FIP10601 – Text 18

Phonon effects on electronic properties

Phonon effect on the electrical conductivity

Our first analysis of the electrical conductivity of metals was based on the Boltzmann equation (Texts 7 and 8). In the linearized version of that equation the collision term can be written as

$$\left(\frac{\partial f(\mathbf{k})}{\partial t}\right)_{\text{col}} = \int \frac{\mathrm{d}^3 k}{(2\pi)^3} \, \mathcal{W}(\mathbf{k}, \mathbf{k}') \left[f(\mathbf{k}') - f(\mathbf{k})\right] \delta(\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}}) \,, \tag{1}$$

where $\mathcal{W}(\mathbf{k}, \mathbf{k}')$ is the cross section for elastic scattering of an electron between the states $\mathbf{k}$ and $\mathbf{k}'$. In a scattering event involving the electron-phonon interaction, the emitted or absorbed phonon has a much smaller energy than that of relevant electrons (near the Fermi level), justifying the use of a linearized form valid for elastic scattering. At thermodynamic equilibrium, we can write (using the notation $\mathbf{k}' = \mathbf{k} + \mathbf{q}$),

$$\mathcal{W}(\mathbf{k}, \mathbf{k} + \mathbf{q}) = \mathcal{W}^a(\mathbf{q}) \, b(\mathbf{q}) + \mathcal{W}^e(-\mathbf{q}) \left[b(-\mathbf{q}) + 1\right] \,, \tag{2}$$

where $\mathcal{W}^a(\mathbf{q})$ and $\mathcal{W}^e(-\mathbf{q})$ are **intrinsic** probabilities of, respectively, absorption and emission of a phonon with the indicated wavevector, and $b(\mathbf{q})$ is the Bose-Einstein distribution (average number of phonons in mode $\mathbf{q}$). Note that $\mathcal{W}(\mathbf{k}, \mathbf{k} + \mathbf{q})$ does not depend explicitly on $\mathbf{k}$, but the distribution functions in Eq. (1) ensure the restriction to electrons near the Fermi surface.

Inspecting the electron-phonon part of the general Fock-space Hamiltonian for electrons and phonons, Eq. (26) of Text 17, we see that the intrinsic absorption and emission probabilities are equal, and given by

$$\mathcal{W}^{\text{ph}}(\mathbf{q}) = |\Gamma_{\mathbf{q}}|^2 \,. \tag{3}$$

From the form of $\Gamma(\mathbf{q})$, Eq. (25) of Text 17, we can deduce that

$$\Gamma_{\mathbf{q}} \sim \sqrt{q} \Rightarrow \mathcal{W}^{\text{ph}}(\mathbf{q}) = \gamma q, \tag{4}$$

where γ is a constant that can be treated as a phenomenological parameter. This form comes from considering that $V(\mathbf{q})$ should be nearly constant due to the local nature of a screened electron-ion interaction, and that the frequencies of acoustic phonons can be approximately taken as **linearly** dependent on $q \equiv |\mathbf{q}|$.

In the relaxation-time approximation we obtained (Text 7)

$$\frac{1}{\tau} = \frac{1}{(2\pi)^3} \int_{S_F} \frac{dS_{\mathbf{k}}}{\hbar v_F} \, \mathcal{W}(\varepsilon_F, \theta) \, (1 - \cos\theta) \,, \tag{5}$$

where $\mathcal{W}(\varepsilon_F, \theta)$ is a simplified notation for $\mathcal{W}(\mathbf{k}, \mathbf{k} + \mathbf{q})$ when calculated for $\mathbf{k}$ and $\mathbf{k} + \mathbf{q}$ both on the Fermi surface, θ being the angle between these wavevectors. From Eqs. (2)–(4), we have

$$\mathcal{W}(\varepsilon_F, \theta) = \gamma q \, [2b(\mathbf{q}) + 1] \,, \tag{6}$$

where we use the fact that the Bose function depends on $\mathbf{q}$ through $\omega(\mathbf{q})$, which is invariant under inversion of the wavevector. Dependence on the scattering angle θ is determined by the transferred wavevector $\mathbf{q}$. A simple geometrical construction shows that

$$\frac{q}{2k_F} = \sin(\theta/2) \,. \tag{7}$$

We are interested in determining how the relaxation time depends on temperature. This dependence comes from the Bose function $b(\mathbf{q})$. Without keeping track of multiplicative constants (since we already have one phenomenological parameter), but concentrating on the functionality with temperature, we first note that dependence on T appears in the combination $\omega(\mathbf{q})/T$. Assuming a linear dispersion relation, $\omega = c\,q$, and turning functions of θ in Eq. (5) into functions of q through Eq. (7), we end up with

$$\frac{1}{\tau} \sim \int q^4 \cotanh\left(\frac{c\,q}{2T}\right) \, dq \,, \tag{8}$$

where we used the (easily verifiable) relationship $2b(q)+1 = \cotanh(c\,q/2T)$. Changing the integration variable to $x \equiv c\,q/T$ generates a prefactor T^5. The upper limit of integration in x may be taken to infinity for low temperature ($T \ll \Theta_D$), so that the remaining integral becomes a constant. The final conclusion is that

$$\frac{1}{\tau} \sim T^5 \tag{9}$$

in the low-temperature regime. Hence, the electric resistivity varies in proportion to T^5 (above a residual contribution from impurity scattering). This behavior is indeed confirmed in experiments.

Interaction between electrons via exchange of virtual phonons

The electron-phonon contribution to electrical resistivity comes from **real** processes of electron scattering by emission or absorption of phonons. Let us now examine in more detail the role of **virtual** processes. At the end of Text 17, we already mentioned that such processes contribute to the electron self-energy, which means that they renormalize

the effective mass. This is the mechanism to **polaron** formation, previously mentioned in our remarks about Fermi-liquid instabilities in Text 15.

The other instability mentioned there in connection to electron-phonon interaction was superconductivity. It arises from an **effective** *electron-electron interaction through phonon exchange*, and we will see that this interaction leads to formation of **electron pairs** near the Fermi surface, with the paired state having lower energy than the Fermi-liquid.

Description of electron pairing in the many-body approach involves *anomalous* single-particle Green's functions (two creation or two annihilation operators), as electron and hole states become mixed. To simplify the analysis, as well as to expand our collection of theoretical methods, we will **not** use the Green's function method. Instead, we will introduce a unitary transformation that explicitly generates a pairing interaction in the transformed Hamiltonian, and its consequences will be analyzed in a mean-field approximation.

Transformation of the Hamiltonian

We begin with the Hamiltonian of electrons and phonons that we obtained in Text 17,

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \sum_{\mathbf{q}} \hbar\omega(\mathbf{q}) \left[a_{\mathbf{q}}^{\dagger} a_{\mathbf{q}} + \frac{1}{2} \right]$$

$$+ \frac{1}{2} \sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{q} \\ \sigma\sigma'}} U(\mathbf{q})\, c_{\mathbf{k}+\mathbf{q},\sigma}^{\dagger} c_{\mathbf{k}'-\mathbf{q},\sigma'}^{\dagger} c_{\mathbf{k}'\sigma'} c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{q}\sigma} \Gamma(\mathbf{q})\, (a_{\mathbf{q}} + a_{-\mathbf{q}}^{\dagger})\, c_{\mathbf{k}+\mathbf{q},\sigma}^{\dagger} c_{\mathbf{k}\sigma}\,. \tag{10}$$

Now, let us define a transformed Hamiltonian

$$\tilde{\mathcal{H}} \equiv e^{-S}\, \mathcal{H}\, e^{S}\,, \tag{11}$$

where S must be an anti-Hermitian operator for the transformation to be unitary. We will initially develop a general analysis of this type of transformation before applying it to our specific problem.

Equation (11) may be expanded as follows:

$$\tilde{\mathcal{H}} = \mathcal{H} + [\mathcal{H}, S] + \frac{1}{2!}[[\mathcal{H}, S], S] + \frac{1}{3!}[[[\mathcal{H}, S], S], S] + \cdots \tag{12}$$

We assume that the Hamiltonian can be decomposed in two parts,

$$\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_1\,, \tag{13}$$

where λ is an auxiliary parameter, which will be eliminated at the end by choosing $\lambda = 1$. Thus,

$$\tilde{\mathcal{H}} = \mathcal{H}_0 + \lambda\mathcal{H}_1 + [\mathcal{H}_0, S] + \lambda[\mathcal{H}_1, S]$$

$$+ \frac{1}{2}[[\mathcal{H}_0, S], S] + \frac{1}{2}\lambda[\mathcal{H}_1, S], S] + \cdots \tag{14}$$

Since the purpose of this transformation is to take into account the effect of $\mathcal{H}_1$, it is obvious that S must be chosen to be null when $\lambda = 0$. This means that S is (at least) linear in λ. So, the linear terms in Eq. (14) are

$$\lambda \mathcal{H}_1 + [\mathcal{H}_0, S] \ . \tag{15}$$

We want to choose S such that $\mathcal{H}_1$ is suppressed from the transformed Hamiltonian in first order. This implies the condition

$$\lambda \mathcal{H}_1 + [\mathcal{H}_0, S] = 0 \ . \tag{16}$$

Assuming that we can solve the eigenvalue problem

$$\mathcal{H}_0 |n\rangle = E_n |n\rangle \ , \tag{17}$$

matrix elements of Eq. (16) in this basis result in

$$\lambda \langle n|\mathcal{H}_1|m\rangle + (E_n - E_m)\langle n|S|m\rangle = 0 \ . \tag{18}$$

Therefore, taking $\lambda = 1$, we obtain

$$\langle n|S|m\rangle = \frac{\langle n|\mathcal{H}_1|m\rangle}{E_m - E_n} \ . \tag{19}$$

This relation determines S through its matrix elements in the basis composed by the eigenvectors of $\mathcal{H}_0$.

Returning to our problem, we will slightly depart from the above scheme in the sense that we will leave the el-el interaction untouched, as an additive term left out of the Hamiltonian for the time being. So, the transformation will involve the non-interacting terms of Eq. (10) as $\mathcal{H}_0$, while $\mathcal{H}_1$ will be the electron-phonon interaction, i.e.,

$$\mathcal{H}_1 = \sum_{\mathbf{kq}\sigma} \Gamma_{\mathbf{q}} \left(a_{\mathbf{q}} + a_{-\mathbf{q}}^\dagger \right) c_{\mathbf{k}+\mathbf{q},\sigma}^\dagger c_{\mathbf{k}\sigma} \ . \tag{20}$$

The states $|n\rangle$ and $|m\rangle$ for which $\mathcal{H}_1$ has nonzero matrix elements differ by one unity (± 1) in the number of phonons, and a changed wavevector for the "scattered" electron. According to Eq. (19), S has nonzero matrix elements between the same states. Therefore, S should have the form

$$S = \sum_{\mathbf{kq}\sigma} \Gamma_{\mathbf{q}} \left(\alpha_{\mathbf{kq}} a_{\mathbf{q}} + \beta_{\mathbf{kq}} a_{-\mathbf{q}}^\dagger \right) c_{\mathbf{k}+\mathbf{q},\sigma}^\dagger c_{\mathbf{k}\sigma} \ . \tag{21}$$

To fully satisfy the relationship between matrix elements of S and $\mathcal{H}_1$, Eq. (19), the coefficients $\alpha_{\mathbf{kq}}$ and $\beta_{\mathbf{kq}}$ should be chosen to present a denominator with the corresponding energy difference between the two states. Therefore, the appropriate choice is

$$\alpha_{\mathbf{kq}} = \frac{1}{\varepsilon_{\mathbf{k}} - (\varepsilon_{\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}})} \tag{22}$$

$$\beta_{\mathbf{kq}} = \frac{1}{\varepsilon_{\mathbf{k}} - (\varepsilon_{\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}})} \ , \tag{23}$$

where we simplified the notation of phonon frequencies (using the wavevector as a subscript), and made use of the relationship $\omega_{-\mathbf{q}} = \omega_{\mathbf{q}}$. By appropriate changes in the summation wavevectors, and using the explicit form of $\Gamma_{\mathbf{q}}$, Eq. (25) of Text 17, we can check that $S^{\dagger} = -S$, confirming that S is an anti-Hermitian operator.

As the relevant regime is of weak electron-phonon coupling (strong coupling yields heavy polarons), we build the effective Hamiltonian keeping only terms up to second order in λ in the generic expansion (14). The linear term is zero by construction. Furthermore, under condition (16), the second-order term in Eq. (14), for $\lambda = 1$, becomes $[\mathcal{H}_1, S]/2$. After evaluating this commutator, the final step is to project $\tilde{\mathcal{H}}$ in the subspace of **zero** phonons (low-temperature limit), obtaining a purely electronic effective Hamiltonian, which has the form

$$\mathcal{H}^{\text{eff}} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{q} \\ \sigma}} \mathcal{V}^{\text{eff}}(\mathbf{k}, \mathbf{q})\, c_{\mathbf{k}+\mathbf{q},\sigma}^{\dagger} c_{\mathbf{k}'-\mathbf{q},\sigma'}^{\dagger}\, c_{\mathbf{k}'\sigma'}\, c_{\mathbf{k}\sigma}\, , \tag{24}$$

where

$$\mathcal{V}^{\text{eff}}(\mathbf{k}, \mathbf{q}) = U(\mathbf{q}) + \frac{2|\Gamma_{\mathbf{q}}|^2\, \hbar\omega_{\mathbf{q}}}{(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}})^2 - (\hbar\omega_{\mathbf{q}})^2}\, . \tag{25}$$

It is important to make the following observations about the effective interaction potential:

- The first term is the Coulomb repulsion between electrons, that had been left out from the above development. Upon a perturbative treatment of e-e interactions, it becomes screened (see Text 15), and can therefore be greatly reduced, allowing the second term to dominate. In other words, we are focusing in the occurence of superconductivity in metals for which the independent-electron approximation is good, allowing to **absorb the effects of $U(\mathbf{q})$ into the periodic potential** to which the electrons are subjected, hence into the energies $\varepsilon_{\mathbf{k}}$. Alternatively, these energies may be interpreted as associated to Fermi-liquid quasi-particles.

- The second term is an effective electron-electron interaction originated from the electron-phonon interaction (phonon exchange). The **virtual** electron-phonon processes involved here **do not conserve energy**. A negative (attractive) potential is favored when the difference of electronic energies in the denominator of Eq. (25) is smaller than the energy of the exchanged phonon. Thus, the most favorable conditions for attractive interaction are:

  - a high-frequency phonon ($\omega_{\mathbf{q}} \sim \omega_D$), whose $\mathbf{q}$ has a magnitude near the Debye wavevector q_D, which is comparable to the Fermi wavevector k_F;
  - electronic energies within a range smaller than the phonon energy around the Fermi surface.

A simple geometric construction, shown in Fig. 1 (assuming a spherical Fermi surface), allows to verify that the wavevectors of the two electrons involved should be nearly antiparallel. We then enforce this restriction ($\mathbf{k}' = -\mathbf{k}$) in the interaction term of $\mathcal{H}^{\text{eff}}$.
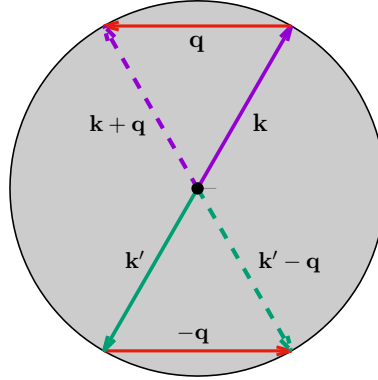
Figure 1: Schematic representation of the wavevectors of two electrons near the Fermi surface and of a large-momentum phonon that they exchange.

Moreover, considering that the total spin is zero, and viewing the system as consisting of **pairs** of electrons with opposite wavevectors (*Cooper pairs*), we assume that **each pair** has zero total spin (*singlet pairing*). This kind of pairing preserves time-reversal invariance, as the paired electrons occupy individual states related by a time-reversal transformation.

Based on these arguments, and changing the notation so that $\mathbf{k} + \mathbf{q} \rightarrow \mathbf{k}'$, we rewrite Eqs. (24) and (25) in the form

$$\mathcal{H}^{\text{eff}} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}}\, c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{k}'} \mathcal{V}(\mathbf{k}, \mathbf{k}')\, c_{\mathbf{k}'\uparrow}^{\dagger} c_{-\mathbf{k}'\downarrow}^{\dagger} c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}\,, \qquad (26)$$

$$\mathcal{V}(\mathbf{k}, \mathbf{k}') = \begin{cases} -\dfrac{2|\Gamma_{\mathbf{k}'-\mathbf{k}}|^2}{\hbar\omega_{\mathbf{k}'-\mathbf{k}}}\,, & |\bar{\varepsilon}_{\mathbf{k}}| \sim |\bar{\varepsilon}_{\mathbf{k}'}| < \hbar\omega_D\,,\ |\mathbf{k}' - \mathbf{k}| \sim q_D\,, \\[2em] 0\,, & \text{other energies.} \end{cases} \qquad (27)$$

Note that the effective interaction has been neglected in the wavevector range in which it would be repulsive, since its effect would be equivalent to the Coulomb repulsion, being also absorbed in the band energies. The effective Hamiltonian in Eq. (26) is known as the *BCS Hamiltonian*, proposed by **B**ardeen, **C**ooper, and **S**chrieffer. It provides the basis to study superconductivity, as discussed in the following section.

BCS Hamiltonian – Superconductivity

From now on, we will **implicitly** assume that single-particle energies $\varepsilon_{\mathbf{k}}$ are measured relative to the chemical potential, dropping the *bar* above $\varepsilon_{\mathbf{k}}$ of our previous notation.

Once more we stress the fact that the interaction term in Eq. (26) may be seen as involving annihilation of an electron pair with wavevectors $\mathbf{k}$ and $-\mathbf{k}$, and creation of a pair with

wavevectors $\mathbf{k}'$ and $-\mathbf{k}'$. Since pairing should lead to a qualitative change in the nature of the ground state with respect to a Fermi liquid, it is not convenient to treat the interaction perturbatively. The simplest alternative approach is a **mean-field approximation**, which mathematically amounts to a "decoupling" of operator products.

Given two generic operators A_1 and A_2, their product can be approximately decoupled as

$$A_1 A_2 \simeq \langle A_1 \rangle A_2 + \langle A_2 \rangle A_1 - \langle A_1 \rangle \langle A_2 \rangle \,. \tag{28}$$

The neglected part is quadratic in the differences between each operator and its average value. If the product $A_1 A_2$ is part of a Hamiltonian, the problem becomes self-consistent, since average values now appear in the Hamiltonian with which they are to be evaluated.

We use this to decouple the interaction term in the BCS Hamiltonian, Eq. (26), with A_1 and A_2 corresponding to a pair-creation and a pair-annihilation operator, respectively. We then have

$$
\begin{aligned}
c^\dagger_{\mathbf{k}'\uparrow} c^\dagger_{-\mathbf{k}'\downarrow} c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} &= \langle c^\dagger_{\mathbf{k}'\uparrow} c^\dagger_{-\mathbf{k}'\downarrow} \rangle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \\
&\quad + c^\dagger_{\mathbf{k}'\uparrow} c^\dagger_{-\mathbf{k}'\downarrow} \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle \\
&\quad - \langle c^\dagger_{\mathbf{k}'\uparrow} c^\dagger_{-\mathbf{k}'\downarrow} \rangle \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle \,.
\end{aligned}
\tag{29}
$$

Note that the original product conserves the number of particles, while the decoupled terms only do it on the average, provided the averages of pair-creation and pair-annihilation operators are equal. Taking into account that these averages will appear in the mean-field Hamiltonian in products with the interaction, we define

$$\Delta_{\mathbf{k}} \equiv -\sum_{\mathbf{k}'} \mathcal{V}(\mathbf{k}, \mathbf{k}') \langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \rangle = -\sum_{\mathbf{k}'} \mathcal{V}(\mathbf{k}, \mathbf{k}') \langle c^\dagger_{\mathbf{k}'\uparrow} c^\dagger_{-\mathbf{k}'\downarrow} \rangle \,. \tag{30}$$

The choice of $\Delta_{\mathbf{k}}$ as a real quantity is not general, but does lead to a self-consistent solution in the case of a homogeneous system.

The effective potential $\mathcal{V}(\mathbf{k}, \mathbf{k}')$, given by Eq. (27), can be greatly simplified. Taking into account that the phonon wavevector is essentially of magnitude q_D, $\omega_{\mathbf{k}'-\mathbf{k}}$ may be replaced by ω_D in the region where the potential is nonzero. By the same reason, Eq. (4) implies that $\Gamma(\mathbf{q})$ is approximately constant. Then, $\mathcal{V}(\mathbf{k}, \mathbf{k}')$ is constant (and negative) in the region where it is not null, so that it may be written in the form

$$\mathcal{V}(\mathbf{k}, \mathbf{k}') = \begin{cases} -\mathcal{V}/N, & \text{for } |\varepsilon_{\mathbf{k}}|, |\varepsilon_{\mathbf{k}'}| < \hbar\omega_D \\ 0, & \text{otherwise}, \end{cases} \tag{31}$$

where $\mathcal{V}$ is a *pairing coupling constant*. The factor $1/N$ comes from $|\Gamma_{\mathbf{k}'-\mathbf{k}}|^2$ in Eq. (27), taking into account Eqs. (20) and (26) **of Text 17** in the case of a nearly local electron-ion interaction. The relevant physical quantities depend on the value of $\mathcal{V}$, which enters the

Hamiltonian through $\Delta_{\mathbf{k}}$, as seen in Eqs. (30) and (31). Thus, the Hamiltonian (which we now denote simply by $\mathcal{H}$) becomes

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}}\, c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} - \sum_{\mathbf{k}} \Delta_{\mathbf{k}}\, (c_{-\mathbf{k}\downarrow}\, c_{\mathbf{k}\uparrow} + c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger) + \sum_{\mathbf{k}} \Delta_{\mathbf{k}} \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}\rangle$$

$$= \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}}\, (c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}\uparrow} + c_{-\mathbf{k}\downarrow}^\dagger c_{-\mathbf{k}\downarrow}) - \sum_{\mathbf{k}} \Delta_{\mathbf{k}}\, (c_{-\mathbf{k}\downarrow}\, c_{\mathbf{k}\uparrow} + c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger) + \sum_{\mathbf{k}} \Delta_{\mathbf{k}} \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}\rangle . \quad (32)$$

In the last line we explicitly summed over spin states, and changed the sign of one of the summation wavevectors so that we always have the combinations $(\mathbf{k}\uparrow)$ and $(-\mathbf{k}\downarrow)$. Note that $\Delta_{\mathbf{k}}$ is nonzero only for $\mathbf{k}$ in the region where $\mathcal{V}(\mathbf{k},\mathbf{k}') \neq 0$. Out of this region, the Hamiltonian is reduced to that of an electron gas.

Diagonalization

The mean-field BCS Hamiltonian, Eq. (32), is a single-particle Hamiltonian, but *non-diagonal*. To obtain single-particle excitation energies we must *diagonalize* it. This easily accomplished if we rewrite the Hamiltonian using an explicit matrix form,

$$\mathcal{H} = \sum_{\mathbf{k}} (c_{\mathbf{k}\uparrow}^\dagger \quad c_{-\mathbf{k}\downarrow}) \begin{pmatrix} \varepsilon_{\mathbf{k}} & -\Delta_{\mathbf{k}} \\ -\Delta_{\mathbf{k}} & -\varepsilon_{\mathbf{k}} \end{pmatrix} \begin{pmatrix} c_{\mathbf{k}\uparrow} \\ c_{-\mathbf{k}\downarrow}^\dagger \end{pmatrix} + \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} + \sum_{\mathbf{k}} \Delta_{\mathbf{k}} \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}\rangle . \quad (33)$$

Note that we used $c_{-\mathbf{k}\downarrow}^\dagger c_{-\mathbf{k}\downarrow} = 1 - c_{-\mathbf{k}\downarrow} c_{-\mathbf{k}\downarrow}^\dagger$, which generated the sum of free-electron energies, and a minus sign in the last diagonal element of the square matrix. Diagonalization of this matrix involves calculating the roots of a determinant,

$$\begin{vmatrix} \lambda - \varepsilon_{\mathbf{k}} & \Delta_{\mathbf{k}} \\ \Delta_{\mathbf{k}} & \lambda + \varepsilon_{\mathbf{k}} \end{vmatrix} = 0 . \quad (34)$$

The solution is

$$\lambda = \pm E_{\mathbf{k}} , \qquad E_{\mathbf{k}} \equiv \sqrt{\varepsilon_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}^2} . \quad (35)$$

Leaving the details as an **EXERCISE**, we observe that the corresponding eigenvectors allow us to obtain new fermion operators as combinations of the original ones,

$$\alpha_{\mathbf{k}} = u_{\mathbf{k}}\, c_{\mathbf{k}\uparrow} - v_{\mathbf{k}}\, c_{-\mathbf{k}\downarrow}^\dagger ,$$
$$\beta_{\mathbf{k}} = u_{\mathbf{k}}\, c_{-\mathbf{k}\downarrow} + v_{\mathbf{k}}\, c_{\mathbf{k}\uparrow}^\dagger , \quad (36)$$

with

$$u_{\mathbf{k}}^2 = \frac{1}{2}\left[1 + \frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}}\right] , \qquad v_{\mathbf{k}}^2 = \frac{1}{2}\left[1 - \frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}}\right] . \quad (37)$$

A simple form results for the Hamiltonian in terms of these new operators,

$$\mathcal{H} = \sum_{\mathbf{k}} E_{\mathbf{k}}(\alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} + \beta_{\mathbf{k}}^\dagger \beta_{\mathbf{k}}) + E_0 , \quad (38)$$

where

$$E_0 = \sum_{\mathbf{k}} \left[\varepsilon_{\mathbf{k}} - E_{\mathbf{k}} + \Delta_{\mathbf{k}} \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle \right] \ . \tag{39}$$

Eq. (38) describes single-particle excitations out of a condensate of Cooper pairs, which is the new ground-state. From Eqs. (30) and (31) we see that $\Delta_{\mathbf{k}}$ is nearly independent of $\mathbf{k}$ (i.e., $\simeq \Delta$) in the region where it is nonzero. The important point here is to notice that there is a minimum energy Δ for single-particle excitations in the superconducting state. Even though these excitations are fermionic, the system is no longer a Fermi liquid. It has an **interaction-induced *gap*** in the energy spectrum around the $\mathbf{k}$-space surface that would be the FS in the absence of pairing. We have not evaluated Δ, which must be done self-consistently since it appears in the Hamiltonian. With further development, it can be verified that the self-consistent solution for an attractive pairing potential (as assumed here) implies that $\Delta > 0$ in the BCS ground-state, and that this is the actual ground-state, having lower energy than the Fermi liquid. In addition, a statistical analysis shows that the gap survives at finite temperature, going to zero at a critical temperature T_c, above which the system becomes a normal Fermi liquid.

Superconductivity

The new state obtained with the BCS Hamiltonian is identified as a *superconducting* state. The meaning of "state" here is not that of a quantum state but of a phase of matter. We will not develop in this course a detailed study of superconductivity, whose phenomenology is quite rich. We will just add a comment that may justify why this gapped state is identified as *superconductivity*. One of the most remarkable characteristics of a superconductor is the absence of electrical resistivity, which can be observed as **no relaxation** of an electric current established in the system (with a convenient geometry, e.g., a ring). This can be understood if we look back at what happens in a normal metal. As we have seen before, the current relaxation in a quantum model of a metal is interpreted as the effect of **nearly elastic** collisions that reduce the total momentum of the conduction electrons, counteracting the action of an external electric field. This works as a consequence of the existence of a Fermi surface. However, if there is a gap **around this surface**, such collisions cannot occur because the available states to scattered electrons are separated by a finite energy.