{q}\downarrow} c_{\mathbf{k}\uparrow}, \quad (2.3b)$$

$$\rho_{\mathbf{k}\sigma}(\mathbf{q})=c_{\mathbf{k}+\mathbf{q}\sigma}^\dagger c_{\mathbf{k}\sigma}, \quad (2.3c)$$

⁵ G. Rickayzen, Phys. Rev. **115**, 795 (1959).

⁶ T. Tsuneto, Phys. Rev. **118**, 1029 (1960).

⁷ D. M. Ginsberg, P. L. Richards, and M. Tinkham, Phys. Rev. Letters **3**, 337 (1959).

⁸ N. N. Bogoliubov, Nuovo cimento **7**, 794 (1958).

⁹ J. G. Valatin, Nuovo cimento **7**, 843 (1958).

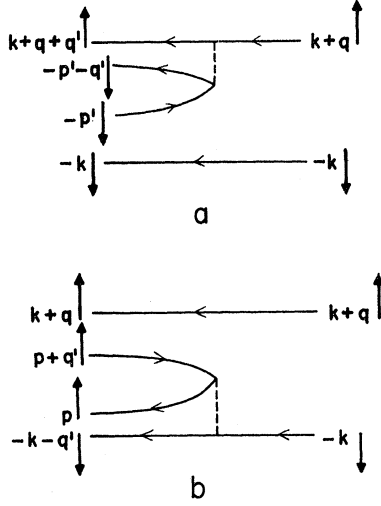


FIG. 1. The two vertices occurring in the full equations of motion for $b_k^\dagger(\mathbf{q})$. In the linearized equations only vertices with certain values of \mathbf{p}' and \mathbf{q}' are retained.

which create excitations with a fixed total momentum $\hbar\mathbf{q}$. It is helpful to consider the full-time development of these operators as being built up from the infinitesimal change of the operators in a time interval δt ; for example,

$$\delta b_k^\dagger(\mathbf{q}, t) = b_k^\dagger(\mathbf{q}, t + \delta t) - b_k^\dagger(\mathbf{q}, t) = (1/i\hbar)[H, b_k^\dagger(\mathbf{q}, t)]\delta t. \quad (2.4)$$

In the absence of the interaction V , the commutator reduces to $(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}})b_k^\dagger(\mathbf{q}, t)$ so that except for a phase factor, the operators are independent of time. We call any operator μ_α^\dagger an eigenoperator if its time dependence is given simply by a phase factor. The equation of motion,

$$[H, \mu_\alpha^\dagger] = \hbar\Omega_\alpha \mu_\alpha^\dagger, \quad (2.5)$$

for the operator guarantees that μ_α^\dagger , when applied to an eigenstate $|\beta\rangle$ of H , creates an eigenstate $|\alpha\rangle$ of H with an excitation energy $\hbar\Omega_\alpha$. From the Hermitian conjugate of (2.5) it follows that μ_α has the inverse effect of μ_α^\dagger . That is, while μ_α^\dagger adds energy to the system, μ_α subtracts energy, so that μ_α^\dagger and μ_α may be thought of as creation and annihilation operators of excitations of the system. A knowledge of the eigenoperators and their eigenenergies allows one to calculate dynamic properties of the system as well as the thermodynamic functions.

In certain cases the state $\mu_\alpha^\dagger|\beta\rangle$ may vanish identically; for example, if μ_α^\dagger creates pairs of fermions in states already occupied in $|\beta\rangle$. Another example is if the operator μ_α^\dagger scatters excitations already present in the initial state, in which case μ_α^\dagger vanishes when applied to the ground state. Both cases will be dealt with in the next section.

In the presence of the interaction V , the commutator (2.4) is complicated by the presence of terms involving four single-particle operators (c and c^\dagger 's). Therefore, the bilinear operators b^\dagger , b , and ρ are no longer eigenoperators of H and one must include products of four,

six, . . . , etc., single operators to form the μ_α^\dagger 's in this case. The question arises whether there is a consistent approximation in which the eigenoperators are represented as linear combinations of the bilinear operators b^\dagger , b , and ρ alone. Consider a typical term in the commutator arising from the interaction potential

$$\begin{aligned} & \frac{1}{2}V(\mathbf{p}, \mathbf{p}+\mathbf{q})[c_{\mathbf{p}+\mathbf{q}'\uparrow}c_{-\mathbf{p}'-\mathbf{q}'\downarrow}c_{-\mathbf{p}'\downarrow}c_{\mathbf{p}\uparrow}, b_k^\dagger(\mathbf{q})] \\ & = \frac{1}{2}V(\mathbf{p}, \mathbf{p}+\mathbf{q})\{c_{\mathbf{k}+\mathbf{q}+\mathbf{q}'\uparrow}c_{-\mathbf{p}'-\mathbf{q}'\downarrow}c_{-\mathbf{p}'\downarrow}c_{-\mathbf{k}\downarrow}^{\dagger}\delta_{\mathbf{p}, \mathbf{k}+\mathbf{q}} \\ & \quad - c_{\mathbf{k}+\mathbf{q}'\uparrow}c_{\mathbf{p}+\mathbf{q}'\uparrow}c_{-\mathbf{k}-\mathbf{q}'\downarrow}c_{\mathbf{p}\uparrow}^{\dagger}\delta_{\mathbf{p}', \mathbf{k}}\}. \end{aligned} \quad (2.6)$$

This expression is shown in diagrammatic form in Fig. 1. In the diagram, time is increasing from right to left with the incoming particles in states $\mathbf{k}+\mathbf{q}\uparrow$ and $-\mathbf{k}\downarrow$ entering from the right. The first term on the right-hand side of (2.6) is represented by Fig. 1(a) in which the interaction, represented by a dashed line, scatters the spin-up incoming particle to $\mathbf{k}+\mathbf{q}+\mathbf{q}'\uparrow$, creating a particle and a hole in states $-\mathbf{p}'-\mathbf{q}'\downarrow$ and $-\mathbf{p}'\downarrow$, respectively. In Fig. 1(b) the analogous process for the spin-down particle given by the second term in (2.6) is shown. If at time $t=0$ a pair of single particles is excited, at time δt there is a finite probability that a particle-hole pair has been created from the background of particles in the Fermi sea, with the incoming particles scattering to new states. In the next interval of time a similar process may occur involving any of the four excitations, and in general the "bare" incoming particles will create a complicated cascade of excitations leading to a decay of the initial state. In the generalized random phase approximation one keeps only those terms in the commutator which conserve the number of excitations allowing for both forward and backward propagation in time (see below). This procedure corresponds to a linearization of the equations of motion by replacing two single-particle operators in each term by a c -number given by the expectation value of this pair of operators with respect to a fixed state. If this state is chosen to be the BCS ground state, defined by

$$|\psi_0\rangle = \prod_{\mathbf{k}} [u_{\mathbf{k}} + v_{\mathbf{k}}b_{\mathbf{k}}^\dagger(0)] |0\rangle, \quad (2.7)$$

where $|0\rangle$ is the state with no particles present, conservation of momentum and spin leads to nonzero average values only for the operators $b_{\mathbf{k}}^\dagger(0)$, $b_{\mathbf{k}}(0)$, and $\rho_{\mathbf{k}\sigma}(0) \equiv n_{\mathbf{k}\sigma}$. In terms of the parameters $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$, these averages are

$$\langle\psi_0|b_{\mathbf{k}}^\dagger(0)|\psi_0\rangle = \langle\psi_0|b_{\mathbf{k}}(0)|\psi_0\rangle^* = u_{\mathbf{k}}v_{\mathbf{k}}, \quad (2.8a)$$

$$\langle\psi_0|n_{\mathbf{k}\sigma}|\psi_0\rangle = v_{\mathbf{k}}^2. \quad (2.8b)$$

The parameters $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are given by

$$u_{\mathbf{k}} = + (1 + \epsilon_{\mathbf{k}}/E_{\mathbf{k}})^{\frac{1}{2}}, \quad (2.9a)$$

$$v_{\mathbf{k}} = + (1 - \epsilon_{\mathbf{k}}/E_{\mathbf{k}})^{\frac{1}{2}}, \quad (2.9b)$$

where

$$E_{\mathbf{k}} = + (\epsilon_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}^2)^{\frac{1}{2}}, \quad (2.10)$$

and $\Delta_{\mathbf{k}}$ satisfies

$$\Delta_{\mathbf{k}} = \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') \frac{\Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}}. \quad (2.11)$$

This prescription gives a unique linearization of the equations of motion since for $q \neq 0$ there is at most one pair of operators with zero total momentum and spin in each term. The terms retained within this approximation are shown in Fig. 2.

(1) As shown in Fig. 2(a), the conventional particle-particle scattering vertex arises from the first term in (2.6) when $\mathbf{p}' = \mathbf{k}$. The factor of $\frac{1}{2}$ in front of V is cancelled by the term in the interaction with spins opposite to those in (2.6). This cancellation of the factor of $\frac{1}{2}$ occurs in each vertex.

(2) Another possibility, shown in Figs. 2(b) and 2(c), is for the scattered incoming particle to enter a bound state with the other incoming particle, the outgoing excitations being the particle-hole pair created from the sea. This possibility is allowed for in the linearization by including the finite average $\langle \psi_0 | b_{\mathbf{k}}^\dagger(0) | \psi_0 \rangle$, which may be regarded as the amplitude for the pair to enter the $q=0$ bound state, which is macroscopically occupied in $|\psi_0\rangle$. Since a finite fraction of all the electrons occupy this bound state in the superconducting state (corresponding to the finite fraction of helium atoms occupying the $k=0$ state is superfluid He^4), the small fluctuation $\sim N^{\frac{1}{2}}$ in the number of pairs N described by (2.7) leads to no difficulties in a large system. Notice that in Figs. 2(b) and 2(c), the incoming pair of particles is transformed into a particle-hole pair by the interaction. Therefore, $b_{\mathbf{k}}^\dagger(\mathbf{q})$ and $\rho_{\mathbf{k}\sigma}(\mathbf{q})$ are coupled in the equations of motion.

(3) In addition, there is the possibility that the scattered incoming particle enters the bound state with the particle created from the sea, leaving the hole and the other incoming particles as the outgoing excitations, as shown in Figs. 2(d) and 2(e). Due to the presence of the bound state, the incoming spin-up particle in Fig. 2(d) is transformed into a hole in the state of opposite momentum and spin. In the next instant of time the inverse process may occur. It is clear that the equations of motion are simplified if one introduces "quasi-particle" operators $\gamma_{\mathbf{k}\sigma}^\dagger$ which are the proper linear combinations of particle and hole creation operators to account for these processes. The appropriate transformation, introduced first by Bogoliubov and by Valatin, is

$$\gamma_{\mathbf{k}0}^\dagger = u_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger - v_{\mathbf{k}} c_{-\mathbf{k}\downarrow}, \quad (2.12a)$$

$$\gamma_{\mathbf{k}1}^\dagger = u_{\mathbf{k}} c_{-\mathbf{k}\downarrow}^\dagger + v_{\mathbf{k}} c_{\mathbf{k}\uparrow}. \quad (2.12b)$$

For mathematical simplicity we will follow Rickayzen by expressing the final linearized equations in terms of quasi-particle variables.

(4) The exchange contributions to the single-particle lines are shown in Figs. 2(f) and 2(g). As is well known, they lead to an anomalously low density of states at the Fermi surface in the normal metal unless a screened interaction is introduced. This point is discussed below. The exchange self-energy vertex can be accounted for, along with process (3), by the quasi-particle transformation (2.12).

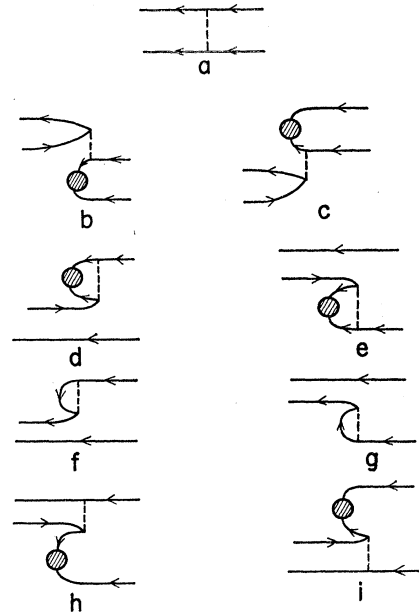


FIG. 2. The vertices retained in the full linearized equation of motion for $b_{\mathbf{k}}^\dagger(\mathbf{q})$. Vertices f , g , h , and i were neglected by Anderson and by Rickayzen. The particle-hole excitons are obtained only if the interactions shown in h and i are included.

(5) Finally, the unscattered incoming particle may enter the bound state with the particle created from the sea, leaving the hole and scattered particle as the outgoing excitations, as shown in Figs. 2(h) and 2(i). As in process (2), the pair of incoming particles is transformed into a particle-hole pair by the interaction. In the limit $q \rightarrow 0$, process (2) is more important than (5) in forming the plasmon state. Since the momentum transfer is always $\hbar\mathbf{q}$ in the former process, the large matrix element of the Coulomb interaction $4\pi e^2/q^2$ dominates the latter vertex in which the momentum transfer $\hbar\mathbf{q}'$ may assume any value. Anderson and Rickayzen have neglected processes (4) and (5), suggesting that their effect is primarily to renormalize the single-particle energies and the effective interaction.

The terms occurring in the linearized equation of motion for $\rho_{\mathbf{k}\sigma}(\mathbf{q})$ are shown in Fig. 3 and bear a close resemblance to those shown in Fig. 2. In the conventional RPA for the excitations in the normal state, only the polarization vertex [Fig. 3(b)] is retained. The so-called exchange scattering correction shown in Fig. 3(a), when combined with the polarization vertex, approximates the time evolution of $\rho_{\mathbf{k}\sigma}(\mathbf{q})$ by graphs of the type shown in Fig. 4. In the limit $q \rightarrow 0$, the exchange correction to the plasmon frequency vanishes. Since matrix elements of the equations of motion are taken with respect to RPA eigenstates, two pairs may be spontaneously created from the vacuum and may interact with the incoming excitations as in Fig. 4. This process may be viewed as a propagation of the excitations backward in time, familiar in the Green's function formulation of the problem.

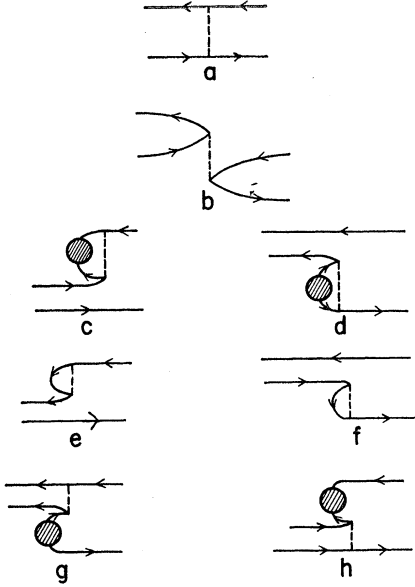


FIG. 3. The vertices retained in the full linearized equation of motion for $\rho_{\mathbf{k}\uparrow}(\mathbf{q})$. Vertices *a*, *e*, and *f* were neglected by Anderson and Rickayzen.

In the generalized RPA for the superconducting state the presence of the bound state gives rise to the vertices represented in Figs. 3(c), (d), (g), and (h), so that an incoming particle-hole pair can be transformed into either a pair of particles or a pair of holes. Therefore, the operators $b_{\mathbf{k}\uparrow}(\mathbf{q})$ and $b_{\mathbf{k}+\mathbf{q}}(-\mathbf{q})$ are coupled by the density operator $\rho_{\mathbf{k}\sigma}(\mathbf{q})$. The vertices occurring in the time development of $b_{\mathbf{k}\uparrow}(\mathbf{q})$ are identical to those in Fig. 2 except that all arrows are reversed and the momentum \mathbf{q} is replaced by $-\mathbf{q}$.

We turn now to the question of screening. Within the random-phase approximation to the normal state, the screened interaction line is represented in the limit of small wave-vector \mathbf{q} by a sum of diagrams of the form shown in Fig. 5. Rickayzen has shown that the dielectric constant is essentially unaffected by the pairing correlations occurring in the superconducting state. It is

$$[H, b_{\mathbf{k}\uparrow}(\mathbf{q})] = (\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}+\mathbf{q}}) b_{\mathbf{k}\uparrow}(\mathbf{q}) + V_D(\mathbf{q}) \rho(\mathbf{q}) (u_{\mathbf{k}} v_{\mathbf{k}} + u_{\mathbf{k}+\mathbf{q}} v_{\mathbf{k}+\mathbf{q}}) + \Delta_{\mathbf{k}} \rho_{\mathbf{k}\uparrow}(\mathbf{q}) + \Delta_{\mathbf{k}+\mathbf{q}} \rho_{-\mathbf{k}-\mathbf{q}\downarrow}(\mathbf{q}) - (1 - v_{\mathbf{k}}^2 - v_{\mathbf{k}+\mathbf{q}}^2) \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') b_{\mathbf{k}'\uparrow}(\mathbf{q}), \quad (2.15a)$$

$$[H, b_{\mathbf{k}+\mathbf{q}}(-\mathbf{q})] = -(\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}+\mathbf{q}}) b_{\mathbf{k}+\mathbf{q}}(-\mathbf{q}) - V_D(\mathbf{q}) \rho(\mathbf{q}) (u_{\mathbf{k}} v_{\mathbf{k}} + u_{\mathbf{k}+\mathbf{q}} v_{\mathbf{k}+\mathbf{q}}) - \Delta_{\mathbf{k}} \rho_{-\mathbf{k}-\mathbf{q}\downarrow}(\mathbf{q}) - \Delta_{\mathbf{k}+\mathbf{q}} \rho_{\mathbf{k}\uparrow}(\mathbf{q}) - (1 - v_{\mathbf{k}}^2 - v_{\mathbf{k}+\mathbf{q}}^2) \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') b_{\mathbf{k}'\uparrow}(-\mathbf{q}), \quad (2.15b)$$

$$[H, \rho_{\mathbf{k}\uparrow}(\mathbf{q})] = (\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}}) \rho_{\mathbf{k}\uparrow}(\mathbf{q}) + (v_{\mathbf{k}}^2 - v_{\mathbf{k}+\mathbf{q}}^2) V_D(\mathbf{q}) \rho(\mathbf{q}) + \Delta_{\mathbf{k}} b_{\mathbf{k}\uparrow}(\mathbf{q}) - \Delta_{\mathbf{k}+\mathbf{q}} b_{\mathbf{k}+\mathbf{q}}(-\mathbf{q}) + u_{\mathbf{k}} v_{\mathbf{k}} \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') b_{\mathbf{k}'\uparrow}(\mathbf{q}) - u_{\mathbf{k}+\mathbf{q}} v_{\mathbf{k}+\mathbf{q}} \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') b_{\mathbf{k}'\uparrow}(-\mathbf{q}), \quad (2.15c)$$

$$[H, \rho_{-\mathbf{k}-\mathbf{q}\downarrow}(\mathbf{q})] = (\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}) \rho_{-\mathbf{k}-\mathbf{q}\downarrow}(\mathbf{q}) - (v_{\mathbf{k}}^2 - v_{\mathbf{k}+\mathbf{q}}^2) V_D(\mathbf{q}) \rho(\mathbf{q}) - \Delta_{\mathbf{k}} b_{\mathbf{k}+\mathbf{q}}(\mathbf{q}) + \Delta_{\mathbf{k}+\mathbf{q}} b_{\mathbf{k}\uparrow}(\mathbf{q}) + u_{\mathbf{k}+\mathbf{q}} v_{\mathbf{k}+\mathbf{q}} \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') b_{\mathbf{k}'\uparrow}(\mathbf{q}) - u_{\mathbf{k}} v_{\mathbf{k}} \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') b_{\mathbf{k}'\uparrow}(-\mathbf{q}). \quad (2.15d)$$

The density operator $\rho(\mathbf{q})$ is given by

$$\rho(\mathbf{q}) = \sum_{\mathbf{k}, \sigma} c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger} c_{\mathbf{k}\sigma}.$$

As mentioned above, the equations can be considerably simplified by transforming to quasi-particle

variables. The Anderson-Rickayzen equations are then: casily seen that the vertices 2(b), 2(c), and 3(b) are automatically screened within the RPA through the presence of the polarization vertex [Fig. 3(b)] in the linearized equations. For example, when the vertex 2(b) is followed in time by a series of vertices 3(b), the effect is to replace the bare interaction line in 2(b) by the screened line shown in Fig. 5. Therefore in vertices 2(b), 2(c), and 3(b), the unscreened interaction V_D must be used. The potential V_D is given by

$$V_D(\mathbf{q}) = \frac{4\pi e^2}{q^2} + \frac{|v_q^i|^2}{\Omega^2 - (\omega_q^i)^2}, \quad (2.13)$$

where $\hbar\Omega$ is the energy of the excitation involved. Also, v_q^i is the bare electron-phonon interaction matrix element introduced by Bardeen and Pines¹⁰ and ω_q^i is the bare phonon frequency. It is essential, however, to introduce the interaction screened by the dynamical dielectric constant in the remaining vertices since it is impossible to replace the bare interaction line by the screened line through an iteration of vertices occurring in the linearized equations. The screened potential is of the form

$$V(\mathbf{k}, \mathbf{k}+\mathbf{q}) = \frac{4\pi e^2}{q^2 \kappa(\mathbf{q}, \omega_{\mathbf{k}, \mathbf{q}})}, \quad (2.14a)$$

where the dynamical dielectric constant is given by

$$\kappa(\mathbf{q}, \omega_{\mathbf{k}, \mathbf{q}}) = 1 + 4\pi\alpha_{\text{ion}}(\mathbf{q}, \omega_{\mathbf{k}, \mathbf{q}}) + 4\pi\alpha_{el}(\mathbf{q}, \omega_{\mathbf{k}, \mathbf{q}}) \simeq 1 - (\omega_q^i)^2 / \omega_{\mathbf{k}, \mathbf{q}}^2 + k_s^2 / q^2. \quad (2.14b)$$

Here, $\hbar\omega_{\mathbf{k}, \mathbf{q}} = \epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}}$ and k_s is the electronic screening wave number. In a more complete treatment involving coupled equations of motion for the electrons and the lattice, the energy $\hbar\omega_{\mathbf{k}, \mathbf{q}}$ would presumably be given in terms of the quasi-particle excitation energies.

For simplicity, we neglect the vertices shown in Figs. 2(h), 2(i), and 3(a). We also neglect the exchange self-energy correction since it simply renormalizes the single-particle energies. With these approximations, one obtains the equations first given by Anderson:

variables. The Anderson-Rickayzen equations are then:

$$[H, \gamma_{\mathbf{k}+\mathbf{q}\uparrow}^{\dagger} \gamma_{\mathbf{k}\uparrow}] = (E_{\mathbf{k}+\mathbf{q}} + E_{\mathbf{k}}) \gamma_{\mathbf{k}+\mathbf{q}\uparrow}^{\dagger} \gamma_{\mathbf{k}\uparrow} + V_D(\mathbf{q}) m(\mathbf{k}, \mathbf{q}) \rho(\mathbf{q}) - \frac{1}{2} l(\mathbf{k}, \mathbf{q}) A_{\mathbf{k}}(\mathbf{q}) + \frac{1}{2} n(\mathbf{k}, \mathbf{q}) B_{\mathbf{k}}(\mathbf{q}), \quad (2.16a)$$

¹⁰ J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

$$\begin{aligned}
 [H, \gamma_{k+q} \gamma_{k0}] & \\
 &= -(E_{k+q} + E_k) \gamma_{k+q} \gamma_{k0} - V_D(\mathbf{q}) m(\mathbf{k}, \mathbf{q}) \rho(\mathbf{q}) \\
 &\quad - \frac{1}{2} l(\mathbf{k}, \mathbf{q}) A_k(\mathbf{q}) - \frac{1}{2} n(\mathbf{k}, \mathbf{q}) B_k(\mathbf{q}), \quad (2.16b)
 \end{aligned}$$

$$[H, \gamma_{k+q, \sigma} \gamma_{k, \sigma}] = (E_{k+q} - E_k) \gamma_{k+q, \sigma} \gamma_{k, \sigma}. \quad (2.16c)$$

The coherence factors are defined by

$$l(\mathbf{k}, \mathbf{q}) = u_k u_{k+q} + v_k v_{k+q}, \quad (2.17a)$$

$$m(\mathbf{k}, \mathbf{q}) = u_k v_{k+q} + v_k u_{k+q}, \quad (2.17b)$$

$$n(\mathbf{k}, \mathbf{q}) = u_k u_{k+q} - v_k v_{k+q}, \quad (2.17c)$$

$$\dot{p}(\mathbf{k}, \mathbf{q}) = u_k v_{k+q} - v_k u_{k+q}, \quad (2.17d)$$

and the three collective variables are

$$\begin{aligned}
 A_k(\mathbf{q}) &= -\sum_{k'} V(\mathbf{k}, \mathbf{k}') [b_{k'}^\dagger(\mathbf{q}) - b_{k'+q}(-\mathbf{q})] \\
 &= -\sum_{k'} V(\mathbf{k}, \mathbf{k}') [l(\mathbf{k}', \mathbf{q}) (\gamma_{k'+q} \gamma_{k'}^\dagger \\
 &\quad - \gamma_{k'+q} \gamma_{k'}^\dagger) + \dot{p}(\mathbf{k}', \mathbf{q}) \\
 &\quad \times (\gamma_{k'+q} \gamma_{k'}^\dagger - \gamma_{k'+q} \gamma_{k'+q+1})], \quad (2.18a)
 \end{aligned}$$

$$\begin{aligned}
 B_k(\mathbf{q}) &= \sum_{k'} V(\mathbf{k}, \mathbf{k}') [b_{k'}(\mathbf{q})^\dagger + b_{k'+q}(-\mathbf{q})] \\
 &= \sum_{k'} V(\mathbf{k}, \mathbf{k}') [n(\mathbf{k}', \mathbf{q}) (\gamma_{k'+q} \gamma_{k'}^\dagger \\
 &\quad + \gamma_{k'+q} \gamma_{k'}^\dagger) - m(\mathbf{k}', \mathbf{q}) (\gamma_{k'+q} \gamma_{k'}^\dagger \\
 &\quad + \gamma_{k'+q} \gamma_{k'+q+1})], \quad (2.18b)
 \end{aligned}$$

$$\begin{aligned}
 \rho(\mathbf{q}) &= \sum_{k, \sigma} \rho_{k\sigma}(\mathbf{q}) \\
 &= \sum_{k'} [m(\mathbf{k}', \mathbf{q}) (\gamma_{k'+q} \gamma_{k'}^\dagger + \gamma_{k'+q} \gamma_{k'}^\dagger) \\
 &\quad + n(\mathbf{k}', \mathbf{q}) (\gamma_{k'+q} \gamma_{k'}^\dagger + \gamma_{k'+q} \gamma_{k'+q+1})]. \quad (2.18c)
 \end{aligned}$$

From (2.16c) we see that half of the normal mode operators are of the form $\gamma_{k+q} \gamma_{k\sigma}$, which has the eigenvalue $E_{k+q} - E_k$. These operators describe scattering of excitations already present in the initial state and vanish when applied to the ground state. Since we will always take matrix elements of the equations of motion between the ground state and an excited state, these quasi-particle conserving operators may be safely neglected.

III. SOLUTIONS OF EQUATIONS OF MOTION

For the analysis of the plasmon and exciton modes at temperature $T=0$ we begin with the Anderson-Rickayzen equations of motion (2.16) for the pair operators $\gamma_{k+q} \gamma_{k1}^\dagger$ and $\gamma_{k+q} \gamma_{k0}$. It must be kept in mind that the equations have been linearized with respect to the ground state involving s -state pairing between electrons of opposite spin and momentum, as our results depend critically upon this fact. The collective variables defined by (2.18) are substituted into the equations in order to obtain them in a form involving only the Bogoliubov-Valatin quasi-particle operators:

$$\begin{aligned}
 [H, \gamma_{k+q} \gamma_{k1}^\dagger] & \\
 &= v_k(\mathbf{q}) \gamma_{k+q} \gamma_{k1}^\dagger + V_D(\mathbf{q}) m(\mathbf{k}, \mathbf{q}) \\
 &\quad \times \sum_{k'} m(\mathbf{k}', \mathbf{q}) (\gamma_{k'+q} \gamma_{k'}^\dagger + \gamma_{k'+q} \gamma_{k'}^\dagger) \\
 &\quad + \frac{1}{2} l(\mathbf{k}, \mathbf{q}) \sum_{k'} V(\mathbf{k}, \mathbf{k}') l(\mathbf{k}', \mathbf{q}) (\gamma_{k'+q} \gamma_{k'}^\dagger \\
 &\quad - \gamma_{k'+q} \gamma_{k'}^\dagger) + \frac{1}{2} n(\mathbf{k}, \mathbf{q}) \sum_{k'} V(\mathbf{k}, \mathbf{k}') n(\mathbf{k}', \mathbf{q}) \\
 &\quad \times (\gamma_{k'+q} \gamma_{k'}^\dagger + \gamma_{k'+q} \gamma_{k'+q+1}). \quad (3.1a)
 \end{aligned}$$

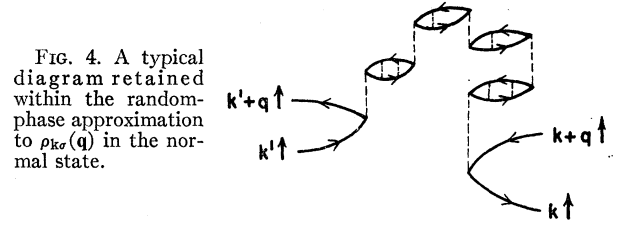


FIG. 4. A typical diagram retained within the random-phase approximation to $\rho_{k\sigma}(\mathbf{q})$ in the normal state.

$$\begin{aligned}
 [H, \gamma_{k+q} \gamma_{k0}] & \\
 &= -v_k(\mathbf{q}) \gamma_{k+q} \gamma_{k0} - V_D(\mathbf{q}) m(\mathbf{k}, \mathbf{q}) \\
 &\quad \times \sum_{k'} m(\mathbf{k}', \mathbf{q}) (\gamma_{k'+q} \gamma_{k'}^\dagger + \gamma_{k'+q} \gamma_{k'}^\dagger) \\
 &\quad + \frac{1}{2} l(\mathbf{k}, \mathbf{q}) \sum_{k'} V(\mathbf{k}, \mathbf{k}') l(\mathbf{k}', \mathbf{q}) (\gamma_{k'+q} \gamma_{k'}^\dagger \\
 &\quad - \gamma_{k'+q} \gamma_{k'}^\dagger) - \frac{1}{2} n(\mathbf{k}, \mathbf{q}) \sum_{k'} V(\mathbf{k}, \mathbf{k}') n(\mathbf{k}', \mathbf{q}) \\
 &\quad \times (\gamma_{k'+q} \gamma_{k'}^\dagger + \gamma_{k'+q} \gamma_{k'+q+1}). \quad (3.1b)
 \end{aligned}$$

Those operators $\mu_\alpha^\dagger(\mathbf{q})$ are now considered which are linear combinations of the bilinear products of γ_k 's and γ_k^\dagger 's appearing in the two equations of motion (3.1), and which create one elementary excitation of type α . Thus we desire

$$\mu_\alpha^\dagger(\mathbf{q}) = \sum_{\mathbf{k}} [\varphi_\alpha(\mathbf{k}, \mathbf{q}) \gamma_{k+q} \gamma_{k1}^\dagger + \chi_\alpha(\mathbf{k}, \mathbf{q}) \gamma_{k+q} \gamma_{k0}], \quad (3.2)$$

with

$$H \mu_\alpha^\dagger(\mathbf{q}) |0\rangle = [\hbar \Omega_\alpha(\mathbf{q}) + W_0] \mu_\alpha^\dagger(\mathbf{q}) |0\rangle, \quad (3.3)$$

where $|0\rangle$ is not the original ground state of BCS, but the renormalized ground state with $\mu_\alpha(\mathbf{q}) |0\rangle = 0$. The quantity $\hbar \Omega_\alpha(\mathbf{q})$ represents the energy of the excitation created by the operator $\mu_\alpha^\dagger(\mathbf{q})$. The elementary excitation $\mu_\alpha^\dagger(\mathbf{q})$ may be any one of the three types involved in the theory: a pair of excited quasi-particles in scattering states, a plasmon, or an exciton.

From Eq. (3.3) and the discussion of Sec. II, we have $[H, \mu_\alpha^\dagger(\mathbf{q})] |0\rangle = \hbar \Omega_\alpha(\mathbf{q}) \mu_\alpha^\dagger(\mathbf{q}) |0\rangle$. Since the commutator $[H, \mu_\alpha^\dagger(\mathbf{q})]$ is related to the time derivative of $\mu_\alpha^\dagger(\mathbf{q})$, the matrix element of $\mu_\alpha^\dagger(\mathbf{q})$ between the ground state $|0\rangle$ and the state $|1(\mathbf{q}, \alpha)\rangle$ containing one excitation of energy $\hbar \Omega_\alpha(\mathbf{q})$ must have the time dependence $\exp[i\Omega_\alpha(\mathbf{q})t]$. Now, Eq. (3.2), expresses $\mu_\alpha^\dagger(\mathbf{q})$, within the RPA, as a linear combination of the bilinear products $\gamma_{k+q} \gamma_{k1}^\dagger$ and $\gamma_{k+q} \gamma_{k0}$, so that we may write the inverse transformations as

$$\gamma_{k+q} \gamma_{k1}^\dagger = \sum_{\beta} [f_{\beta}(\mathbf{k}, \mathbf{q}) \mu_{\beta}^\dagger(\mathbf{q}) + \tilde{f}_{\beta}(\mathbf{k}, \mathbf{q}) \mu_{\beta}(-\mathbf{q})], \quad (3.4a)$$

$$\gamma_{k+q} \gamma_{k0} = \sum_{\beta} [g_{\beta}(\mathbf{k}, \mathbf{q}) \mu_{\beta}^\dagger(\mathbf{q}) + \tilde{g}_{\beta}(\mathbf{k}, \mathbf{q}) \mu_{\beta}(-\mathbf{q})]. \quad (3.4b)$$

Taking matrix elements of Eq. (3.4) between $|0\rangle$ and $|1(\mathbf{q}, \alpha)\rangle$ and using the orthonormality property of the excited states, we find

$$\begin{aligned}
 \langle 1(\mathbf{q}, \alpha) | \gamma_{k+q} \gamma_{k1}^\dagger | 0 \rangle & \\
 &= \sum_{\beta} f_{\beta}(\mathbf{k}, \mathbf{q}) \langle 1(\mathbf{q}, \alpha) | \mu_{\beta}^\dagger(\mathbf{q}) | 0 \rangle \\
 &= f_{\alpha}(\mathbf{k}, \mathbf{q}) \exp[i\Omega_{\alpha}(\mathbf{q})t], \quad (3.5a)
 \end{aligned}$$

$$\langle 1(\mathbf{q}, \alpha) | \gamma_{k+q} \gamma_{k0} | 0 \rangle = g_{\alpha}(\mathbf{k}, \mathbf{q}) \exp[i\Omega_{\alpha}(\mathbf{q})t]. \quad (3.5b)$$

The solution for the exciton mode dispersion relation is dependent on taking matrix elements of the equations

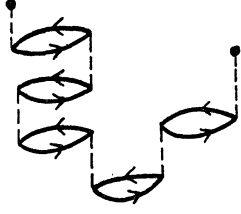


FIG. 5. The random-phase approximation to the screened interaction line.

of motion (3.1) between the states $|0\rangle$ and $|1(\mathbf{q}, \alpha)\rangle$ and using the relations (3.5a) and (3.5b) so that we obtain a set of c -number equations. The resultant system of linear equations may then be solved for the normal mode frequencies and the transformation coefficients f and g .

By taking matrix elements of (3.1), we obtain:

$$\begin{aligned} & [\hbar\Omega_\alpha(\mathbf{q}) - \nu_k(\mathbf{q})] f_\alpha(\mathbf{k}, \mathbf{q}) \\ &= V_D(\mathbf{q}) m(\mathbf{k}, \mathbf{q}) \sum_{\mathbf{k}'} m(\mathbf{k}', \mathbf{q}) [f_\alpha(\mathbf{k}', \mathbf{q}) + g_\alpha(\mathbf{k}', \mathbf{q})] \\ &+ \frac{1}{2} l(\mathbf{k}, \mathbf{q}) \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') l(\mathbf{k}', \mathbf{q}) [f_\alpha(\mathbf{k}', \mathbf{q}) - g_\alpha(\mathbf{k}', \mathbf{q})] \\ &+ \frac{1}{2} n(\mathbf{k}, \mathbf{q}) \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') n(\mathbf{k}', \mathbf{q}) \\ &\quad \times [f_\alpha(\mathbf{k}', \mathbf{q}) + g_\alpha(\mathbf{k}', \mathbf{q})], \quad (3.6a) \end{aligned}$$

$$\begin{aligned} & [\hbar\Omega_\alpha(\mathbf{q}) + \nu_k(\mathbf{q})] g_\alpha(\mathbf{k}, \mathbf{q}) \\ &= -V_D(\mathbf{q}) m(\mathbf{k}, \mathbf{q}) \sum_{\mathbf{k}'} m(\mathbf{k}', \mathbf{q}) [f_\alpha(\mathbf{k}', \mathbf{q}) + g_\alpha(\mathbf{k}', \mathbf{q})] \\ &+ \frac{1}{2} l(\mathbf{k}, \mathbf{q}) \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') l(\mathbf{k}', \mathbf{q}) [f_\alpha(\mathbf{k}', \mathbf{q}) - g_\alpha(\mathbf{k}', \mathbf{q})] \\ &- \frac{1}{2} n(\mathbf{k}, \mathbf{q}) \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') n(\mathbf{k}', \mathbf{q}) \\ &\quad \times [f_\alpha(\mathbf{k}', \mathbf{q}) + g_\alpha(\mathbf{k}', \mathbf{q})]. \quad (3.6b) \end{aligned}$$

From (3.6) it is evident that an explicit form for $V(\mathbf{k}, \mathbf{k}')$ must be chosen in order to proceed further. As emphasized in the foregoing, the BCS ground state about which the Anderson-Rickayzen equations have been linearized is one involving s -state pairing. Thus in the absence of crystalline anisotropy, the $q \rightarrow 0$ solutions must transform according to the irreducible representations of the full rotation group, i.e., the spherical harmonics. Because of this fact, we expand the two-body potential $V(\mathbf{k}, \mathbf{k}')$ in terms of spherical

harmonics. The coordinate system is chosen so that \mathbf{q} lies along the polar axis with θ and φ the polar and azimuthal angles of the wave vector of \mathbf{k}' and Θ and Φ the analogous quantities for \mathbf{k} . If ζ is the angle between \mathbf{k}' and \mathbf{k} , the use of the addition theorem gives

$$\begin{aligned} V(\mathbf{k}, \mathbf{k}') &= \sum_{l=0}^{\infty} \bar{V}_l(k, k') Y_{l0}(\zeta) \\ &= \sum_{l=0}^{\infty} V_l(k, k') \sum_{m=-l}^l Y_{lm}(\theta, \varphi)^* Y_{lm}(\Theta, \Phi), \quad (3.7) \end{aligned}$$

where

$$V_l(k, k') = (4\pi/2l+1)^{1/2} \bar{V}_l(k, k').$$

A further approximation is made in setting $V_l(k, k') = V_l$, a nonzero constant, for $|\epsilon| < \hbar\omega_c$ and zero otherwise. The quantity $\hbar\omega_c$ is the average phonon energy of the order of the Debye energy. We define the coupling constant g_L by

$$g_L = -N(0) V_L / 4\pi. \quad (3.8)$$

The BCS coupling constant is related to g_0 by

$$g_0 = -N(0) V_0 / 4\pi = N(0) V_{\text{BCS}} > 0.$$

It is convenient to introduce three new variables

$$\begin{aligned} \Lambda_{lm}(\mathbf{q}) &= \sum_{\mathbf{k}} n(\mathbf{k}, \mathbf{q}) V_l Y_{lm}(\theta, \varphi)^* \\ &\quad \times [f(\mathbf{k}, \mathbf{q}) + g(\mathbf{k}, \mathbf{q})], \quad (3.9a) \end{aligned}$$

$$\begin{aligned} \Gamma_{lm}(\mathbf{q}) &= \sum_{\mathbf{k}} l(\mathbf{k}, \mathbf{q}) V_l Y_{lm}(\theta, \varphi)^* \\ &\quad \times [f(\mathbf{k}, \mathbf{q}) - g(\mathbf{k}, \mathbf{q})], \quad (3.9b) \end{aligned}$$

$$Z(\mathbf{q}) = V_D(\mathbf{q}) \sum_{\mathbf{k}} m(\mathbf{k}, \mathbf{q}) [f(\mathbf{k}, \mathbf{q}) + g(\mathbf{k}, \mathbf{q})], \quad (3.9c)$$

where the subscript α has been dropped from both sides of the equations for simplicity. Equations (3.6) then express the transformation coefficients f and g in terms of the new variables Λ , Γ , and Z . By substituting these expressions into the defining relationships (3.9), we obtain the following coupled integral equations to determine the eigenfrequency $\Omega(\mathbf{q})$:

$$\begin{aligned} \Lambda_{LM}(\mathbf{q}) &= V_L \sum_{\mathbf{k}} n(\mathbf{k}, \mathbf{q}) \frac{1}{[\hbar\Omega(\mathbf{q})]^2 - \nu_k(\mathbf{q})^2} \{ 2\nu_k(\mathbf{q}) m(\mathbf{k}, \mathbf{q}) Z(\mathbf{q}) Y_{LM}^*(\theta, \varphi) + \nu_k(\mathbf{q}) n(\mathbf{k}, \mathbf{q}) \sum_{l,m} Y_{LM}^*(\theta, \varphi) \\ &\quad \times Y_{lm}(\theta, \varphi) \Lambda_{lm}(\mathbf{q}) + \hbar\Omega(\mathbf{q}) l(\mathbf{k}, \mathbf{q}) \sum_{l,m} Y_{LM}^*(\theta, \varphi) Y_{lm}(\theta, \varphi) \Gamma_{lm}(\mathbf{q}) \}, \quad (3.10a) \end{aligned}$$

$$\begin{aligned} \Gamma_{LM}(\mathbf{q}) &= V_L \sum_{\mathbf{k}} l(\mathbf{k}, \mathbf{q}) \frac{1}{[\hbar\Omega(\mathbf{q})]^2 - \nu_k(\mathbf{q})^2} \{ 2\hbar\Omega(\mathbf{q}) m(\mathbf{k}, \mathbf{q}) Z(\mathbf{q}) Y_{LM}^*(\theta, \varphi) + \hbar\Omega(\mathbf{q}) n(\mathbf{k}, \mathbf{q}) \sum_{l,m} Y_{LM}^*(\theta, \varphi) \\ &\quad \times Y_{lm}(\theta, \varphi) \Lambda_{lm}(\mathbf{q}) + \nu_k(\mathbf{q}) l(\mathbf{k}, \mathbf{q}) \sum_{l,m} Y_{LM}^*(\theta, \varphi) Y_{lm}(\theta, \varphi) \Gamma_{lm}(\mathbf{q}) \}, \quad (3.10b) \end{aligned}$$

$$\begin{aligned} Z(\mathbf{q}) &= V_D(\mathbf{q}) \sum_{\mathbf{k}} m(\mathbf{k}, \mathbf{q}) \frac{1}{[\hbar\Omega(\mathbf{q})]^2 - \nu_k(\mathbf{q})^2} \{ 2\nu_k(\mathbf{q}) m(\mathbf{k}, \mathbf{q}) Z(\mathbf{q}) + \nu_k(\mathbf{q}) n(\mathbf{k}, \mathbf{q}) \sum_{l,m} Y_{lm}(\theta, \varphi) \Lambda_{lm}(\mathbf{q}) \\ &\quad + \hbar\Omega(\mathbf{q}) l(\mathbf{k}, \mathbf{q}) \sum_{l,m} Y_{lm}(\theta, \varphi) \Gamma_{lm}(\mathbf{q}) \}. \quad (3.10c) \end{aligned}$$

From these three equations it is immediately seen that one good quantum number for the description of an

excitation is the magnetic quantum number M . In the sum over \mathbf{k} , the angular integration requires $m = M$, as

the only φ -dependent quantities involved are the spherical harmonics. Thus, M is a good quantum number regardless of the center-of-mass momentum $\hbar\mathbf{q}$.

(1) $\mathbf{q} \rightarrow \mathbf{0}$ Case

In the case of zero center-of-mass momentum, Eqs. (3.10) give L as an additional good quantum number. This follows since neither the coherence factors nor the energy $\nu_{\mathbf{k}}(\mathbf{q})$ of the quasi-particle pair are dependent on the polar angle in this case. The angular part of the sum $\sum_{\mathbf{k}}$ then reduces to

$$\int Y_{LM}^*(\theta, \varphi) Y_{lm}(\theta, \varphi) d\omega_k = \delta_{Ll} \delta_{Mm}.$$

The sum $\sum_{\mathbf{k}}$ is converted into an integral by letting

$$\sum_{\mathbf{k}} \rightarrow [v/(2\pi)^3] \int dk k^2 d\omega_k,$$

where the volume v of the normalization box is taken as unity. The radial integrals over k are all of the form

$$I_{ab\dots 0} = \frac{1}{(2\pi)^3} \int \frac{a(\mathbf{k}, 0)b(\mathbf{k}, 0)\dots}{(\hbar\Omega)^2 - \nu_{\mathbf{k}}(0)^2} k^2 dk, \quad (3.11)$$

where each of the quantities a, b, c, \dots is one of the coherence factors, the energy $\nu_{\mathbf{k}}(0)$ of the independent quasi-particles, or the excitation energy $\hbar\Omega$. The integration over the magnitude of \mathbf{k} is replaced by an integration over the Bloch state energy $\epsilon_{\mathbf{k}}$, as measured from the Fermi surface, by setting

$$k^2 dk = (m/\hbar^2)^{3/2} (2E_F)^{1/2} d\epsilon = 2\pi^2 N(0) d\epsilon, \quad (3.12)$$

where we have made the approximation of a constant density of states. The approximation leads to an error of order $\hbar\omega_c/E_F = 10^{-3}$. The integrals $I_{ab\dots 0}$ are only performed over the region $-\hbar\omega_c < \epsilon < \hbar\omega_c$ since the potentials V_l have been set equal to zero outside this energy band. Using (3.12), Eqs. (3.10a) and (3.10b) for the $q \rightarrow 0$ case are written as

$$(1 - V_L I_{\nu n^0}) \Lambda_{LM} - V_L I_{\hbar\Omega n^0} \Gamma_{LM} = \lim_{q \rightarrow 0} Z(\mathbf{q}) 2V_L I_{\nu n^0} \delta_{L0}, \quad (3.13a)$$

$$-V_L I_{\hbar\Omega n^0} \Lambda_{LM} + (1 - V_L I_{\nu l^0}) \Gamma_{LM} = \lim_{q \rightarrow 0} Z(\mathbf{q}) 2V_L I_{\hbar\Omega l^0} \delta_{L0}. \quad (3.13b)$$

From these equations it is seen that the direct Coulomb interaction $4\pi e^2/q^2$ involved in $Z(\mathbf{q})$ only appears for the $L=M=0$ state. It will be shown below that this state has a solution corresponding to a plasma oscillation with the usual plasmon energy

$$\hbar\Omega_p = \hbar(4\pi n e^2/m)^{1/2} \sim 10 \text{ ev}$$

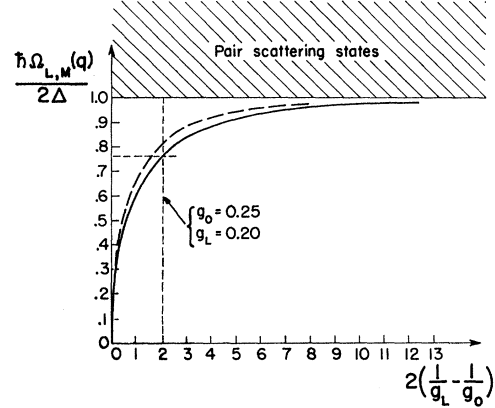


FIG. 6. The L -state exciton energy in the limit $q \rightarrow 0$ as a function of the L -wave coupling constant g_L , where s state pairing in the ground state has been assumed. The solid curve is based on the Anderson-Rickayzen equations while the slightly higher dashed curve includes the effect of the vertices shown in Figs. 2(h) and 2(i) for $g_0 = 0.25$. For $g_L > g_0$ the L -state exciton energy is imaginary. If g_L is the largest coupling constant, the linearization should be carried out with respect to L -state pairing in the ground state.

and lies far above the gap $2\Delta \sim 10^{-3}$ ev. In this section only the $M \neq 0$ cases will be considered, in which the right-hand sides of Eqs. (2.13) become zero. Since the integrand of $I_{\hbar\Omega n^0}$ is odd about the Fermi surface within the constant density of states approximation, $I_{\hbar\Omega n^0}$ vanishes and there is no coupling between the Λ and Γ modes. The excitation energies for the $L \neq 0$ modes with zero center-of-mass momentum are then determined by the conditions:

$$(1 - V_L I_{\nu n^0}) = 0, \quad (\Lambda_{LM} \text{ mode}), \quad (3.14a)$$

$$(1 - V_L I_{\nu l^0}) = 0, \quad (\Gamma_{LM} \text{ mode}). \quad (3.14b)$$

Setting $x = (\hbar\Omega/2\Delta) \leq 1$ in the integrals $I_{\nu n^0}$ and $I_{\nu l^0}$ and using the definition (3.8) of the coupling constant g_L , Eqs. (3.13) become:

$$\left(\frac{1}{g_L} - \frac{1}{g_0} \right) = - \left(\frac{\arcsin x}{x} \right) (1 - x^2)^{1/2} \quad (\Lambda_{LM} \text{ mode}), \quad (3.15a)$$

$$\left(\frac{1}{g_L} - \frac{1}{g_0} \right) = \frac{x \arcsin x}{(1 - x^2)^{1/2}}, \quad (\Gamma_{LM} \text{ mode}). \quad (3.15b)$$

Values of $x = (\hbar\Omega/2\Delta)$ are plotted as a function of the left-hand sides of these equations in Fig. 6. The plot shows that when g_L becomes larger than g_0 , the frequency Ω of the Γ_{LM} mode becomes imaginary, indicating that the system is unstable when described by a ground state formed with s -state pairing. Therefore, if g_L is the largest coupling constant present, the ground state should be formed from pair functions having L -type symmetry. The pair spin function is singlet or triplet depending on whether L is even or odd, since the wave function describing the exciton state must be antisymmetric on the interchange of all coordinates of the quasi-particle pair involved.

The growth of the Γ_{LM} modes for $g_L > g_0$ also indicates that the Λ_{LM} modes have no physical existence. As is seen in Fig. 6, a Λ_{LM} exciton cannot exist unless $g_L > g_0$. However, when such a coupling strength is reached, the corresponding Γ_{LM} exciton is unstable so that the system decays before the Λ_{LM} mode can come into existence. Figure 6 also indicates the $2L$ -fold M degeneracy of $q=0$ L -state excitons.

It should also be mentioned that a continuum of scattering state solutions is obtained from (3.14b) corresponding to the vanishing of the denominator of the integrand. One such state exists between two successive unperturbed levels, $E_k + E_{k+q}$. Although the energy of a scattering state solution is unaltered from its value in the absence of interactions, its wave function is strongly modified since each particle is surrounded by a depletion of the same type of particle leading to the backflow picture mentioned above.

(2) q Finite Case

From Eq. (3.10) it is seen that L is not strictly a good quantum number for the case of finite \mathbf{q} since the coherence factors and $\nu_{\mathbf{k}}(\mathbf{q})$ now have a polar angle dependence. Because of the complexity of this dependence, the sum $\sum_{\mathbf{k}}$ cannot be carried out exactly.

We approximate

$$\epsilon_{\mathbf{k}+\mathbf{q}} = \epsilon_{\mathbf{k}} + \frac{\hbar^2 \mathbf{k} \cdot \mathbf{q}}{m} + \frac{\hbar^2 q^2}{2m},$$

by

$$\epsilon_{\mathbf{k}+\mathbf{q}} \simeq \epsilon_{\mathbf{k}} + \beta\mu, \tag{3.15c}$$

where $\beta = \hbar v_0 q$, $\mu = \cos\theta$, and v_0 is the velocity of a particle at the Fermi surface. This leads to an error of order $q/k_F \ll 1$. The integral $I_{ab\dots}$ are of the same form as those in the $q=0$ case. To perform the angular integral, we expand the denominator of the integrand

$$I_{ab\dots} = \frac{1}{(2\pi)^3} \int \frac{a(\mathbf{k}, \mathbf{q}) b(\mathbf{k}, \mathbf{q}) \dots}{(\hbar\Omega)^2 - \nu_{\mathbf{k}}(\mathbf{q})^2} k^2 dk, \tag{3.16}$$

in powers of β . This procedure is valid so long as $\beta < \hbar\Omega - 2\Delta$. The integrals over k are then of the form

$$I_{ab\dots} = I_{ab\dots}^0 + \mu I_{ab\dots}^1 + \mu^2 I_{ab\dots}^2 + \dots, \tag{3.17}$$

with superscripts indicating the powers of β involved. Keeping terms through order β^2 and using the relations

$$\cos\theta = \mu = (4\pi/3) Y_{10}(\theta)$$

and

$$\cos^2\theta = \mu^2 = \frac{2}{3} (4\pi/5) Y_{20}(\theta) + (4\pi/3) Y_{00},$$

the equations for Λ and Γ (3.10) become

$$\begin{aligned} \Lambda_{LM}(\mathbf{q}) = V_L \int d\omega \left\{ 2 \left(\frac{4\pi}{3} \right)^{\frac{1}{2}} I_{\nu m n^1} Z(\mathbf{q}) Y_{LM}^* Y_{10} + \left[\left((4\pi)^{\frac{1}{2}} I_{\nu n^2} + \frac{(4\pi)^{\frac{1}{2}}}{3} I_{\nu n^2} \right) Y_{00} + \frac{2}{3} \left(\frac{4\pi}{5} \right)^{\frac{1}{2}} I_{\nu n^2} Y_{20} \right] \right. \\ \left. \times \sum_l Y_{LM}^* Y_{lm} \Lambda_{lM}(\mathbf{q}) + \left(\frac{4\pi}{3} \right)^{\frac{1}{2}} I_{\hbar\Omega l n^1} Y_{10} \sum_l Y_{LM}^* Y_{lm} \Gamma_{lM}(\mathbf{q}) \right\}, \tag{3.18a} \end{aligned}$$

$$\begin{aligned} \Gamma_{LM}(\mathbf{q}) = V_L \int d\omega \left\{ 2 \left[\left((4\pi)^{\frac{1}{2}} I_{\hbar\Omega l m^0} + \frac{(4\pi)^{\frac{1}{2}}}{3} I_{\hbar\Omega l m^2} \right) Y_{00} + \frac{2}{3} \left(\frac{4\pi}{5} \right)^{\frac{1}{2}} I_{\hbar\Omega l m^2} Y_{20} \right] Z(\mathbf{q}) Y_{LM}^* \right. \\ \left. + \left(\frac{4\pi}{3} \right)^{\frac{1}{2}} I_{\hbar\Omega l n^1} Y_{10} \sum_l Y_{LM}^* Y_{lm} \Lambda_{lM}(\mathbf{q}) + \left[\left((4\pi)^{\frac{1}{2}} I_{\nu l^2} + \frac{(4\pi)^{\frac{1}{2}}}{3} I_{\nu l^2} \right) Y_{00} \right. \right. \\ \left. \left. + \frac{2}{3} \left(\frac{4\pi}{5} \right)^{\frac{1}{2}} I_{\nu l^2} Y_{20} \right] \sum_l Y_{LM}^* Y_{lm} \Gamma_{lM}(\mathbf{q}) \right\}. \tag{3.18b} \end{aligned}$$

With the relation

$$\int d\omega Y_{l_3 m_3}^* Y_{l_2 m_2} Y_{l_1 m_1} = \left[\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)} \right]^{\frac{1}{2}} C(l_1, l_2, l_3; m_1, m_2, m_3) C(l_1, l_2, l_3; 0, 0, 0),$$

where the C 's are usual Clebsch-Gordan coefficients,¹¹ Eqs. (3.18) become

$$\begin{aligned} \Lambda_{LM}(\mathbf{q}) = V_L \left\{ 2 \left(\frac{4\pi}{3} \right)^{\frac{1}{2}} I_{\nu m n^1} Z(\mathbf{q}) \delta_{L1} \delta_{M0} + \left((4\pi)^{\frac{1}{2}} I_{\nu n^2} + \frac{(4\pi)^{\frac{1}{2}}}{3} I_{\nu n^2} \right) \sum_l \left[\frac{2l+1}{4\pi(2L+1)} \right]^{\frac{1}{2}} C(0L; 0MM) \right. \\ \left. \times C(0L; 000) \Lambda_{lM}(\mathbf{q}) + \frac{2}{3} \left(\frac{4\pi}{5} \right)^{\frac{1}{2}} I_{\nu n^2} \sum_l \left[\frac{5(2l+1)}{4\pi(2L+1)} \right]^{\frac{1}{2}} C(2L; 0MM) C(2L; 000) \Lambda_{lM}(\mathbf{q}) \right. \\ \left. + \left(\frac{4\pi}{3} \right)^{\frac{1}{2}} I_{\hbar\Omega l n^1} \sum_l \left[\frac{3(2l+1)}{4\pi(2L+1)} \right]^{\frac{1}{2}} C(1L; 0MM) C(1L; 000) \Gamma_{lM}(\mathbf{q}) \right\}, \tag{3.19a} \end{aligned}$$

¹¹ Refer to M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

$$\begin{aligned} \Gamma_{LM}(\mathbf{q}) = & V_L \left\{ 2 \left[\left((4\pi)^{\frac{1}{2}} I_{k\Omega l m^0} + \frac{(4\pi)^{\frac{1}{2}}}{3} I_{h\Omega l m^2} \right) \delta_{L0} \delta_{M0} + \frac{2}{3} \left(\frac{4\pi}{5} \right)^{\frac{1}{2}} I_{k\Omega l m^2} \delta_{L2} \delta_{M2} \right] Z(\mathbf{q}) \right. \\ & + \left((4\pi)^{\frac{1}{2}} I_{\nu l^0} + \frac{(4\pi)^{\frac{1}{2}}}{3} I_{\nu l^2} \right) \sum_l \left[\frac{2l+1}{4\pi(2L+1)} \right]^{\frac{1}{2}} C(0lL; 0MM) C(0lL; 000) \Gamma_{LM}(\mathbf{q}) \\ & + \frac{2}{3} \left(\frac{4\pi}{5} \right)^{\frac{1}{2}} I_{\nu l^2} \sum_l \left[\frac{5(2l+1)}{4\pi(2L+1)} \right]^{\frac{1}{2}} C(2lL; 0MM) C(2lL; 000) \Gamma_{LM}(\mathbf{q}) \\ & \left. + \left(\frac{4\pi}{3} \right)^{\frac{1}{2}} I_{h\Omega l m^1} \sum_l \left[\frac{3(2l+1)}{4\pi(2L+1)} \right]^{\frac{1}{2}} C(1lL; 0MM) C(1lL; 000) \Lambda_{LM}(\mathbf{q}) \right\}. \quad (3.19b) \end{aligned}$$

As in the $q \rightarrow 0$ case, the Coulomb field represented by the presence of the $Z(q)$ term does not couple into the equations of motion except for the longitudinal modes $M=0$. Discussion of this case is deferred and the transverse cases $M \neq 0$ are now considered. For a given $M \neq 0$, Eqs. (3.19) represent a set of $2N$ linear simultaneous equations in Λ_{LM} and Γ_{LM} , where N is the number of terms present in the spherical harmonic decomposition of the two-body interaction (3.7). It follows that for a given set of V_L 's the normal mode frequencies of the system may be obtained by setting the determinant of the coefficients of the Λ_{LM} 's and Γ_{LM} 's equal to zero. Once the frequencies have been obtained, the Λ_{LM} 's, Γ_{LM} 's, and the transformation coefficients f and g may be determined.

For simplicity we consider the case for which all but two of the V_L 's vanish. It is assumed that the two-body potential consists of a term V_0 , corresponding to the BCS parameter and another, V_L , representing the angular dependence of the interaction. Since M has been taken as nonzero, it is seen that the simplified V_0 and V_L potential allows the modes to be characterized

by a quantum number L within the approximations of the calculation, due to Λ_{0M} and Γ_{0M} vanishing identically for $M \neq 0$. Thus, we may speak of a p -, d -, ... state exciton when the additional term in the potential has $L=1, 2, \dots$ type angular dependence.

If the potential contains s - and p -wave potentials,

$$\begin{aligned} V(\mathbf{k}, \mathbf{k}') = & V_0 Y_{00}^*(\theta, \varphi) Y_{00}(\Theta, \Phi) \\ & + V_1 Y_{1,\pm 1}^*(\theta, \varphi) Y_{1,\pm 1}(\Theta, \Phi), \quad (3.20) \end{aligned}$$

the dispersion relations obtained from (3.19) are found to be

$$\frac{1}{V_1} = (I_{\nu n^0} + \frac{1}{3} I_{\nu n^2}), \quad [\Lambda_{1,\pm 1}(\mathbf{q}) \text{ modes}], \quad (3.21a)$$

$$\frac{1}{V_1} = (I_{\nu l^0} + \frac{1}{5} I_{\nu l^2}), \quad [\Gamma_{1,\pm 1}(\mathbf{q}) \text{ modes}]. \quad (3.21b)$$

We discard the Λ mode since it does not exist if the system is stable. The dispersion relation (3.21b) for the $\Gamma_{1,\pm 1}(\mathbf{q})$ mode, when rewritten in terms of explicit expressions for the integrals $I_{\nu l^0}$ and $I_{\nu l^2}$ becomes

$$(q\xi_0)^2 = 30x^5 \left\{ \frac{2 \left(\frac{1}{g_1} - \frac{1}{g_0} \right) - \frac{2x \arcsin x}{(1-x^2)^{\frac{1}{2}}}}{x(9+2x^2) + \frac{2(3x^2-6)}{(1-x^2)^{\frac{1}{2}}} \arcsin x + \frac{3}{2} x^4 \frac{\arcsin x}{(1-x^2)^{\frac{1}{2}}}} \right\}, \quad (3.22)$$

where $x = \hbar\Omega_{1,\pm 1}/2\Delta < 1$. This dispersion relation is plotted in Fig. 7 for two values of g_1 with $g_0=0.25$. From the figure, it is seen that the curve intersects the origin for $g_1=g_0$. For a value $g_1 < g_0$ there is a minimum value of $x=x_m$ given by $(1/g_1 - 1/g_0) = x_m \arcsin x_m / (1-x_m^2)^{\frac{1}{2}}$, in agreement with the results of the last section for the $q \rightarrow 0$ case.

(3) The s -State Exciton

The above discussion was restricted to that of the transverse, $M \neq 0$, excitations in which the Coulomb interaction term $Z(\mathbf{q})$ did not enter into the equations

for $\Lambda_{LM}(\mathbf{q})$ and $\Gamma_{LM}(\mathbf{q})$. Before discussing the $M=0$ cases, it should be emphasized that the equations of motion (3.1) which are the basis of this paper are those linearized by Anderson about the BCS ground state based on s -state pairing of the electrons. As Anderson^{3,12} has pointed out, it is the s -state exciton which corresponds to a plasmon excitation, due to $Z(\mathbf{q})$ coupling into the equations of motion.

The $L=0$ mode is considered in the $q \rightarrow 0$ limit. Because of the singular nature of the direct interaction, it is not possible to set $q=0$ in the calculation, so that

¹² K. Yosida, Progr. Theoret. Phys. (Kyoto) 21, 731 (1959).

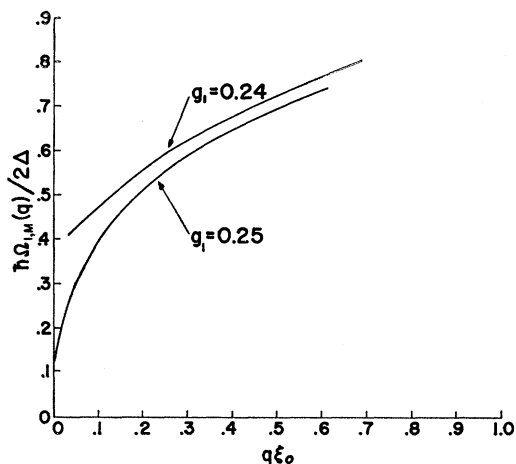


FIG. 7. The p -state exciton energy as a function of momentum \mathbf{q} for $g_0=0.25$ and $g_1=0.24$ or 0.25 . The parameter ξ_0 is the coherence length $\sim 10^{-4}$ cm. Notice that the exciton states are strongly bound only for $q^{-1} > \xi_0$.

the limit $q \rightarrow 0$ must be taken. For our starting point, we consider Eq. (3.13b) for the $\Gamma_{00}(\mathbf{q})$ mode in the

$$1 = \lim_{q \rightarrow 0} 8\pi V_D(q) \left\{ \frac{I_{\hbar\Omega lm}^0(I_{\hbar\Omega lm}^0 + I_{\hbar\Omega lm}^2/3)V_0 + (I_{\nu m}^0 + I_{\nu m}^2/3)(1 - V_0 I_{\nu l}^0)}{1 - V_0 I_{\nu l}^0} \right\}. \quad (3.25)$$

Since $V_D(q) \sim 1/q^2$, Eq. (3.26) indicates that in order for the limit to be finite, the terms in the numerator which are independent of q must vanish:

$$(I_{\hbar\Omega lm}^0)^2 V_0 + I_{\nu m}^0(1 - V_0 I_{\nu l}^0) = 0. \quad (3.26)$$

The validity of (3.26) is shown by considering the explicit form of the integrals involved:

$$I_{\nu m}^0 = \int_{-\hbar\omega_c}^{\hbar\omega_c} \frac{2N(\epsilon)\Delta^2/E}{(\hbar\Omega)^2 - 4E^2} d\epsilon, \quad (3.27a)$$

$$\begin{aligned} I_{\hbar\Omega lm}^0 &= \hbar\Omega \int_{-\hbar\omega_c}^{\hbar\omega_c} \frac{N(\epsilon)\Delta/E}{(\hbar\Omega)^2 - 4E^2} d\epsilon \\ &= \hbar\Omega \int_{-\hbar\omega_c}^{\hbar\omega_c} N(\epsilon) \left\{ \frac{\Delta}{(\hbar\Omega)^2 E} \right. \\ &\quad \left. + \frac{\Delta}{E} \left(\frac{1}{(\hbar\Omega)^2 - 4E^2} - \frac{1}{(\hbar\Omega)^2} \right) \right\} d\epsilon \\ &= \left\{ \frac{-2\Delta}{\hbar\Omega V_0} + \int_{-\hbar\omega_c}^{\hbar\omega_c} \frac{N(\epsilon)4\Delta E}{\hbar\Omega[(\hbar\Omega)^2 - 4E^2]} d\epsilon \right\} \\ &= \frac{2\Delta}{\hbar\Omega} \left\{ -\frac{1}{V_0} + I_{\nu l}^0 \right\}, \end{aligned} \quad (3.27b)$$

where the BCS integral equation¹ for V_0 has been used to obtain the first term on the right. With the use of

$q \rightarrow 0$ case:

$$(1 - V_0 I_{\nu l}^0) \Gamma_{00} = \lim_{q \rightarrow 0} Z(\mathbf{q}) 2V_0 I_{\hbar\Omega lm}^0. \quad (3.23)$$

From the definitions (3.5) and (3.9) an expression for $Z(\mathbf{q})$ is obtained:

$$\begin{aligned} Z(\mathbf{q}) &= \frac{V_D(q)}{1 - 8\pi V_D(q)(I_{\nu m}^0 + I_{\nu m}^2/3)} \left\{ \left(\frac{4\pi}{3} \right)^{\frac{1}{2}} I_{\nu m}^0 \Lambda_{10}(\mathbf{q}) \right. \\ &\quad \left. + \left((4\pi)^{\frac{1}{2}} I_{\hbar\Omega lm}^0 + \frac{(4\pi)^{\frac{1}{2}}}{3} I_{\hbar\Omega lm}^2 \right) \Gamma_{00}(\mathbf{q}) \right. \\ &\quad \left. + \frac{2}{3} \left(\frac{4\pi}{5} \right)^{\frac{1}{2}} I_{\hbar\Omega lm}^2 \Gamma_{20}(\mathbf{q}) \right\}. \end{aligned} \quad (3.24)$$

Since the $L=0$ mode excitation energy is being considered, only the $\Gamma_{00}(\mathbf{q})$ term in (3.24) need be used in substituting for $Z(\mathbf{q})$ into (3.23). Rearrangement of terms then gives:

these relations, (3.26) becomes:

$$\begin{aligned} \frac{2\Delta}{\hbar\Omega} V_0 \left(-\frac{1}{V_0} + I_{\nu l}^0 \right) \hbar\Omega \int_{-\hbar\omega_c}^{\hbar\omega_c} \frac{N(\epsilon)\Delta/E d\epsilon}{(\hbar\Omega)^2 - 4E^2} \\ + 2 \int_{-\hbar\omega_c}^{\hbar\omega_c} \frac{N(\epsilon)\Delta^2/E}{(\hbar\Omega)^2 - 4E^2} (1 - V_0 I_{\nu l}^0) d\epsilon = 0. \end{aligned}$$

With the validity of (3.26) established, (3.25) reduces to

$$1 = \lim_{q \rightarrow 0} \frac{8\pi V_D(\mathbf{q})}{3} \left\{ \frac{V_0 I_{\hbar\Omega lm}^0 I_{\hbar\Omega lm}^2 + I_{\nu m}^2(1 - V_0 I_{\nu l}^0)}{1 - V_0 I_{\nu l}^0} \right\}. \quad (3.28)$$

To determine the existence of a plasma oscillation for the $L=0$ mode, (3.28) must have a solution for $x = (\hbar\Omega/2\Delta) \gg 1$. Under this condition the term $V_0 I_{\nu l}^0$ in the denominator is much less than unity and may be dropped. The integrals involved in (3.28) are evaluated for $x \gg 1$ so that, to order $1/x^2$, (3.28) reduced to

$$1 = \frac{\pi^2}{6x^2} V_D(\mathbf{q}) q^2 N(0) \xi_0^2. \quad (3.29)$$

Using $V_D(q) = 4\pi e^2/q^2$ and $e^2 \xi_0^2 N(0) = (3/2\pi^3)(\hbar\omega_p/2\Delta)^2$, where $\omega_p^2 = 4\pi n e^2/m$, (3.29) gives $\Omega = \omega_p$ so that the excitation frequency of this mode is the plasma frequency.

(4) The $L=1, M=0$ Mode

To complete the investigation of the collective states present when only the V_0 and V_1 terms are kept in the potential expansion (3.7), we must determine the dispersion relation for the $\Gamma_{10}(\mathbf{q})$ mode. Setting $M=0$ is (3.19b) we obtain two simultaneous equations involving $\Gamma_{00}(\mathbf{q})$ and $\Gamma_{10}(\mathbf{q})$. There is no mixing of these modes in the equations. The Γ_{00} dispersion relation gives the plasma frequency as discussed above while the $\Gamma_{10}(\mathbf{q})$ mode dispersion relation becomes

$$1/V_1 = (I_{\nu l^2} + \frac{3}{5}I_{\nu l^2}). \quad (3.30)$$

In Sec. III (2) we found the dispersion relation for the $\Gamma_{1\pm 1}(\mathbf{q})$ modes to be

$$1/V_1 = (I_{\nu l^2} + \frac{1}{5}I_{\nu l^2}). \quad (3.21b)$$

Thus the $\Gamma_{10}(\mathbf{q})$ dispersion relation can be obtained by letting $\mathbf{q} \rightarrow \mathbf{q}\sqrt{3}$ in (3.22), indicating that for a given wave vector \mathbf{q} the excitation energy of the longitudinal $\Gamma_{10}(\mathbf{q})$ mode is raised above that of the transverse $\Gamma_{1\pm 1}(\mathbf{q})$ modes.

IV. CORRECTIONS TO THE ANDERSON-RICKAYZEN EQUATIONS

We consider here the terms in the linearized equations neglected by Anderson and Rickayzen. For simplicity we treat these terms only in the $\mathbf{q} \rightarrow 0$ case. In the equation for $b_k^\dagger(\mathbf{q})$, the terms shown in Figs. 2(h) and 2(i) were neglected. They contribute the factor

$$-u_k v_k \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') (\Delta_{\mathbf{k}'}/2E_{\mathbf{k}'}) \times (\gamma_{\mathbf{k}'0} \gamma_{\mathbf{k}'1}^\dagger + \gamma_{\mathbf{k}'1} \gamma_{\mathbf{k}'0}) \quad (4.1)$$

to the right-hand side of (3.1a) in the limit $\mathbf{q} \rightarrow 0$, while the negative of this factor is added to the right-hand side of (3.1b). The exchange scattering vertex shown in Fig. 3(a) was neglected in the equation for $\rho_{k\sigma}(q)$. Its contribution,

$$\sum_{\mathbf{k}'} c_{\mathbf{k}'+\mathbf{q}\sigma}^\dagger c_{\mathbf{k}'\sigma} [V(\mathbf{k}', \mathbf{k}) v_{\mathbf{k}+\mathbf{q}^2} - V(\mathbf{k}+\mathbf{q}, \mathbf{k}'+\mathbf{q}) v_{\mathbf{k}^2}], \quad (4.2)$$

vanishes as $\mathbf{q} \rightarrow 0$ and does not affect the energy of the exciton states in this limit. The inclusion of (4.1) adds the term

$$-\frac{1}{2} \frac{\Delta_{\mathbf{k}}}{E_{\mathbf{k}}} \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}') \frac{\Delta_{\mathbf{k}'}}{E_{\mathbf{k}'}} (f_{\mathbf{k}'} + g_{\mathbf{k}'}) \quad (4.3)$$

to the right-hand side of (3.6a) and the negative of this term to the right-hand side of (3.6b). Introducing the variable

$$R_{\mathbf{k}} = \sum_{\mathbf{k}'} \frac{\Delta_{\mathbf{k}}}{E_{\mathbf{k}}} V(\mathbf{k}, \mathbf{k}') (f_{\mathbf{k}'} + g_{\mathbf{k}'}), \quad (4.4)$$

one finds the $M \neq 0$ exciton states satisfy the set of

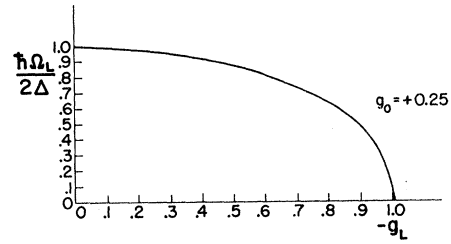


FIG. 8. The energy of the L -state particle-hole exciton as a function of the L -wave coupling constant g_L with $g_0=0.25$. For $g_L > 0$ the particle-particle exciton described by Figs. 6 and 7 is bound while for $g_L < 0$ the particle-hole exciton is bound. In the absence of the direct interaction V_D , the s -state exciton is essentially a bound particle-particle (and hole-hole) pair. With the inclusion of long-range Coulomb interactions, the s -state exciton becomes a plasmon described as a particle-hole pair.

coupled equations:

$$\Gamma_{LM} = \Gamma_{LM} V_L \sum_{\mathbf{k}} \frac{2E_{\mathbf{k}}}{(\hbar\Omega)^2 - 4E_{\mathbf{k}}^2} - R_{LM} V_L \sum_{\mathbf{k}} \left(\frac{\Delta_{\mathbf{k}}}{E_{\mathbf{k}}} \right) \frac{\hbar\Omega}{(\hbar\Omega)^2 - 4E_{\mathbf{k}}^2}, \quad (4.5)$$

$$R_{LM} = \Gamma_{LM} V_L \sum_{\mathbf{k}} \left(\frac{\Delta_{\mathbf{k}}}{E_{\mathbf{k}}} \right) \frac{\hbar\Omega}{(\hbar\Omega)^2 - 4E_{\mathbf{k}}^2} - R_{LM} V_L \sum_{\mathbf{k}} \frac{2\Delta_{\mathbf{k}}^2}{E_{\mathbf{k}} [(\hbar\Omega)^2 - 4E_{\mathbf{k}}^2]}.$$

Setting the determinant of the coefficients equal to zero, one finds the dispersion relation

$$\left(\frac{1}{V_L} + I_{\nu m^2} \right) \left(\frac{1}{V_L} - I_{\nu l^2} \right) + (I_{\hbar\Omega l m^0})^2 = 0, \quad (4.6)$$

or

$$\left(\frac{1}{g_L} + \frac{\arcsin x}{x(1-x^2)^{1/2}} \right) \left(\frac{1}{g_L} - \frac{1}{g_0} - \frac{x \arcsin x}{(1-x^2)^{1/2}} \right) + \frac{(\arcsin x)^2}{1-x^2} = 0, \quad (4.7)$$

for the energy of the Γ_{LM} exciton. The modification of the $\mathbf{q} \rightarrow 0$ exciton energy given by (4.7) is shown in Fig. 6 for $g_0=0.25$ and is seen to be small. A new type of excitation follows from (4.7) for $g_L < 0$, that is, a repulsive rather than attractive L -wave interaction between electrons. The energy of this state is shown in Fig. 8 as a function of $-g_L$ for $g_0=0.25$. From the form of the coherence factors entering the dispersion relation it appears the new state should be interpreted as a bound electron-hole pair in close analogy with the exciton states occurring in insulators. This interpretation is consistent with the fact that the electron-hole interaction is attractive when the corresponding elec-

tron-electron interaction is repulsive. Thus the electron-hole exciton arises solely from the terms neglected in the Anderson-Rickayzen equations.

V. CONCLUSIONS

While we have approximated the L th spherical harmonic of the two-body interaction by a separable potential, $V_L(\mathbf{k}, \mathbf{k}') = -V_L$ for $|\epsilon_{\mathbf{k}}|, |\epsilon_{\mathbf{k}'}| < \hbar\omega_c$ and zero, otherwise, in general, if the potential is independent of crystallographic orientation, the numbers L and M remain good quantum numbers for the excitations in the limit $\mathbf{q} \rightarrow 0$. For a nonseparable potential, i.e., if $V_L(\mathbf{k}, \mathbf{k}')$ is not of the form $\varphi_L(\mathbf{k})\varphi_L^*(\mathbf{k}')$, there may be more than one exciton state for a given L and M . While the excitons should give a negligible contribution to the specific heat, it may prove possible to observe the

thermally-excited odd L excitons (spin waves) by magnetic-resonance techniques. Since the precursor infrared absorption observed in Pb and Hg by Ginsberg, Richards, and Tinkham may be due to creation of excitons, it would be interesting to carry out an explicit calculation of the absorption coefficient for a thin-film geometry in an attempt to reconcile the difference between Tsuneto's prediction and experiment. We are at present calculating the infrared absorption due to hole-particle excitons.

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