11

Phonons, photons, and electrons

When the sky is illumined with crystal
Then gladden my road and broaden my path
And clothe me in light.
–From "The Book of the Dead," Ancient Egypt
Translated by Robert Hillyer

In this chapter we turn to phonons, photons, and their interactions with electrons. These interactions play an important role in condensed matter physics. At room temperature, the resistivity of metals results mainly from electron–phonon inter-action. At low temperature, this interaction is responsible for the superconducting properties of many metals. On the other hand, the electron–photon interaction plays a dominant role in light scattering by solids, from which we derive a great deal of information about excitation modes in solids. Much of our knowledge about energy bands in crystals has been obtained through optical absorption experiments, whose interpretation relies on an understanding of how electrons and photons interact.

We begin by discussing lattice vibrations in crystals and show that, upon quantization, the vibrational modes are described in terms of phonons, which are particle-like excitations that carry energy and momentum. We will see that the effect of lattice vibrations on electronic states is to cause scattering, whereby electrons change their states by emitting or absorbing phonons. Similarly, the interaction of electrons with an electromagnetic field will be represented as scattering processes in which electrons emit or absorb photons.

A discussion of lattice vibrations in the general case of a three-dimensional crystal with a basis of more than one atom is somewhat complicated. To keep the presentation simple, we consider in detail the simplest case, a one-dimensional crystal with only one atom per unit cell. Next, we consider a diatomic chain, and then indicate briefly how things look in three dimensions. The reader interested in a treatment of the general case of a three-dimensional crystal with more than one atom per primitive cell will find a detailed presentation in Appendix C.
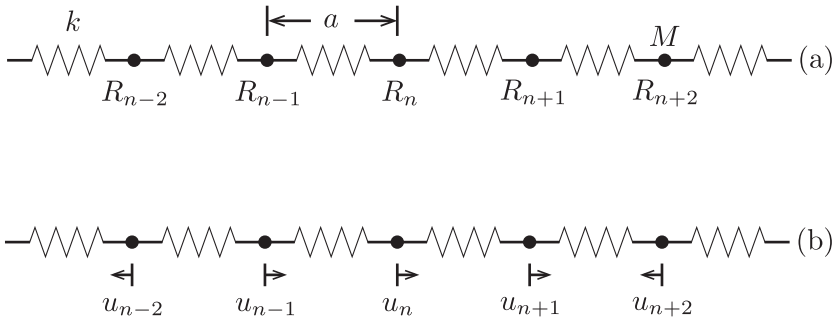
Figure 11.1 A line of atoms, each of mass M, connected by massless springs of force constant k. (a) The atoms sit at their equilibrium positions, with the equilibrium position of atom n being R_n. In equilibrium, the separation between neighboring atoms is a. (b) The atoms are displaced from equilibrium, with the displacement of atom n being u_n.

11.1 Lattice vibrations in one dimension

The simplest case we can deal with is a one-dimensional crystal with one atom per unit cell. Consider a line of N atoms ($N \gg 1$), each of mass M. In equilibrium, the position of atom n is $R_n = na$, and the separation between adjacent atoms is a. We model the interatomic interactions by massless springs, each of force constant k, which connect neighboring atoms (see Figure 11.1). When atoms vibrate, they are displaced from equilibrium. Let u_n be the displacement from equilibrium of atom n. We adopt periodic boundary conditions: $u_1 = u_{N+1}$. Newton's second law gives

$$M\ddot{u}_n = k(u_{n+1} - 2u_n + u_{n-1}). \tag{11.1}$$

This is a set of N coupled differential equations ($n = 1, 2, \dots N$). The general approach to solving such a set of coupled equations is to first find the normal modes; the general solution is then obtained by writing the displacements as linear combinations of these modes. In a normal mode all atoms vibrate with the same wave vector and frequency. Denoting wave vector as q and frequency as ω_q, atom n in a normal mode has a displacement given by

$$u_n = A \exp[i(q R_n - \omega_q t)] = A \exp[i(qna - \omega_q t)] \tag{11.2}$$

where A is a constant. Inserting this into Eq. (11.1), we obtain

$$-M\omega_q^2 = k(e^{iqa} - 2 + e^{-iqa}) = 2k[\cos(qa) - 1].$$

Writing $\cos(qa) = 1 - 2\sin^2(qa/2)$, the frequency can be expressed as

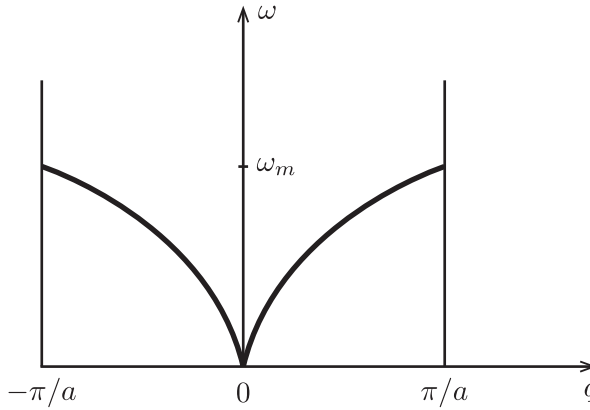$$\omega_q = \omega_m|\sin(qa/2)|, \quad \omega_m = (4k/M)^{1/2}. \tag{11.3}$$

Figure 11.2 A plot of ω vs. q for values of q in the first Brillouin zone. The crystal is one-dimensional, with one atom per primitive cell.

The relation between ω_q and q is known as the dispersion relation. We note the following:

1. Periodic boundary conditions, applied to Eq. (11.2), give the allowed values for q, namely

$$q = 0, \pm 2\pi/L, \pm 4\pi/L, \ldots$$

   where $L = Na$ is the length of the line of atoms.
2. It follows from Eqs (11.2) and (11.3) that

$$\omega_q = \omega_{-q} = \omega_{q+2\pi/a}, \quad u_n(q) = u_n(q + 2\pi/a).$$

3. As $q \to 0$, $\omega_q = vq$, where $v = \omega_m a/2$.

The second remark implies that it is sufficient to restrict the values of q to the first Brillouin zone (FBZ): $-\pi/a < q \leqslant \pi/a$. The number of normal modes is equal to the number of q-points within the FBZ, which is exactly equal to N. Since $L \gg a$, the first remark means that the separation between neighboring values of q is too small compared to the width of the FBZ; hence, when plotting ω vs q, we may consider q to be continuous. Such a plot is shown in Figure 11.2. Regarding the third remark, the fact that $\omega \to 0$ as $q \to 0$ is obvious on physical grounds: as $q \to 0$, neighboring atoms undergo equal displacements during the vibration, and the restoring forces vanish. The fact that ω approaches zero linearly in q in the long wavelength limit ($q \to 0$) assigns the name "acoustic branch" to the branch in the dispersion in Figure 11.2; v is the speed of sound in this one-dimensional crystal. The general solution of the equation of motion, Eq. (11.1), is a linear combination

of the normal modes,

$$u_n = \frac{1}{\sqrt{NM}} \sum_{q \in \text{FBZ}} Q_q e^{iqR_n}, \tag{11.4}$$

where the factor $e^{-i\omega_q t}$ is absorbed into the expansion coefficients Q_q and the factor $1/\sqrt{NM}$ is inserted for later convenience. In effect, Eq. (11.4) is a Fourier expansion of the displacement u_n. The expansion coefficients Q_q are called normal coordinates. They satisfy the relation $Q_q^* = Q_{-q}$, which is a consequence of the fact that the displacement u_n is real.

Our next task is to construct an expression for the energy of the line of atoms in terms of the normal coordinates. The kinetic energy is given by

$$T = (M/2) \sum_{n=1}^{N} \dot{u}_n^2 = \frac{1}{2N} \sum_n \sum_{qq'} \dot{Q}_q \dot{Q}_{q'} e^{i(q+q')R_n},$$

where $q, q' \in$ FBZ. Summing first over n ($\sum_n e^{i(q+q')R_n} = N\delta_{q',-q}$), we find

$$T = (1/2) \sum_q \dot{Q}_q \dot{Q}_{-q}. \tag{11.5}$$

The potential energy is the elastic energy of the springs,

$$V = (k/2) \sum_{n=1}^{N} (u_{n+1} - u_n)^2. \tag{11.6}$$

From Eq. (11.4), we can write

$$u_{n+1} - u_n = \frac{1}{\sqrt{NM}} \sum_q Q_q e^{iqR_n}(e^{iqa} - 1).$$

The potential energy is thus given by

$$V = \frac{k}{2NM} \sum_n \sum_{qq'} Q_q Q_{q'}(e^{iqa} - 1)(e^{iq'a} - 1)e^{i(q+q')R_n}.$$

Carrying out the summation over n first, we obtain

$$V = \frac{k}{2M} \sum_q Q_q Q_{-q} |e^{iqa} - 1|^2 = \frac{2k}{M} \sum_q Q_q Q_{-q} \sin^2(qa/2).$$

Using Eq. (11.3), the above expression becomes

$$V = (1/2) \sum_q \omega_q^2 Q_q Q_{-q}. \tag{11.7}$$

The Lagrangian $L = T - V$ is thus a function of the normal coordinates. The canonical momentum conjugate to Q_q is

$$P_q = \partial L / \partial \dot{Q}_q = \dot{Q}_{-q}. \tag{11.8}$$

The Hamiltonian, in terms of the dynamical variables Q_q and P_q, is

$$H = \left(\sum_q P_q \dot{Q}_q - L \right)_{\dot{Q}_q = P_{-q}}. \tag{11.9}$$

Substituting $T - V$ for L, we find

$$H = \frac{1}{2} \sum_q \left(P_q P_{-q} + \omega_q^2 Q_q Q_{-q} \right). \tag{11.10}$$

The quantum theory of lattice vibrations of the one-dimensional monatomic crystal is obtained by treating the dynamical variables Q_q and P_q as operators that satisfy the commutation relations

$$[Q_q, Q_{q'}] = [P_q, P_{q'}] = 0, \quad [Q_q, P_{q'}] = i\hbar \delta_{qq'}. \tag{11.11}$$

Analogous to the case of the harmonic oscillator (see Section 1.2), we introduce two new operators,

$$a_q = (2\hbar\omega_q)^{-1/2}(\omega_q Q_q + i P_{-q}), \quad a_q^\dagger = (2\hbar\omega_q)^{-1/2}(\omega_q Q_{-q} - i P_q). \tag{11.12}$$

These operators satisfy the commutation relations

$$[a_q, a_{q'}] = [a_q^\dagger, a_{q'}^\dagger] = 0, \quad [a_q, a_{q'}^\dagger] = \delta_{qq'}. \tag{11.13}$$

It is straightforward to show that, in terms of these operators, the Hamiltonian is

$$H = \sum_q \hbar\omega_q (a_q^\dagger a_q + 1/2). \tag{11.14}$$

The Hamiltonian is seen to be a collection of N independent harmonic oscillators. The eigenvalues are $\sum_q \hbar\omega_q(n_q + 1/2)$, where n_q is a non-negative integer. The ground state is obtained when $n_q = 0$ for all values of q. We interpret n_q as the number of particle-like excitations, called phonons, that occupy the normal mode specified by q; each phonon has energy $\hbar\omega_q$ and wave number q. The operator $a_q^\dagger(a_q)$ is interpreted as a creation (annihilation) operator that creates (annihilates) a phonon of wave number q and energy $\hbar\omega_q$. The commutation relations satisfied by a_q and $a_q^\dagger$ mean that phonons are bosonic particles. Since the quantum number $q \in$ FBZ completely specifies a vibrational mode, phonons are spinless particles.

A phonon of wave number q represents a traveling wave of wavelength $\lambda = 2\pi/|q|$. Therefore, a phonon of wave number $q = 0$ does not exist; the $q = 0$ normal mode represents a translation of the whole crystal, not a traveling wave.
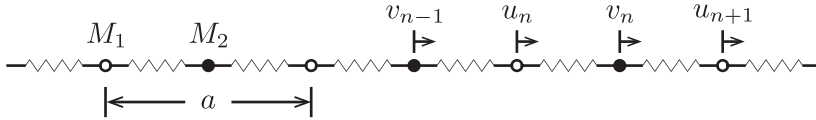
Figure 11.3 A linear diatomic chain with lattice constant a. The two different atoms have masses M_1 and M_2. Neighboring atoms are connected by springs of force constant k. In unit cell n, the displacements from equilibrium of the atoms of masses M_1 and M_2 are u_n and v_n, respectively.

11.2 One-dimensional diatomic lattice

We now consider a one-dimensional diatomic lattice (Figure 11.3). The two different atoms in a unit cell have masses M_1 and M_2, and their equilibrium separation is $a/2$. Neighboring atoms are assumed to be connected by massless springs, each of force constant k. We denote by u_n and v_n, respectively, the displacements from equilibrium of the atoms of masses M_1 and M_2, located in unit cell n. Newton's second law yields the following equations:

$$M_1 \ddot{u}_n = k(v_n - 2u_n + v_{n-1}) \tag{11.15}$$

$$M_2 \ddot{v}_n = k(u_{n+1} - 2v_n + u_n). \tag{11.16}$$

These constitute a set of $2N$ coupled differential equations, where N is the number of unit cells. To find the normal modes, we consider the trial solutions

$$u_n = u e^{i(q R_n - \omega_q t)}, \qquad v_n = v e^{i(q R_n - \omega_q t)}, \tag{11.17}$$

where $R_n = na$. Inserting these solutions into Eqs (11.15) and (11.16), we obtain the following homogeneous algebraic equations involving u and v:

$$(-M_1 \omega_q^2 + 2k)u - k(1 + e^{-iqa})v = 0 \tag{11.18}$$

$$-k(1 + e^{iqa})u + (-M_2 \omega_q^2 + 2k)v = 0. \tag{11.19}$$

A nontrivial solution exists only if the determinant of the coefficients of u and v vanishes. The result is the following expression:

$$\omega_q^2 = \frac{k}{\mu} \pm k \sqrt{\frac{1}{\mu^2} - \frac{4\sin^2(qa/2)}{M_1 M_2}} \tag{11.20}$$

where $\mu = M_1 M_2/(M_1 + M_2)$ is the reduced mass of the two atoms in the unit cell. A plot of ω vs q reveals that the dispersion curves consist of two branches (see Figure 11.4). The lower branch is the acoustic branch, while the upper one is
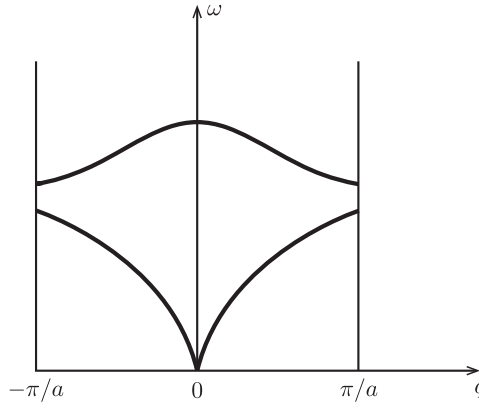
Figure 11.4 Dispersion curves for a linear diatomic chain with lattice constant a. The lower (upper) branch is the acoustic (optical) branch.

the optical branch. As $q \to 0$,

$$\omega = \sqrt{\frac{ka^2}{2(M_1 + M_2)}}\, q \quad \text{(acoustic)}, \quad \omega = \sqrt{2k/\mu} \quad \text{(optical)}. \qquad (11.21)$$

At the Brillouin zone edges ($q = \pm\pi/a$) we find, based on Eq. (11.20), that

$$\omega = \sqrt{\frac{2k}{\max(M_1, M_2)}} \quad \text{(acoustic)}, \qquad \omega = \sqrt{\frac{2k}{\min(M_1, M_2)}} \quad \text{(optical)} \qquad (11.22)$$

where $\max(M_1, M_2)$ is the larger of M_1 and M_2, and $\min(M_1, M_2)$ is the smaller of the two masses. At $q = 0$, Eqs (11.18), (11.19), and (11.21) give

$$u/v = 1 \quad \text{(acoustic)}, \qquad u/v = -M_2/M_1 \quad \text{(optical)}. \qquad (11.23)$$

At the Brillouin zone center ($q = 0$), all atoms vibrate in phase in the acoustic mode, undergoing equal displacements; the vanishing of the frequency results from the absence of any restoring forces. In the optical mode, on the other hand, adjacent atoms vibrate out of phase (see Figure 11.5). We note that the optical mode is excited by infrared light, hence the name "optical mode."

If we were to construct a quantum theory of lattice vibrations for the diatomic chain, we would find the following Hamiltonian:

$$H = \sum_{q \in \text{FBZ}} \sum_{\lambda=1}^{2} \hbar\omega_{q\lambda}(a_{q\lambda}^{\dagger} a_{q\lambda} + 1/2). \qquad (11.24)$$
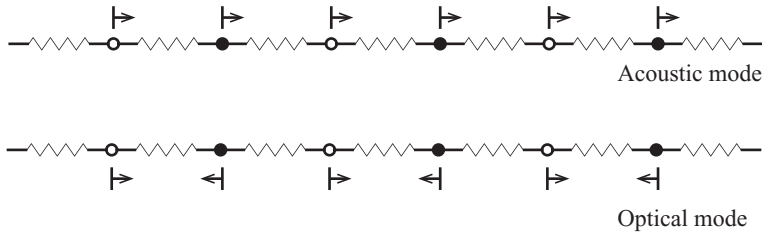
Figure 11.5 The acoustic (upper figure) and optical (lower figure) modes at the Brillouin zone center ($q = 0$) of a linear diatomic chain.

Here, the index λ refers to the phonon branch. There are two branches, an acoustic one and an optical one. The operator $a_{q\lambda}^{\dagger}$ ($a_{q\lambda}$) creates (annihilates) a phonon of wave number q, branch index λ, and energy $\hbar\omega_{q\lambda}$.

11.3 Phonons in three-dimensional crystals

We now briefly indicate how the one-dimensional case is generalized to three dimensions. A detailed account is given in Appendix C.

We consider a crystal consisting of N unit cells with a basis of r atoms. The displacement from equilibrium of atom l ($l = 1, 2, \ldots, r$) in unit cell n ($n = 1, 2, \ldots, N$) is denoted by $\mathbf{u}_{nl}$. Since there are Nr atoms in the crystal and each atom vibrates in three dimensions, there are $3Nr$ degrees of freedom; consequently, there is a total of $3Nr$ normal modes. In a normal mode, all atoms vibrate with the same wave vector and frequency. A normal mode is specified by a wave vector $\mathbf{q} \in$ FBZ (there are N such vectors) and a branch index $\lambda = 1, 2, \ldots, 3r$. In a normal mode with coordinates ($\mathbf{q}\lambda$),

$$\mathbf{u}_{nl} \propto (M_l)^{-1/2} \boldsymbol{\epsilon}_{\lambda}^{(l)}(\mathbf{q}) e^{i(\mathbf{q} \cdot \mathbf{R}_n - \omega_{\mathbf{q}\lambda} t)},$$

where M_l is the mass of atom l and $\boldsymbol{\epsilon}_{\lambda}^{(l)}$ is a polarization vector that determines the direction of the displacement $\mathbf{u}_{nl}$ relative to the wave vector $\mathbf{q}$. In a purely longitudinal normal mode, $\boldsymbol{\epsilon}_{\lambda}^{(l)} \parallel \mathbf{q}$, while in a purely transverse mode, $\boldsymbol{\epsilon}_{\lambda}^{(l)} \perp \mathbf{q}$. The general solution of the equations of motion is a linear combination of the $3Nr$ normal modes,

$$\mathbf{u}_{nl} = (NM_l)^{-1/2} \sum_{\mathbf{q}\lambda} Q_{\mathbf{q}\lambda} \boldsymbol{\epsilon}_{\lambda}^{(l)}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_n}. \tag{11.25}$$

The time-dependent coefficients $Q_{\mathbf{q}\lambda}$ are called normal coordinates. Since $\mathbf{u}_{nl}^* = \mathbf{u}_{nl}$ (displacements are real), it follows that $Q_{\mathbf{q}\lambda}^* = Q_{-\mathbf{q}\lambda}$ and $\boldsymbol{\epsilon}_{\lambda}^{(l)*}(\mathbf{q}) = \boldsymbol{\epsilon}_{\lambda}^{(l)}(-\mathbf{q})$. The Hamiltonian can be expressed in terms of the normal coordinates $Q_{\mathbf{q}\lambda}$ and their

conjugate momenta $P_{\mathbf{q}\lambda}$:

$$H = (1/2) \sum_{\mathbf{q}\lambda} (P_{\mathbf{q}\lambda} P_{-\mathbf{q}\lambda} + \omega_{\mathbf{q}\lambda}^2 Q_{\mathbf{q}\lambda} Q_{-\mathbf{q}\lambda}). \qquad (11.26)$$

Passage to a quantum theory of lattice vibrations is accomplished by treating the dynamical variables $Q_{\mathbf{q}\lambda}$ and $P_{\mathbf{q}\lambda}$ as operators that satisfy the commutation relations

$$[Q_{\mathbf{q}\lambda}, Q_{\mathbf{q}'\lambda'}] = [P_{\mathbf{q}\lambda}, P_{\mathbf{q}'\lambda'}] = 0, \quad [Q_{\mathbf{q}\lambda}, P_{\mathbf{q}'\lambda'}] = i\hbar \delta_{\mathbf{q}\mathbf{q}'} \delta_{\lambda\lambda'}. \qquad (11.27)$$

We introduce two new operators $a_{\mathbf{q}\lambda}$ and $a_{\mathbf{q}\lambda}^{\dagger}$ such that

$$Q_{\mathbf{q}\lambda} = \sqrt{\frac{\hbar}{2\omega_{\mathbf{q}\lambda}}} (a_{\mathbf{q}\lambda} + a_{-\mathbf{q}\lambda}^{\dagger}) \qquad (11.28)$$

$$P_{\mathbf{q}\lambda} = i\sqrt{\frac{\hbar\omega_{\mathbf{q}\lambda}}{2}} (a_{\mathbf{q}\lambda}^{\dagger} - a_{-\mathbf{q}\lambda}). \qquad (11.29)$$

Note that $Q_{-\mathbf{q}\lambda} = Q_{\mathbf{q}\lambda}^{\dagger}$. The new operators satisfy the commutation relations

$$[a_{\mathbf{q}\lambda}, a_{\mathbf{q}'\lambda'}] = [a_{\mathbf{q}\lambda}^{\dagger}, a_{\mathbf{q}'\lambda'}^{\dagger}] = 0, \quad [a_{\mathbf{q}\lambda}, a_{\mathbf{q}'\lambda'}^{\dagger}] = \delta_{\mathbf{q}\mathbf{q}'} \delta_{\lambda\lambda'}. \qquad (11.30)$$

In terms of these operators, the Hamiltonian can be written as

$$H = \sum_{\mathbf{q}\lambda} \hbar\omega_{\mathbf{q}\lambda} (a_{\mathbf{q}\lambda}^{\dagger} a_{\mathbf{q}\lambda} + 1/2). \qquad (11.31)$$

The operator $a_{\mathbf{q}\lambda}^{\dagger}$ ($a_{\mathbf{q}\lambda}$) is interpreted as a creation (annihilation) operator of a phonon of wave vector $\mathbf{q}$, branch index λ, and energy $\hbar\omega_{\mathbf{q}\lambda}$.

Finally, we note that there are three acoustic phonon branches with a zero frequency at the Brillouin zone center ($\mathbf{q} = 0$), and $3r - 3$ optical phonon branches with nonvanishing frequencies.

11.4 Phonon statistics

The Hamiltonian given in Eq. (11.31) describes a system of noninteracting phonons. Its eigenvalues are $\sum_{\mathbf{q}\lambda}(n_{\mathbf{q}\lambda} + 1/2)\hbar\omega_{\mathbf{q}\lambda}$, where $n_{\mathbf{q}\lambda} = 0, 1, 2\dots$ is a non-negative integer, interpreted as the number of phonons of wave vector $\mathbf{q}$, branch index λ, and energy $\hbar\omega_{\mathbf{q}\lambda}$. In the ground state, $n_{\mathbf{q}\lambda} = 0$ for all values of $\mathbf{q}$ and λ. We now calculate $\langle n_{\mathbf{q}\lambda} \rangle_0$, the average number of phonons occupying the normal mode ($\mathbf{q}\lambda$), for a system of noninteracting phonons in equilibrium at temperature T. The subscript "0" refers to a noninteracting system.

When the system is in equilibrium at temperature T, any particular normal mode ($\mathbf{q}\lambda$) may be occupied by any number of phonons. The probability that n phonons

occupy the mode $(\mathbf{q}\lambda)$ is $e^{-\beta n\hbar\omega_{\mathbf{q}\lambda}}/\sum_{n=0}^{\infty}e^{-\beta n\hbar\omega_{\mathbf{q}\lambda}}$. Hence,

$$\langle n_{\mathbf{q}\lambda}\rangle_0 = \sum_{n=0}^{\infty}ne^{-\beta n\hbar\omega_{\mathbf{q}\lambda}}\left/\sum_{n=0}^{\infty}e^{-\beta n\hbar\omega_{\mathbf{q}\lambda}}\right..$$

The evaluation of the above expression is straightforward: the denominator is a geometric series, while the numerator is proportional to the derivative, with respect to β, of the same series. We obtain

$$\langle n_{\mathbf{q}\lambda}\rangle_0 = \frac{1}{e^{\beta\hbar\omega_{\mathbf{q}\lambda}}-1} \equiv n_{\omega_{\mathbf{q}\lambda}}. \tag{11.32}$$

As expected, phonons obey Bose–Einstein statistics. The important point here (and the reason for going through the derivation) is the absence of a chemical potential: $\mu = 0$, as Eq. (11.32) indicates. The vanishing of the chemical potential results from the fact that the number of phonons in the system is unrestricted: an arbitrary number of phonons can occupy a normal mode $(\mathbf{q}\lambda)$.

11.5 Electron–phonon interaction: rigid-ion approximation

The basic idea underlying the electron–phonon interaction is simple, as illustrated in Figure 11.6. When ions sit at their equilibrium positions, the state of an electron is described by a Bloch function of wave vector $\mathbf{k}$ (and spin projection σ and band index n). A phonon disturbs the lattice, and ions move out of their equilibrium positions. This causes a change in the potential seen by the electron (the potential no longer has the periodicity of the lattice). This change, in turn, scatters the electron into another state with wave vector $\mathbf{k}'$.

In this section, we calculate the electron–phonon interaction within the rigid-ion approximation: in it, the potential field of an ion is assumed to be rigidly attached to the ion as it moves. This is an approximation because, in reality, as a nucleus moves, it does not rigidly carry along the electronic charge that surrounds it. In the rigid-ion approximation, the interaction between an electron and an ion depends on the distance that separates them. This approximation is reasonable for simple metals, but it is not adequate for polar crystals, where ionic vibrations produce an electric field which acts on the electron.

For simplicity of notation, we assume that there is one atom per unit cell; the extension to a crystal with a basis is straightforward. The interaction of an electron at position $\mathbf{r}_j$ with the ions is given by

$$V_{e-i} = \sum_n V(\mathbf{r}_j - \mathbf{R}_n - \mathbf{u}_n) \simeq \sum_n V(\mathbf{r}_j - \mathbf{R}_n) - \sum_n \mathbf{u}_n.\nabla V(\mathbf{r}_j - \mathbf{R}_n).$$
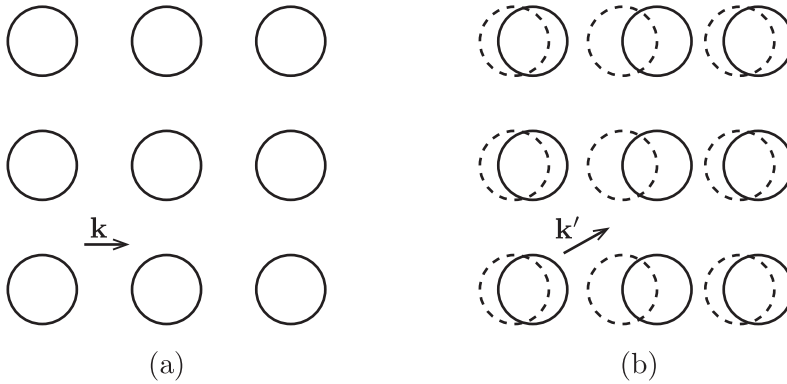
Figure 11.6 (a) An electron is in the Bloch state $|n\mathbf{k}\sigma\rangle$. As long as the lattice is static, the electron remains in this state. (b) In the presence of a phonon, the ions in the lattice vibrate, and the electron sees a different ionic potential than it does in (a). The change in the potential energy of the electron acts as a time-dependent perturbation that can scatter the electron into the stationary states $|n'\mathbf{k}'\sigma\rangle$.

$V(\mathbf{r}_j - \mathbf{R}_n - \mathbf{u}_n)$ is the interaction energy of the electron with the ion in unit cell n when the ion is displaced from equilibrium by $\mathbf{u}_n$. The gradient is with respect to the electron coordinates. The above equation is no more than a Taylor expansion of V_{e-i} to first order in the displacement; higher orders are ignored due to the smallness of the ionic displacement as compared to the spacing between neighboring ions. The first term in the expansion is the periodic potential energy which results from the interaction of the electron with the static ions at their equilibrium positions; when combined with the electron's kinetic energy, this term gives rise to the Bloch Hamiltonian whose eigenfunctions are the Bloch functions. The second term, when summed over all electrons, is the electron–phonon interaction:

$$H_{e-\text{phonon}} = -\sum_{jn} \mathbf{u}_n . \nabla V(\mathbf{r}_j - \mathbf{R}_n). \tag{11.33}$$

The displacement $\mathbf{u}_n$ is now written in terms of the normal coordinates (see Eq. [11.25]); we obtain

$$H_{e-\text{phonon}} = \frac{-1}{\sqrt{NM}} \sum_n \sum_{\mathbf{q}\lambda} Q_{\mathbf{q}\lambda} e^{i\mathbf{q}.\mathbf{R}_n} \sum_j \boldsymbol{\epsilon}_\lambda . \nabla V(\mathbf{r}_j - \mathbf{R}_n). \tag{11.34}$$

In this expression, the sum over the electrons is identified as a one-body operator of the form $\sum_j h(\mathbf{r}_j)$; its second quantized form is

$$\sum_j \boldsymbol{\epsilon}_\lambda . \nabla V(\mathbf{r}_j - \mathbf{R}_n) = \sum_{\mathbf{k}\mathbf{k}'\sigma} \left(\int \psi^*_{\mathbf{k}'\sigma}(\mathbf{r}) \boldsymbol{\epsilon}_\lambda . \nabla V(\mathbf{r} - \mathbf{R}_n) \psi_{\mathbf{k}\sigma}(\mathbf{r}) d^3r \right) c^\dagger_{\mathbf{k}'\sigma} c_{\mathbf{k}\sigma}$$
$$\tag{11.35}$$

where $\psi_{\mathbf{k}\sigma}(\mathbf{r})$ and $\psi_{\mathbf{k}'\sigma}(\mathbf{r})$ are Bloch functions. In writing the above equation, we have assumed that there is only one partially filled band (as is the case in simple metals) and that electrons scatter within this band; we thus ignored the band index when writing the Bloch functions. Furthermore, no spin flip can occur when an electron is scattered by lattice vibrations.

We recall that, according to Bloch's theorem (Section 2.3),

$$\psi_{\mathbf{k}\sigma}(\mathbf{r} + \mathbf{R}_n) = e^{i\mathbf{k}.\mathbf{R}_n}\psi_{\mathbf{k}\sigma}(\mathbf{r}). \tag{11.36}$$

We can take advantage of this property: in the integral in Eq. (11.35), we replace the integration variable $\mathbf{r}$ with $\mathbf{r} + \mathbf{R}_n$; then

$$\sum_j \boldsymbol{\epsilon}_\lambda.\boldsymbol{\nabla} V(\mathbf{r}_j - \mathbf{R}_n) = \sum_{\mathbf{k}\mathbf{k}'\sigma} e^{i(\mathbf{k}-\mathbf{k}').\mathbf{R}_n}\left(\int \psi_{\mathbf{k}'\sigma}^*(\mathbf{r})\boldsymbol{\epsilon}_\lambda.\boldsymbol{\nabla} V(\mathbf{r})\psi_{\mathbf{k}\sigma}(\mathbf{r})d^3r\right) c_{\mathbf{k}'\sigma}^\dagger c_{\mathbf{k}\sigma}.$$

We insert this into Eq. (11.34) and carry out the summation over n:

$$\sum_n e^{i(\mathbf{k}-\mathbf{k}'+\mathbf{q}).\mathbf{R}_n} = N\sum_{\mathbf{G}} \delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}+\mathbf{G}}, \tag{11.37}$$

where $\mathbf{G}$ is a reciprocal lattice vector. Equation (11.34) becomes

$$H_{e-\text{phonon}} = -\sqrt{N/M}\sum_{\mathbf{k}\sigma}\sum_{\mathbf{q}\lambda}\sum_{\mathbf{G}} \boldsymbol{\epsilon}_\lambda.\mathbf{T}(\mathbf{k}, \mathbf{q}, \mathbf{G}\sigma)c_{\mathbf{k}+\mathbf{q}+\mathbf{G}\sigma}^\dagger c_{\mathbf{k}\sigma} Q_{\mathbf{q}\lambda}. \tag{11.38}$$

Here,

$$\mathbf{T}(\mathbf{k}, \mathbf{q}, \mathbf{G}\sigma) = \int \psi_{\mathbf{k}+\mathbf{q}+\mathbf{G}\sigma}^*(\mathbf{r})\boldsymbol{\nabla} V(\mathbf{r})\psi_{\mathbf{k}\sigma}(\mathbf{r})d^3r. \tag{11.39}$$

We can proceed a bit further if we adopt the effective mass approximation: $\psi_{\mathbf{k}}(\mathbf{r}) \simeq (1/\sqrt{V})e^{i\mathbf{k}.\mathbf{r}}$, $\epsilon_{\mathbf{k}} \simeq \hbar^2 k^2/2m^*$, where V is the volume of the crystal and m^* is the effective electron mass. This approximation is adequate for simple metals. Expanding $V(\mathbf{r})$ in a Fourier series,

$$V(\mathbf{r}) = (1/V)\sum_{\mathbf{p}} V_{\mathbf{p}}e^{i\mathbf{p}.\mathbf{r}} \Rightarrow \boldsymbol{\nabla} V = (i/V)\sum_{\mathbf{p}} \mathbf{p}V_{\mathbf{p}}e^{i\mathbf{p}.\mathbf{r}},$$

making use of the relation

$$\int e^{i(\mathbf{p}-\mathbf{q}-\mathbf{G}).\mathbf{r}}d^3r = V\delta_{\mathbf{p},\mathbf{q}+\mathbf{G}},$$

and writing $Q_{\mathbf{q}\lambda}$ in terms of phonon creation and annihilation operators (see Eq. [11.28]), we finally obtain

$$H_{e-\text{phonon}} = -\frac{i}{V}\sum_{\mathbf{k}\sigma}\sum_{\mathbf{q}\lambda}\sum_{\mathbf{G}} \sqrt{\frac{N\hbar}{2M\omega_{\mathbf{q}\lambda}}}V_{\mathbf{q}+\mathbf{G}}(\mathbf{q} + \mathbf{G}).\boldsymbol{\epsilon}_\lambda(\mathbf{q})c_{\mathbf{k}+\mathbf{q}+\mathbf{G}\sigma}^\dagger c_{\mathbf{k}\sigma}(a_{\mathbf{q}\lambda} + a_{-\mathbf{q}\lambda}^\dagger).$$
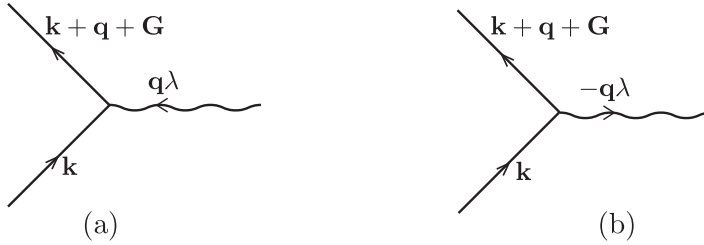
$$\tag{11.40}$$

Figure 11.7 A pictorial representation of electron–phonon interaction. (a) An electron is scattered from state $|\mathbf{k}\sigma\rangle$ into state $|\mathbf{k}+\mathbf{q}+\mathbf{G}\sigma\rangle$ by absorbing a phonon of wave vector $\mathbf{q}$ and branch index λ. (b) Here, scattering occurs by the emission of a phonon with coordinates $(-\mathbf{q}\lambda)$.

For a crystal with a basis of r atoms: $l = 1, 2, \ldots, r$, the above expression is modified as follows: $M \to M_l$, $V_{\mathbf{q}+\mathbf{G}} \to V_{\mathbf{q}+\mathbf{G}}^{(l)}$, $\boldsymbol{\epsilon}_\lambda(\mathbf{q}) \to \boldsymbol{\epsilon}_\lambda^{(l)}(\mathbf{q})$, and an extra summation $\sum_{l=1}^{r}$ is carried out.

We make the following remarks regarding the electron–phonon interaction:

(1) The interaction is seen to be a sum of terms, with each term representing a scattering process in which an electron is scattered from state $|\mathbf{k}\sigma\rangle$ into state $|\mathbf{k}+\mathbf{q}+\mathbf{G}\sigma\rangle$ by either emitting or absorbing a phonon. The scattering process is depicted in Figure 11.7.

(2) The wave vectors $\mathbf{q}$, $\mathbf{k}$, and $\mathbf{k}' = \mathbf{k}+\mathbf{q}+\mathbf{G}$ must all lie in the first Brillouin zone (FBZ). Hence, in summing over $\mathbf{G}$, there is only one term in the summation for any fixed $\mathbf{k}$ and $\mathbf{q}$; $\mathbf{G}$ is the one reciprocal lattice vector which, when added to $\mathbf{k}+\mathbf{q}$, carries it back into the FBZ. If $\mathbf{k}+\mathbf{q} \in$ FBZ, then $\mathbf{G} = 0$; otherwise, $\mathbf{G} \neq 0$. Electron scattering processes (by the emission or absorption of a phonon) for which $\mathbf{G} = 0$ are called normal processes. A process for which $\mathbf{G} \neq 0$ is called an Umklapp process. Normal and Umklapp processes are depicted in Figure 11.8.

(3) We restrict further discussion to normal processes only: $\mathbf{G} = 0$. The factor $\mathbf{q}.\boldsymbol{\epsilon}_\lambda(\mathbf{q})$ in Eq. (11.40) implies that electrons interact only with longitudinal phonons. In isotropic media, phonon polarization vectors are actually either longitudinal or transverse.

(4) We write the electron–phonon interaction in the following form:

$$H_{e-\text{phonon}} = \sum_{\mathbf{k}\sigma} \sum_{\mathbf{q}\lambda} M_{\mathbf{q}\lambda} c_{\mathbf{k}+\mathbf{q}\sigma}^\dagger c_{\mathbf{k}\sigma} (a_{\mathbf{q}\lambda} + a_{-\mathbf{q}\lambda}^\dagger). \qquad (11.41)$$

The matrix element $M_{\mathbf{q}\lambda}$ is a measure of the strength of the electron–phonon interaction. Its mathematical form depends on the kind of approximations one
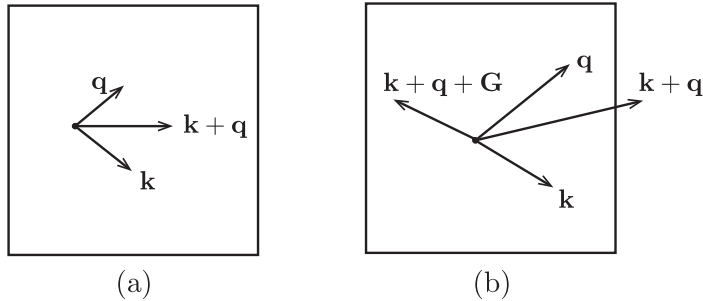
Figure 11.8 Normal and Umklapp processes in a two-dimensional square lattice of lattice constant a. The square shown in the figure is the FBZ; its side is $2\pi/a$. In the scattering process, an electron of wave vector $\mathbf{k}$ absorbs a phonon of wave vector $\mathbf{q}$ or emits a phonon of wave vector $-\mathbf{q}$. (a) The wave vector $\mathbf{k} + \mathbf{q} \in$ FBZ; the scattering process is normal. (b) $\mathbf{k} + \mathbf{q} \notin$ FBZ; a reciprocal lattice vector $\mathbf{G}$ must be added to carry $\mathbf{k} + \mathbf{q}$ back into the FBZ, so the scattering process is Umklapp.

makes (Ziman, 1960). Since H_{e-ph} is Hermitian, it follows that

$$M_{\mathbf{q}\lambda}^* = M_{-\mathbf{q}\lambda}. \tag{11.42}$$

Let us consider the case of an isotropic medium (a cubic crystal, for example) with only one atom per unit cell. In this case, there is one longitudinal acoustic branch and two transverse acoustic branches. Electrons interact only with the longitudinal phonons. Assuming that the crystal is a metal, the Coulomb potential of the ions is screened by the conduction electrons. Since ions move very slowly compared to electrons, we can assume that the screening is static, similar to the screening of a fixed charged impurity. The screened Coulomb potential of an ion is thus taken to be $4\pi Ze/q^2\varepsilon(\mathbf{q}, 0)$, where Ze is the ionic charge and $\varepsilon(\mathbf{q}, 0)$ is the static dielectric function. For small values of q, this is given by $4\pi Ze/(q^2 + q_{TF}^2) \simeq 4\pi Ze/q_{TF}^2$, where q_{TF} is the Thomas–Fermi wave number. The electron–ion interaction energy thus has the Fourier component $V_{\mathbf{q}} = -4\pi Ze^2/q_{TF}^2$. Under these assumptions, it follows from Eq. (11.40) that the electron–phonon interaction matrix element depends on $\mathbf{q}$ only and is given by

$$M_{\mathbf{q}} = \frac{i}{V}\sqrt{\frac{N\hbar}{2M\omega_{\mathbf{q}}}}\frac{4\pi Ze^2}{q_{TF}^2}\mathbf{q}.\boldsymbol{\epsilon}_\lambda(\mathbf{q}). \tag{11.43}$$

Note that because $\boldsymbol{\epsilon}_\lambda(-\mathbf{q}) = \boldsymbol{\epsilon}_\lambda^*(\mathbf{q})$, $M_{\mathbf{q}}$ satisfies the relation $M_{\mathbf{q}}^* = M_{-\mathbf{q}}$, as it should. Often in the literature $\mathbf{q}.\boldsymbol{\epsilon}_\lambda(\mathbf{q})$ is replaced by q, which is the magnitude of $\mathbf{q}$; this is not quite accurate, for then the equality $M_{\mathbf{q}}^* = M_{-\mathbf{q}}$ is not satisfied. Note further that $M_{\mathbf{q}=0} = 0$: in a normal mode, with $\mathbf{q} = \mathbf{0}$, the periodicity of the

lattice is preserved, Bloch states are still the stationary states of the system, and no scattering takes place.

11.6 Electron–LO phonon interaction in polar crystals

We indicated in the previous section that the rigid-ion approximation is not adequate for polar crystals, where the electric field associated with longitudinal optical (LO) vibrations acts on the electrons. We consider the simplest case of a cubic polar crystal with two ions per unit cell; the ions have equal but opposite charges. Moreover, we only consider vibrations in the long wavelength limit. Even in this case, the calculation of the electron–LO phonon coupling is not easy. We relegate the details to Appendix D. Here, we simply summarize the main results.

(1) There is no electric field associated with transverse optical (TO) modes.
(2) The electric field associated with a longitudinal optical (LO) mode exerts a restoring force on the ions, in addition to the short-range restoring forces that are present in the absence of an electric field. The result is that the LO–phonon frequency is higher than the TO–phonon frequency. In the long wavelength limit ($q \to 0$), we find

$$\omega_{\mathrm{LO}}^2 = \frac{\varepsilon(0)}{\varepsilon(\infty)} \omega_{\mathrm{TO}}^2 \,, \tag{11.44}$$

where $\varepsilon(0) = \varepsilon(\mathbf{q} \to 0, \omega = 0)$ is the static dielectric constant (measured by applying a static electric field to the crystal) and $\varepsilon(\infty) = \varepsilon(\mathbf{q} = 0, \omega \gg \omega_{\mathrm{phonon}})$ is the high-frequency dielectric constant of the crystal (it is the square of the refractive index of the crystal). The above relation is known as the Lyddane–Sachs–Teller (LST) relation.
(3) The electron–LO phonon interaction takes the form:

$$H_{e-\mathrm{LO}} = \sum_{ss'} \sum_{\mathbf{k}\sigma} {\sum_{\mathbf{q}}}' M_{\mathbf{q}}^{ss'} c_{s'\mathbf{k}+\mathbf{q}\sigma}^{\dagger} c_{s\mathbf{k}\sigma} (a_{\mathbf{q}} + a_{-\mathbf{q}}^{\dagger}). \tag{11.45}$$

The prime on the summation indicates that the $\mathbf{q} = 0$ term is excluded, $a_{\mathbf{q}}^{\dagger}(a_{\mathbf{q}})$ creates (annihilates) an LO–phonon of wave vector $\mathbf{q}$, and $c_{s\mathbf{k}\sigma}^{\dagger}(c_{s\mathbf{k}\sigma})$ creates (annihilates) an electron in state $|s\mathbf{k}\sigma\rangle$, where s is the band index. The matrix element $M_{\mathbf{q}}^{ss'}$ is given by

$$M_{\mathbf{q}}^{ss'} = i\omega_{\mathrm{LO}} \left[\frac{1}{\epsilon(\infty)} - \frac{1}{\epsilon(0)} \right]^{1/2} \left(\frac{2\pi\hbar e^2}{V q^2 \omega_{\mathrm{LO}}} \right)^{1/2} \boldsymbol{\epsilon}_L(\mathbf{q}).\hat{\mathbf{q}} \langle s'\mathbf{k} + \mathbf{q}\sigma | e^{i\mathbf{q}.\mathbf{r}} | s\mathbf{k}\sigma \rangle. \tag{11.46}$$

Here, V is the crystal volume, $\hat{\mathbf{q}}$ is the unit vector in the direction of $\mathbf{q}$, and $\epsilon_L(\mathbf{q})$ is the LO–phonon unit polarization vector.

If we assume that electron scattering by phonons takes place in only one band, the sum over s and s' in Eq. (11.45) is no longer there. If we also approximate the Bloch functions by plane waves, the matrix element $\langle s'\mathbf{k} + \mathbf{q}\sigma | e^{i\mathbf{q}\cdot\mathbf{r}} | s\mathbf{k}\sigma \rangle$ becomes equal to unity.

11.7 Phonon Green's function

In previous chapters, we defined the retarded and advanced Green's functions for bosons in terms of the ensemble average of the commutator of an annihilation and a creation operator. The imaginary-time Green's function was also defined in terms of the ensemble average of the time-ordered product of an annihilation and a creation operator. Although a similar definition for the phonon Green's function may be adopted, this is not the most convenient one. This is because the linear combination $a_{\mathbf{q}\lambda} + a^{\dagger}_{-\mathbf{q}\lambda}$ appears in the electron–phonon interaction. It is this particular combination that is employed in the definition of the phonon Green's function.

11.7.1 Definitions

The phonon retarded Green's function is defined by

$$d^R(\mathbf{q}\lambda, t) = -i\theta(t)\langle [\phi_{\mathbf{q}\lambda}(t), \phi^{\dagger}_{\mathbf{q}\lambda}(0)] \rangle, \tag{11.47}$$

where $\theta(t)$ is the step function,

$$\phi_{\mathbf{q}\lambda} = a_{\mathbf{q}\lambda} + a^{\dagger}_{-\mathbf{q}\lambda} \tag{11.48}$$

is the phonon field operator, and $\phi_{\mathbf{q}\lambda}(t) = e^{iHt/\hbar}\phi_{\mathbf{q}\lambda}(0)e^{-iHt/\hbar}$. In Eq. (11.47), the average is over a canonical ensemble,

$$\langle \cdots \rangle = Tr(e^{-\beta H} \dots)/Tr(e^{-\beta H}). \tag{11.49}$$

For phonons, canonical and grand canonical ensembles coincide because the chemical potential vanishes, as discussed in Section 11.4.

The phonon imaginary-time (Matsubara) Green's function is defined by

$$d(\mathbf{q}\lambda, \tau) = -\langle T\phi_{\mathbf{q}\lambda}(\tau)\phi^{\dagger}_{\mathbf{q}\lambda}(0)\rangle \tag{11.50}$$

Here, $\phi_{\mathbf{q}\lambda}(\tau) = e^{H\tau/\hbar}\phi_{\mathbf{q}\lambda}(0)e^{-H\tau/\hbar}$, and T is the time-ordering operator,

$$T\phi_{\mathbf{q}\lambda}(\tau)\phi^{\dagger}_{\mathbf{q}\lambda}(0) = \begin{cases} \phi_{\mathbf{q}\lambda}(\tau)\phi^{\dagger}_{\mathbf{q}\lambda}(0) & \tau > 0 \\ \phi^{\dagger}_{\mathbf{q}\lambda}(0)\phi_{\mathbf{q}\lambda}(\tau) & \tau < 0. \end{cases} \tag{11.51}$$

No minus sign is incurred upon interchanging the operators, since they are bosonic. We focus our attention on the imaginary-time Green's function; from it, the retarded function can be obtained by analytic continuation.

11.7.2 Periodicity

As discussed in Chapter 8, the time τ is restricted to the interval $[-\beta\hbar, \beta\hbar]$. Since $\phi_{\mathbf{q}\lambda}$ is a bosonic operator, it follows from the results of Chapter 8 that the phonon Green's function is periodic:

$$d(\mathbf{q}\lambda, \tau > 0) = d(\mathbf{q}\lambda, \tau - \beta\hbar). \tag{11.52}$$

The Fourier expansion of Green's function is given by

$$d(\mathbf{q}\lambda, \tau) = \frac{1}{\beta\hbar} \sum_{m=-\infty}^{\infty} d(\mathbf{q}\lambda, \omega_m) e^{-i\omega_m\tau}, \quad \omega_m = 2\pi m/\beta\hbar \tag{11.53}$$

and the Fourier transform is

$$d(\mathbf{q}\lambda, \omega_m) = \int_0^{\beta\hbar} d(\mathbf{q}\lambda, \tau) e^{i\omega_m\tau} d\tau. \tag{11.54}$$

11.8 Free-phonon Green's function

For a noninteracting system of phonons,

$$d^0(\mathbf{q}\lambda, \tau) = \theta(\tau) d^{0>}(\mathbf{q}\lambda, \tau) + \theta(-\tau) d^{0<}(\mathbf{q}\lambda, \tau). \tag{11.55}$$

The greater and lesser functions are given by

$$d^{0>}(\mathbf{q}\lambda, \tau) = -\langle \phi_{\mathbf{q}\lambda}(\tau)\phi_{\mathbf{q}\lambda}^\dagger(0)\rangle_0, \quad d^{0<}(\mathbf{q}\lambda, \tau) = -\langle \phi_{\mathbf{q}\lambda}^\dagger(0)\phi_{\mathbf{q}\lambda}(\tau)\rangle_0. \tag{11.56}$$

In terms of phonon creation and annihilation operators,

$$d^{0>}(\mathbf{q}\lambda, \tau) = -\left\langle \left(a_{\mathbf{q}\lambda}(\tau) + a_{-\mathbf{q}\lambda}^\dagger(\tau)\right)\left(a_{\mathbf{q}\lambda}^\dagger(0) + a_{-\mathbf{q}\lambda}(0)\right)\right\rangle_0 \tag{11.57}$$

where $a_{\mathbf{q}\lambda}(\tau) = e^{H\tau/\hbar} a_{\mathbf{q}\lambda}(0) e^{-H\tau/\hbar}$ and $a_{-\mathbf{q}\lambda}^\dagger(\tau) = e^{H\tau/\hbar} a_{-\mathbf{q}\lambda}^\dagger(0) e^{-H\tau/\hbar}$. Taking the derivative with respect to τ, we obtain

$$\dot{a}_{\mathbf{q}\lambda}(\tau) = (1/\hbar)[H(\tau), a_{\mathbf{q}\lambda}(\tau)], \quad \dot{a}_{-\mathbf{q}\lambda}^\dagger(\tau) = (1/\hbar)[H(\tau), a_{-\mathbf{q}\lambda}^\dagger(\tau)].$$

Note that $H(0) = H(\tau)$. Since $H = \sum_{\mathbf{q}\lambda} \hbar\omega_{\mathbf{q}\lambda}(a_{\mathbf{q}\lambda}^\dagger a_{\mathbf{q}\lambda} + 1/2)$, the commutators are evaluated easily; we find

$$a_{\mathbf{q}\lambda}(\tau) = e^{-\omega_{\mathbf{q}\lambda}\tau} a_{\mathbf{q}\lambda}, \quad a_{-\mathbf{q}\lambda}^\dagger(\tau) = e^{\omega_{\mathbf{q}\lambda}\tau} a_{-\mathbf{q}\lambda}^\dagger. \tag{11.58}$$

Inserting these into Eq. (11.57), and noting that the terms $\langle a_{\mathbf{q}\lambda} a_{-\mathbf{q}\lambda} \rangle_0$ and $\langle a^\dagger_{-\mathbf{q}\lambda} a^\dagger_{\mathbf{q}\lambda} \rangle_0$ vanish, we obtain

$$d^{0>}(\mathbf{q}\lambda, \tau) = - \left[e^{-\omega_{\mathbf{q}\lambda}\tau} \langle a_{\mathbf{q}\lambda} a^\dagger_{\mathbf{q}\lambda} \rangle_0 + e^{\omega_{\mathbf{q}\lambda}\tau} \langle a^\dagger_{-\mathbf{q}\lambda} a_{-\mathbf{q}\lambda} \rangle_0 \right].$$

The commutation relation between the phonon annihilation and creation operators implies that $a_{\mathbf{q}\lambda} a^\dagger_{\mathbf{q}\lambda} = 1 + a^\dagger_{\mathbf{q}\lambda} a_{\mathbf{q}\lambda}$. Moreover, in thermal equilibrium, $\langle a^\dagger_{\mathbf{q}\lambda} a_{\mathbf{q}\lambda} \rangle_0$ is the occupation number $n_{\omega_{\mathbf{q}\lambda}}$ of the normal mode $(\mathbf{q}\lambda)$, given by Eq. (11.32). Since $\omega_{-\mathbf{q}\lambda} = \omega_{\mathbf{q}\lambda}$, we can write

$$d^{0>}(\mathbf{q}\lambda, \tau) = - \left[e^{-\omega_{\mathbf{q}\lambda}\tau} (1 + n_{\omega_{\mathbf{q}\lambda}}) + e^{\omega_{\mathbf{q}\lambda}\tau} n_{\omega_{\mathbf{q}\lambda}} \right]. \tag{11.59}$$

The observation that $1 + n_{\omega_{\mathbf{q}\lambda}} = -n_{-\omega_{\mathbf{q}\lambda}}$ (easily verified) allows us to write the above expression in another way:

$$d^{0>}(\mathbf{q}\lambda, \tau) = - \left[n_{\omega_{\mathbf{q}\lambda}} e^{\omega_{\mathbf{q}\lambda}\tau} - n_{-\omega_{\mathbf{q}\lambda}} e^{-\omega_{\mathbf{q}\lambda}\tau} \right]. \tag{11.60}$$

Similarly, following the same steps, we can show that

$$d^{0<}(\mathbf{q}\lambda, \tau) = - \left[n_{\omega_{\mathbf{q}\lambda}} e^{-\omega_{\mathbf{q}\lambda}\tau} - n_{-\omega_{\mathbf{q}\lambda}} e^{\omega_{\mathbf{q}\lambda}\tau} \right]. \tag{11.61}$$

Before proceeding to calculate the free-phonon Green's function, let us rewrite the above expressions for $d^{0>}$ and $d^{0<}$ in the following way:

$$d^{0>}(\mathbf{q}\lambda, \tau) = \int_{-\infty}^{\infty} P_d^{0>}(\mathbf{q}\lambda, \epsilon) e^{-\epsilon\tau} \frac{d\epsilon}{2\pi} \tag{11.62a}$$

$$d^{0<}(\mathbf{q}\lambda, \tau) = \int_{-\infty}^{\infty} P_d^{0<}(\mathbf{q}\lambda, \epsilon) e^{-\epsilon\tau} \frac{d\epsilon}{2\pi} \tag{11.62b}$$

where

$$P_d^{0>}(\mathbf{q}\lambda, \epsilon) = 2\pi n_{-\epsilon} \left[\delta(\epsilon - \omega_{\mathbf{q}\lambda}) - \delta(\epsilon + \omega_{\mathbf{q}\lambda}) \right] \tag{11.63a}$$

$$P_d^{0<}(\mathbf{q}\lambda, \epsilon) = -2\pi n_\epsilon \left[\delta(\epsilon - \omega_{\mathbf{q}\lambda}) - \delta(\epsilon + \omega_{\mathbf{q}\lambda}) \right]. \tag{11.63b}$$

The Fourier transform of the free-phonon Green's function is

$$d^0(\mathbf{q}\lambda, \omega_m) = \int_0^{\beta\hbar} d^0(\mathbf{q}\lambda, \tau) e^{i\omega_m \tau} d\tau = \int_0^{\beta\hbar} d^{0>}(\mathbf{q}\lambda, \tau) e^{i\omega_m \tau} d\tau.$$

This is calculated by inserting the expression for $d^{0>}(\mathbf{q}\lambda, \tau)$ from either Eq. (11.60) or Eq. (11.62a); the result is

$$d^0(\mathbf{q}\lambda, \omega_m) = \frac{2\omega_{\mathbf{q}\lambda}}{(i\omega_m)^2 - \omega_{\mathbf{q}\lambda}^2}. \tag{11.64}$$
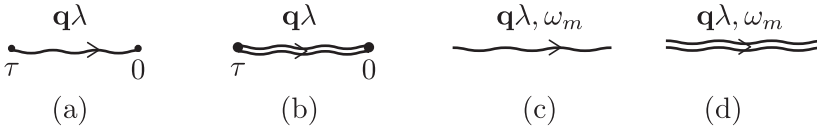
Figure 11.9 Pictorial representation of the phonon Green's function: (a) $d^0(\mathbf{q}\lambda, \tau)$, (b) $d(\mathbf{q}\lambda, \tau)$, (c) $d^0(\mathbf{q}\lambda, \omega_m)$, and (d) $d(\mathbf{q}\lambda, \omega_m)$. Here, d^0 is the noninteracting (free) phonon Green's function, while d is the interacting function.
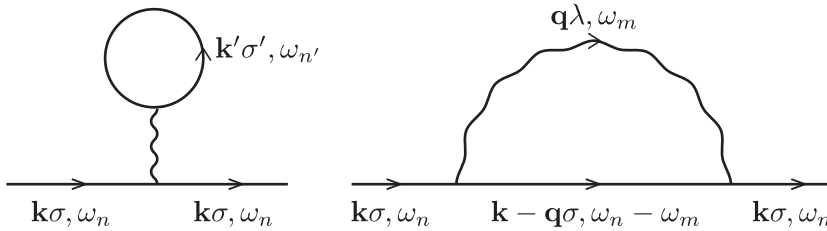

Figure 11.10 The two diagrams of second order in the electron–phonon coupling.

In drawing Feynman diagrams, the phonon Green's function is depicted as in Figure 11.9.

11.9 Feynman rules for the electron–phonon interaction

Treating the electron–phonon interaction as a perturbation, we can expand the electron Green's function to various orders in the perturbation. Since the thermal average of the product of an odd number of phonon field operators is zero, only even orders in the perturbation expansion will survive. The derivation of the Feynman rules from Wick's theorem proceeds in exactly the same way as in Chapter 9. Here, we simply write the rules for calculating the electron Green's function.

(1) At order $2n$ in the electron–phonon interaction (since only even orders survive), draw all topologically distinct diagrams with n phonon lines, two external electron lines, and $2n - 1$ internal electron lines.
(2) To each electron line of coordinates $(\mathbf{k}\sigma, \omega_n)$, assign $g^0(\mathbf{k}\sigma, \omega_n)$.
(3) To each phonon line of coordinates $(\mathbf{q}\lambda, \omega_m)$, assign $|M_{\mathbf{q}\lambda}|^2 d^0(\mathbf{q}\lambda, \omega_m)$.
(4) At each vertex, conserve wave vector, frequency, and spin.
(5) Sum over all internal coordinates.
(6) Multiply each electron loop by -1.
(7) Multiply by the factor $(1/\hbar)^{2n}(-1/\beta\hbar)^n$.

For example, consider the two diagrams that arise in second-order perturbation in the electron–phonon interaction (see Figure 11.10). In the first diagram,
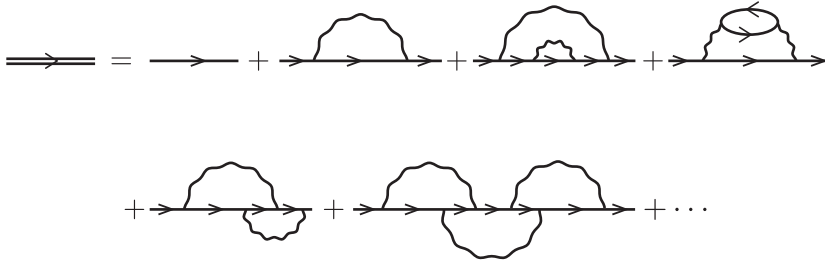
Figure 11.11 Some representative diagrams in the perturbation expansion of the electron Green's function. The perturbation is the electron–phonon interaction.

conservation of wave vector at the vertex implies that the phonon line has zero wave vector. However, the term $\mathbf{q} = \mathbf{0}$ is absent in the electron–phonon interaction, and this diagram should be excluded. Using the Feynman rules, the contribution of the second diagram in Figure 11.10 is

$$\delta g(\mathbf{k}\sigma, \omega_n) = -\frac{1}{\beta\hbar^3} \left[g^0(\mathbf{k}\sigma, \omega_n) \right]^2 \sum_{\mathbf{q}\lambda m} |M_{\mathbf{q}\lambda}|^2 g^0(\mathbf{k} - \mathbf{q}\sigma, \omega_n - \omega_m) d^0(\mathbf{q}\lambda, \omega_m).$$

11.10 Electron self energy

In a simple metal with one partially filled band, electrical conductivity is given by $ne^2\tau/m^*$, where n is the number of electrons per unit volume, m^* is the effective electron mass, and τ is the average lifetime of the electronic states near the Fermi surface (see, e.g., [Omar, 1993]). In a pure metal, the lifetime of an electronic state is determined by the electron–phonon interaction. Here, we calculate the electron self energy that is due to interaction with phonons; the imaginary part of the self energy is related to the lifetime of the electronic state.

We consider a system of electrons and phonons. The Hamiltonian is

$$\bar{H} = \sum_{\mathbf{k}\sigma} \bar{\epsilon}_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \sum_{\mathbf{q}\lambda} \hbar\omega_{\mathbf{q}\lambda}(a_{\mathbf{q}\lambda}^\dagger a_{\mathbf{q}\lambda} + 1/2) + \sum_{\mathbf{k}\sigma} {\sum_{\mathbf{q}\lambda}}' M_{\mathbf{q}\lambda} c_{\mathbf{k}+\mathbf{q}\sigma}^\dagger c_{\mathbf{k}\sigma} \phi_{\mathbf{q}\lambda}.$$

$$(11.65)$$

The first term describes a collection of electrons in the conduction band of a metal; interactions among the electrons are taken in an average way, with the effect being simply a renormalization of the electron mass. The second term is the Hamiltonian for a system of noninteracting phonons, and the third term is the electron–phonon interaction, with the term $\mathbf{q} = \mathbf{0}$ excluded ($M_{\mathbf{q}=0,\lambda} = 0$).

The perturbation expansion of the electron Green's function is depicted in Figure 11.11, where some representative diagrams are shown. The last two diagrams in Figure 11.11 are, in fact, similar to the one-phonon diagram (the second
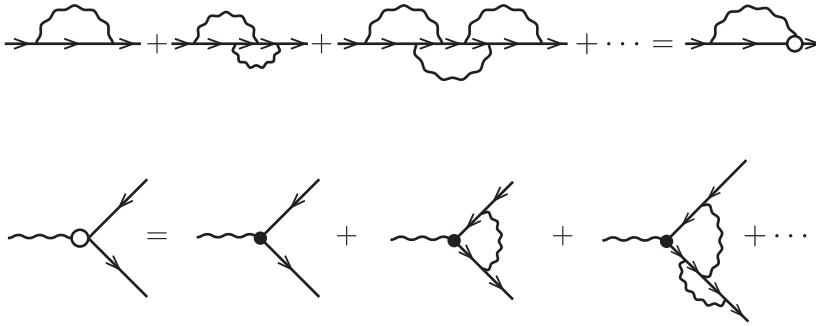
Figure 11.12 Diagrams that can be added to produce a single diagram with a corrected vertex.
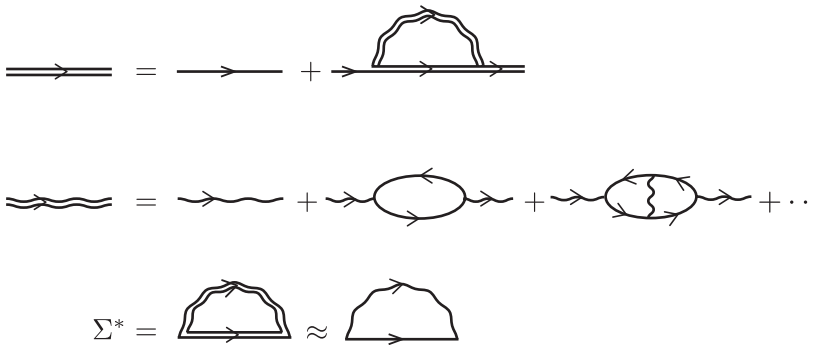

Figure 11.13 Electron and phonon Green's functions for a system of coupled electrons and phonons. Vertex corrections are ignored. The electron proper self energy Σ^* is approximated by replacing full (dressed, or interacting) electron and phonon propagators with bare (noninteracting) propagators.

one on the RHS in the figure), except for some vertex corrections, as shown in Figure 11.12. A remarkable theorem, due to Migdal (Migdal, 1958), states the following:

$$\circ = \bullet \left[1 + O(\sqrt{m^*/M}) \right] \qquad (11.66)$$

where $\circ$ ($\bullet$) is the electron–phonon interaction matrix element in the presence (absence) of vertex corrections, m^* is the effective electron mass, and M is the ion mass. Thus, according to Migdal's theorem, vertex corrections may be ignored, since the error made is of the order of one percent ($\sqrt{m^*/M} \approx 0.01$). With that in mind, the electron Green's function may now be expanded as in Figure 11.13.

In calculating the electron self energy, we approximate the interacting electron and phonon Green's functions by using bare ones. The calculation can be carried out using the Feynman rules that were mentioned in the previous section. We
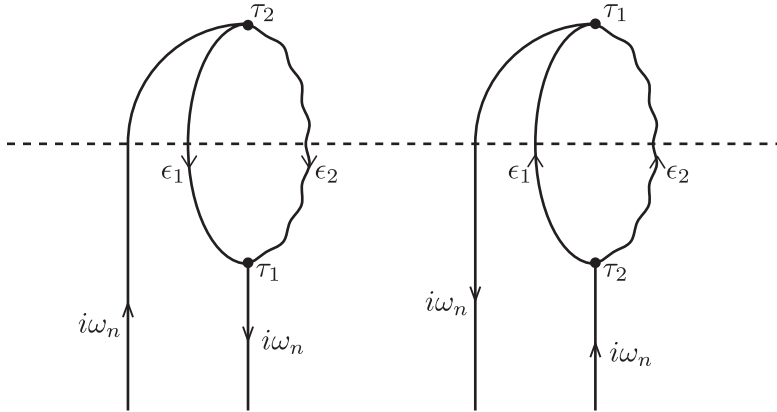
Figure 11.14 The two time-ordered diagrams that are used to calculate the electron self energy that is due to electron–phonon interaction. The external lines have coordinates $(\mathbf{k}\sigma, \omega_n)$. The internal electron line has coordinates $(\mathbf{k} - \mathbf{q}\sigma, \epsilon_1)$, while the internal phonon line has coordinates $(\mathbf{q}\lambda, \epsilon_2)$. The horizontal dashed line is a section.

relegate this approach to the Problems section. Here, we calculate the self energy using Dzyaloshinski's rules for time-ordered diagrams (see Section 9.8). There are two time-ordered diagrams (see Figure 11.14). The self energy is given by

$$\Sigma^*(\mathbf{k}\sigma, \omega_n) = -\frac{1}{\hbar^2} \sum_{\mathbf{q}\lambda} |M_{\mathbf{q}\lambda}|^2 \int_{-\infty}^{\infty} \frac{d\epsilon_1}{2\pi} \int_{-\infty}^{\infty} \frac{d\epsilon_2}{2\pi}$$

$$\times \frac{P_g^{0<}(\mathbf{k} - \mathbf{q}\sigma, \epsilon_1) P_d^{0<}(\mathbf{q}\lambda, \epsilon_2) - P_g^{0>}(\mathbf{k} - \mathbf{q}\sigma, \epsilon_1) P_d^{0>}(\mathbf{q}\lambda, \epsilon_2)}{i\omega_n - \epsilon_1 - \epsilon_2}.$$
(11.67)

The electron spectral functions are

$$P_g^{0>}(\mathbf{k} - \mathbf{q}\sigma, \epsilon) = -2\pi(1 - f_\epsilon)\delta(\epsilon - \bar{\epsilon}_{\mathbf{k}-\mathbf{q}}/\hbar)$$

$$P_g^{0<}(\mathbf{k} - \mathbf{q}\sigma, \epsilon) = 2\pi f_\epsilon \delta(\epsilon - \bar{\epsilon}_{\mathbf{k}-\mathbf{q}}/\hbar)$$

(see Eqs [6.55], [8.32], and [8.34]). The phonon spectral functions are given in Eq. (11.63). Inserting these into the expression for Σ^*, and noting that $n_{\omega_{\mathbf{q}\lambda}} = -1 - n_{-\omega_{\mathbf{q}\lambda}}$, we find that

$$\Sigma^*(\mathbf{k}\sigma, \omega_n) = \frac{1}{\hbar^2} \sum_{\mathbf{q}\lambda} |M_{\mathbf{q}\lambda}|^2 \left[\frac{n_{\omega_{\mathbf{q}\lambda}} + f_{\mathbf{k}-\mathbf{q}}}{i\omega_n - \bar{\epsilon}_{\mathbf{k}-\mathbf{q}}/\hbar + \omega_{\mathbf{q}\lambda}} + \frac{1 + n_{\omega_{\mathbf{q}\lambda}} - f_{\mathbf{k}-\mathbf{q}}}{i\omega_n - \bar{\epsilon}_{\mathbf{k}-\mathbf{q}}/\hbar - \omega_{\mathbf{q}\lambda}} \right].$$
(11.68)

The retarded self energy is obtained by replacing $i\omega_n$ with $\omega + i0^+$:

$$Im\,\Sigma_R^*(\mathbf{k}\sigma, \omega) = \frac{-\pi}{\hbar^2} \sum_{\mathbf{q}\lambda} |M_{\mathbf{q}\lambda}|^2 \left[(n_{\omega_{\mathbf{q}\lambda}} + f_{\mathbf{k}-\mathbf{q}}) \delta(\omega - \bar{\epsilon}_{\mathbf{k}-\mathbf{q}}/\hbar + \omega_{\mathbf{q}\lambda}) \right.$$

$$\left. + (1 + n_{\omega_{\mathbf{q}\lambda}} - f_{\mathbf{k}-\mathbf{q}}) \delta(\omega - \bar{\epsilon}_{\mathbf{k}-\mathbf{q}}/\hbar - \omega_{\mathbf{q}\lambda}) \right]. \tag{11.69}$$

The first (second) term in the brackets corresponds to phonon absorption (emission). The lifetime of an electron in state $|\mathbf{k}\sigma\rangle$ is given by

$$\tau_{\mathbf{k}\sigma} = \frac{-1}{2\,Im\,\Sigma_R^*(\mathbf{k}\sigma, \bar{\epsilon}_{\mathbf{k}}/\hbar)}. \tag{11.70}$$

In writing Eq. (11.70), we have replaced ω in Σ_R^* with $\bar{\epsilon}_{\mathbf{k}}/\hbar$; this is an approximation. In fact, $\hbar\omega$ should be replaced with the shifted energy, which is obtained by solving the equation $\omega - \bar{\epsilon}_{\mathbf{k}}/\hbar + Re\,\Sigma_R^*(\mathbf{k}\sigma, \omega) = 0$.

11.11 The electromagnetic field

In free space, away from charge and current sources, the electromagnetic field is described by the following Maxwell's equations:

$$\nabla.\mathbf{E} = 0 \tag{11.71a}$$

$$\nabla.\mathbf{B} = 0 \tag{11.71b}$$

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} \quad \text{(cgs)}, \quad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (SI) \tag{11.71c}$$

$$\nabla \times \mathbf{B} = \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} \quad \text{(cgs)}, \quad \nabla \times \mathbf{B} = \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \quad (SI). \tag{11.71d}$$

In the following treatment, we use the cgs system of units. The second and third Maxwell's equations are automatically satisfied if we express $\mathbf{E}$ and $\mathbf{B}$ in terms of a scalar potential $\Phi(\mathbf{r}, t)$ and a vector potential $\mathbf{A}(\mathbf{r}, t)$:

$$\mathbf{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}. \tag{11.72}$$

This is because the divergence of a curl is zero ($\nabla.\nabla \times \mathbf{A}$) and the curl of a gradient is zero ($\nabla \times \nabla\Phi = 0$). The first and fourth Maxwell's equations are now written as

$$\nabla^2\Phi + \frac{1}{c}\frac{\partial}{\partial t}(\nabla.\mathbf{A}) = 0 \tag{11.73}$$

$$\nabla \times \nabla \times \mathbf{A} = -\frac{1}{c}\frac{\partial}{\partial t}\nabla\Phi - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A}. \tag{11.74}$$

Using the identity

$$\nabla \times \nabla \times \mathbf{A} = -\nabla^2 \mathbf{A} + \nabla(\nabla.\mathbf{A}), \tag{11.75}$$

we can rewrite Eq. (11.74) in the following form:

$$\nabla^2 \mathbf{A} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A} = \nabla\left(\nabla.\mathbf{A} + \frac{1}{c}\frac{\partial \Phi}{\partial t}\right). \tag{11.76}$$

Simplification is achieved by exploiting a freedom in the choice of Φ and $\mathbf{A}$: under the gauge transformation,

$$\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla\Lambda, \quad \Phi \rightarrow \Phi' = \Phi - \frac{1}{c}\frac{\partial \Lambda}{\partial t},$$

where $\Lambda(\mathbf{r}, t)$ is any smooth function, both $\mathbf{E}$ and $\mathbf{B}$ remain unchanged. Choosing a particular function $\Lambda(\mathbf{r}, t)$ is called "fixing the gauge." In one gauge, called the radiation gauge, $\Lambda(\mathbf{r}, t)$ is chosen such that $\nabla^2\Lambda(\mathbf{r}, t) = -\nabla.\mathbf{A}$ and $(1/c)(\partial\Lambda/\partial t) = \Phi$. Thus, in the radiation gauge, $\Phi' = 0$ and $\nabla.\mathbf{A}' = 0$. Relabeling $(\Phi', \mathbf{A}')$ as $(\Phi, \mathbf{A})$, we can write

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}, \tag{11.77}$$

where $\mathbf{A}$ satisfies the wave equation

$$\nabla^2 \mathbf{A} - \frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} = 0. \tag{11.78}$$

This equation is to be solved subject to the constraint $\nabla.\mathbf{A} = 0$. We assume that the electromagnetic field is enclosed in a large cube of volume $V = L^3$, and that it obeys periodic boundary conditions. Our approach is similar to the one we followed in studying atomic vibrations: we first find the normal modes and then write the general solution as a linear combination of these modes. The normal modes are given by

$$\mathbf{A}^{nor}_{\mathbf{q}\lambda}(\mathbf{r}, t) = \frac{1}{\sqrt{V}}\boldsymbol{\epsilon}_\lambda(\mathbf{q})e^{i(\mathbf{q}.\mathbf{r}-\omega_{\mathbf{q}\lambda}t)}$$

where $\boldsymbol{\epsilon}_\lambda(\mathbf{q})$ is a unit polarization vector. The requirement $\nabla.\mathbf{A} = 0 \Rightarrow \mathbf{q}.\boldsymbol{\epsilon}_\lambda(\mathbf{q}) = 0$; the normal modes are transverse modes, so $\lambda = 1, 2$. Inserting the above expression into the wave equation, we find that the equation is satisfied if $\omega_{\mathbf{q}\lambda} = cq$, independent of λ; henceforth, we write $\omega_{\mathbf{q}}$ and drop the subscript λ. The periodic boundary conditions imply that the allowed values for $\mathbf{q}$ are

$$q_x, q_y, q_z = 0, \pm 2\pi/L, \pm 4\pi/L, \ldots.$$

The general solution of the wave equation is written as

$$\mathbf{A}(\mathbf{r}, t) = \left(\frac{4\pi c^2}{V}\right)^{1/2} \sum_{\mathbf{q}} \sum_{\lambda=1}^{2} A_{\mathbf{q}\lambda} \boldsymbol{\epsilon}_{\lambda}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}}. \tag{11.79}$$

The factor $e^{-i\omega_{\mathbf{q}}t}$ is absorbed into $A_{\mathbf{q}\lambda}$, which satisfies the equation

$$\ddot{A}_{\mathbf{q}\lambda} = -\omega_{\mathbf{q}}^2 A_{\mathbf{q}\lambda}.$$

The expansion coefficients $A_{\mathbf{q}\lambda}$ are the normal coordinates of the electromagnetic field. They are similar to the $Q_{\mathbf{q}\lambda}$ coefficients that appear in the expansion of the ionic displacements in a crystal. The additional factor $(4\pi c^2)^{1/2}$ in Eq. (11.79) is inserted for later convenience. We note that, since $\mathbf{A}(\mathbf{r}, t)$ is real, $\mathbf{A}^*(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}, t)$; it follows that $A_{\mathbf{q}\lambda}^* = A_{-\mathbf{q}\lambda}$ and $\boldsymbol{\epsilon}_{\lambda}^*(\mathbf{q}) = \boldsymbol{\epsilon}_{\lambda}(-\mathbf{q})$. Orthonormality of the normal modes implies that $\boldsymbol{\epsilon}_{\lambda}^*(\mathbf{q}).\boldsymbol{\epsilon}_{\lambda'}(\mathbf{q}) = \delta_{\lambda\lambda'}$.

The electric and magnetic fields are obtained by using Eq. (11.77):

$$\mathbf{E} = -\sqrt{4\pi/V} \sum_{\mathbf{q}\lambda} \dot{A}_{\mathbf{q}\lambda} \boldsymbol{\epsilon}_{\lambda}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}}, \quad \mathbf{B} = i\sqrt{4\pi c^2/V} \sum_{\mathbf{q}\lambda} A_{\mathbf{q}\lambda} \mathbf{q} \times \boldsymbol{\epsilon}_{\lambda}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}}. \tag{11.80}$$

The Lagrangian for the electromagnetic field (Jackson, 1999) is given by

$$L = \frac{1}{8\pi} \int (|\mathbf{E}|^2 - |\mathbf{B}|^2) d^3r \quad \text{(cgs)}. \tag{11.81}$$

Inserting the expressions for $\mathbf{E}$ and $\mathbf{B}$ from Eq. (11.80), and noting that $|\boldsymbol{\epsilon}_{\lambda}(\mathbf{q}) \times \mathbf{q}| = q$ (since $\boldsymbol{\epsilon}_{\lambda}(\mathbf{q}) \perp \mathbf{q}$) and $\omega_{\mathbf{q}} = cq$, we can show that

$$L = \frac{1}{2} \sum_{\mathbf{q}\lambda} \left(\dot{A}_{\mathbf{q}\lambda}\dot{A}_{-\mathbf{q}\lambda} - \omega_{\mathbf{q}}^2 A_{\mathbf{q}\lambda}A_{-\mathbf{q}\lambda}\right). \tag{11.82}$$

The momentum conjugate to $A_{\mathbf{q}\lambda}$ is $P_{\mathbf{q}\lambda} = \partial L/\partial \dot{A}_{\mathbf{q}\lambda} = \dot{A}_{-\mathbf{q}\lambda}$. The Hamiltonian is therefore given by

$$H = \frac{1}{2} \sum_{\mathbf{q}\lambda} \left(P_{\mathbf{q}\lambda} P_{-\mathbf{q}\lambda} + \omega_{\mathbf{q}}^2 A_{\mathbf{q}\lambda}A_{-\mathbf{q}\lambda}\right). \tag{11.83}$$

This is the Hamiltonian for a collection of harmonic oscillators. A quantum theory is obtained in a similar way as we did for phonons:

$$H = \sum_{\mathbf{q}\lambda} \hbar\omega_{\mathbf{q}\lambda} \left(b_{\mathbf{q}\lambda}^{\dagger} b_{\mathbf{q}\lambda} + 1/2\right), \tag{11.84}$$

where

$$A_{\mathbf{q}\lambda} = \sqrt{\frac{\hbar}{2\omega_{\mathbf{q}}}} \left(b_{\mathbf{q}\lambda} + b_{-\mathbf{q}\lambda}^{\dagger}\right), \quad P_{\mathbf{q}\lambda} = i\sqrt{\frac{\hbar\omega_{\mathbf{q}}}{2}} \left(b_{\mathbf{q}\lambda}^{\dagger} - b_{-\mathbf{q}\lambda}\right). \tag{11.85}$$

The quanta of the electromagnetic field are called photons. The operator $b_{\mathbf{q}\lambda}^{\dagger}(b_{\mathbf{q}\lambda})$ creates (annihilates) a photon of wave vector $\mathbf{q}$ and polarization λ.

11.12 Electron–photon interaction

In the presence of an electromagnetic field, described by the vector potential $\mathbf{A}$, the Hamiltonian for an electron in a crystal is

$$H = \frac{1}{2m}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2 + V(\mathbf{r}). \tag{11.86}$$

The electron charge is $-e$, and $V(\mathbf{r})$ is the periodic potential produced by the lattice of ions. We ignore the electron–phonon interaction for now. Expanding Eq. (11.86), we obtain

$$H = H_0 + H', \quad H_0 = p^2/2m + V(\mathbf{r}), \quad H' = \frac{e}{2mc}(\mathbf{p}.\mathbf{A} + \mathbf{A}.\mathbf{p}) + \frac{e^2}{2mc^2}A^2.$$

H_0 is the Hamiltonian for the electron in the absence of the electromagnetic field; its eigenstates $|s\mathbf{k}\sigma\rangle$ are characterized by a band index s, a wave vector $\mathbf{k}$, and a spin projection σ. H', when summed over all electrons, is the electron–photon interaction. The term in H' which is proportional to A^2 involves two-photon scattering processes. For weak fields, this term is generally far less important than the other term which involves single-photon processes; henceforth, the A^2 term will be ignored.

In the radiation gauge ($\nabla.\mathbf{A} = 0$), the two terms $\mathbf{p}.\mathbf{A}$ and $\mathbf{A}.\mathbf{p}$ are equal. To see this, consider the action of $\mathbf{p}.\mathbf{A}$ on any function $f(\mathbf{r})$:

$$\mathbf{p}.\mathbf{A}f(\mathbf{r}) = -i\hbar\nabla.(\mathbf{A}f(\mathbf{r})) = -i\hbar(\nabla.\mathbf{A})f(\mathbf{r}) - i\hbar\mathbf{A}.\nabla f(\mathbf{r})$$

$$= 0 - i\hbar\mathbf{A}.\nabla f(\mathbf{r}) = \mathbf{A}.\mathbf{p}f(\mathbf{r}).$$

The electron–photon interaction Hamiltonian is obtained by summing H' over all electrons:

$$H_{e-\text{photon}} = \frac{e}{mc}\sum_j \mathbf{A}(\mathbf{r}_j, t).\mathbf{p}_j. \tag{11.87}$$

$\mathbf{p}_j$ is the momentum of the jth electron whose position is $\mathbf{r}_j$. Since this is a one-body operator, its second quantized form is

$$H_{e-\text{photon}} = \frac{e}{mc}\sum_{s\mathbf{k}\sigma}\sum_{s'\mathbf{k}'}\langle s'\mathbf{k}'\sigma|\mathbf{A}.\mathbf{p}|s\mathbf{k}\sigma\rangle c_{s'\mathbf{k}'\sigma}^{\dagger}c_{s\mathbf{k}\sigma}.$$

The matrix element is given by

$$\langle s'\mathbf{k}'\sigma|\mathbf{A}.\mathbf{p}|s\mathbf{k}\sigma\rangle = \left(\frac{4\pi c^2}{V\varepsilon(\infty)}\right)^{1/2} \sum_{\mathbf{q}\lambda} A_{\mathbf{q}\lambda}\boldsymbol{\epsilon}_\lambda(\mathbf{q}).\langle s'\mathbf{k}'\sigma|e^{i\mathbf{q}.\mathbf{r}}\mathbf{p}|s\mathbf{k}\sigma\rangle.$$

Note that, in expanding $\mathbf{A}(\mathbf{r}, t)$, we have modified Eq. (11.79), replacing c with $c/n = c/\sqrt{\varepsilon(\infty)}$, where $n = \sqrt{\varepsilon(\infty)}$ is the index of refraction of the medium (the crystal). This is because in $H_{e-\text{photon}}$, $\mathbf{A}(\mathbf{r}, t)$ is the vector potential in the medium, where the speed of light is c/n. The matrix element on the RHS of the above equation is evaluated using Bloch's theorem:

$$I = \langle s'\mathbf{k}'\sigma|e^{i\mathbf{q}.\mathbf{r}}\mathbf{p}|s\mathbf{k}\sigma\rangle = \int u^*_{s'\mathbf{k}'}(\mathbf{r})e^{-i\mathbf{k}'.\mathbf{r}}e^{i\mathbf{q}.\mathbf{r}}\mathbf{p}u_{s\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}.\mathbf{r}}d^3r.$$

Here, $u_{s'\mathbf{k}'}(\mathbf{r})$ and $u_{s\mathbf{k}}(\mathbf{r})$ are periodic functions having the same periodicity as the lattice. Changing variables from $\mathbf{r}$ to $\mathbf{r} + \mathbf{R}_n$, where $\mathbf{R}_n$ is any lattice vector, and using the periodicity property of $u_{s'\mathbf{k}'}(\mathbf{r})$ and $u_{s\mathbf{k}}(\mathbf{r})$, we find

$$I = Ie^{-i(\mathbf{k}'-\mathbf{k}-\mathbf{q}).\mathbf{R}_n}.$$

This means that $\mathbf{k}' = \mathbf{k} + \mathbf{q} + \mathbf{G}$, where $\mathbf{G}$ is a reciprocal lattice vector. Since $\mathbf{k}, \mathbf{k}' \in$ FBZ, $\mathbf{G}$ must carry $\mathbf{k} + \mathbf{q}$ into the FBZ. For visible light, $q \approx 10^5$ cm^{-1}, which is too small compared to the width of the Brillouin zone ($\approx 10^8$ cm^{-1}). Thus, $\mathbf{G}$ is generally equal to zero unless $\mathbf{k}$ is extremely close to the Brillouin zone edge. The electron–photon interaction is therefore given by

$$H_{e-\text{photon}} = \sum_{ss'}\sum_{\mathbf{k}\sigma}\sum_{\mathbf{q}\lambda} P^{ss'}_{\mathbf{k},\mathbf{k}+\mathbf{q}}(\lambda)c^\dagger_{s'\mathbf{k}+\mathbf{q}\sigma}c_{s\mathbf{k}\sigma}(b_{\mathbf{q}\lambda} + b^\dagger_{-\mathbf{q}\lambda}) \tag{11.88}$$

where

$$P^{ss'}_{\mathbf{k},\mathbf{k}+\mathbf{q}}(\lambda) = \frac{e}{m}\left(\frac{2\pi\hbar}{V\omega_{\mathbf{q}}\varepsilon(\infty)}\right)^{1/2}\langle s'\mathbf{k}+\mathbf{q}\sigma|e^{i\mathbf{q}.\mathbf{r}}\boldsymbol{\epsilon}_\lambda(\mathbf{q}).\mathbf{p}|s\mathbf{k}\sigma\rangle. \tag{11.89}$$

The electron–photon interaction is thus seen to be a sum of terms, each of which represents a scattering process whereby an electron in state $|s\mathbf{k}\sigma\rangle$ is scattered into state $|s'\mathbf{k}+\mathbf{q}\sigma\rangle$ by the absorption (emission) of a photon of wave vector $\mathbf{q}$ ($-\mathbf{q}$) and polarization λ.

11.13 Light scattering by crystals

In this section, we discuss the general theory of light scattering by crystals (Van Hove, 1954; Loudon, 1963). In the next section we will focus on the specific case of Raman scattering in insulators.
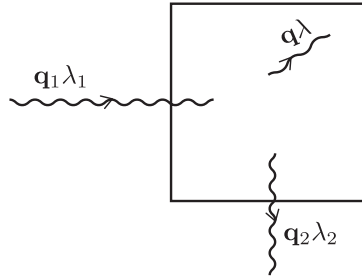
Figure 11.15 Light scattering by a crystal: an incident photon of frequency $\omega_{\mathbf{q}_1 \lambda_1}$ is absorbed, and a photon of frequency $\omega_{\mathbf{q}_2 \lambda_2}$ is emitted. In the process, a quantum of an excitation mode of the crystal is created or annihilated in order to conserve energy and momentum.

Consider a process in which a photon of wave vector $\mathbf{q}_1$ and polarization λ_1 is absorbed by a crystal, and a photon of coordinates $(\mathbf{q}_2 \lambda_2)$ is created. The process is accompanied by the creation or annihilation of a quantum of an excitation mode of the crystal, having coordinates $(\mathbf{q}\lambda)$, such that momentum and energy are conserved. The process is depicted in Figure 11.15.

The scattering process is described by the Hamiltonian

$$H' = \sum_{\mathbf{q}\lambda} \sum_{\mathbf{q}'\lambda'} \sum_{\mathbf{q}''\lambda''} \Gamma(\mathbf{q}'\lambda', \mathbf{q}''\lambda'', \mathbf{q}\lambda) \phi^{\dagger}_{\mathbf{q}\lambda} b^{\dagger}_{\mathbf{q}''\lambda''} b_{\mathbf{q}'\lambda'} \tag{11.90}$$

where $b^{\dagger}_{\mathbf{q}\lambda} (b_{\mathbf{q}\lambda})$ creates (annihilates) a photon of coordinates $(\mathbf{q}\lambda)$, and

$$\phi^{\dagger}_{\mathbf{q}\lambda} = a^{\dagger}_{\mathbf{q}\lambda} + a_{-\mathbf{q}\lambda} \tag{11.91}$$

is the field operator for the excitation mode (phonon or plasmon, for example) of the crystal. Γ is the matrix element for the scattering process; it is determined by considering the detailed mechanism through which the process takes place. In the next section, we will calculate this quantity for the specific case of Raman scattering by an insulating crystal.

The initial and final states of the system, which consists of the photons and the crystal, are denoted by $|I\rangle$ and $|F\rangle$, respectively:

$$|I\rangle = |n_1\rangle |n_2\rangle |i\rangle, \quad |F\rangle = |n_1 - 1\rangle |n_2 + 1\rangle |f\rangle.$$

Here, n_1 is the number of incident photons of coordinates $(\mathbf{q}_1 \lambda_1)$, n_2 is the number of scattered photons of coordinates $(\mathbf{q}_2 \lambda_2)$, $|i\rangle$ is the initial state of the crystal, and $|f\rangle$ is its final state.

The probability per unit time (the transition rate) for scattering from the initial state is given by the Fermi golden rule,

$$W = \frac{2\pi}{\hbar} \sum_F |\langle F|H'|I\rangle|^2 \delta(E_F - E_I). \tag{11.92}$$

E_I and E_F are the energies of the initial and final states. Writing $E_I = \hbar\omega_I$, $E_F = \hbar\omega_F$, and using

$$b_{\mathbf{q}\lambda}|n_{\mathbf{q}\lambda}\rangle = \sqrt{n_{\mathbf{q}\lambda}}|n_{\mathbf{q}\lambda} - 1\rangle, \quad b_{\mathbf{q}\lambda}^\dagger|n_{\mathbf{q}\lambda}\rangle = \sqrt{n_{\mathbf{q}\lambda} + 1}|n_{\mathbf{q}\lambda} + 1\rangle,$$

we obtain

$$W = \frac{2\pi}{\hbar^2} \sum_{\mathbf{q}\lambda} \sum_{\mathbf{q}'\lambda'} \sum_f \Gamma(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}\lambda)\Gamma^*(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}'\lambda')$$

$$\times \langle i|\phi_{\mathbf{q}'\lambda'}|f\rangle\langle f|\phi_{\mathbf{q}\lambda}^\dagger|i\rangle n_1(n_2 + 1)\delta(\omega_f - \omega_i - \omega), \tag{11.93}$$

where $\hbar\omega_i$ ($\hbar\omega_f$) is the energy of the crystal's initial (final) state, and $\hbar\omega = \hbar\omega_1 - \hbar\omega_2$ is the energy transferred to the crystal. Noting that

$$\delta(\omega_f - \omega_i - \omega) = \frac{1}{2\pi} \int_{-\infty}^\infty e^{-i(\omega_f - \omega_i - \omega)t} dt,$$

the expression for W becomes

$$W = \frac{n_1(n_2 + 1)}{\hbar^2} \sum_{\mathbf{q}\lambda} \sum_{\mathbf{q}'\lambda'} \sum_f \Gamma(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}\lambda)\Gamma^*(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}'\lambda')$$

$$\times \int \langle i|\phi_{\mathbf{q}'\lambda'}|f\rangle\langle f|\phi_{\mathbf{q}\lambda}^\dagger|i\rangle e^{-i(\omega_f - \omega_i - \omega)t} dt$$

$$= \frac{n_1(n_2 + 1)}{\hbar^2} \sum_{\mathbf{q}\lambda} \sum_{\mathbf{q}'\lambda'} \sum_f \Gamma(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}\lambda)\Gamma^*(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}'\lambda')$$

$$\times \int \langle i|e^{iHt/\hbar}\phi_{\mathbf{q}'\lambda'}e^{-iHt/\hbar}|f\rangle\langle f|\phi_{\mathbf{q}\lambda}^\dagger|i\rangle e^{i\omega t} dt,$$

where H is the crystal Hamiltonian. The sum over the final states of the crystal is now carried out ($\sum_f |f\rangle\langle f| = 1$); we obtain

$$W = \frac{n_1(n_2 + 1)}{\hbar^2} \sum_{\mathbf{q}\lambda} |\Gamma(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}\lambda)|^2 \int_{-\infty}^\infty \langle i|\phi_{\mathbf{q}\lambda}(t)\phi_{\mathbf{q}\lambda}^\dagger(0)|i\rangle e^{i\omega t} dt. \tag{11.94}$$

The transition rate depends on the initial state of the crystal. At zero temperature, $|i\rangle$ is the ground state $|\Psi_0\rangle$ of the crystal, and its energy is E_0. At finite temperature, other states $|\Psi_n\rangle$ with energy E_n have a nonzero probability of being occupied. Hence, at finite temperature, the matrix element in Eq. (11.94) is replaced by the

thermal average $\langle \phi_{\mathbf{q}\lambda}(t)\phi_{\mathbf{q}\lambda}^{\dagger}(0)\rangle$, which is the correlation function $C(\mathbf{q}\lambda, t)$ of the excitation mode in the crystal. The integral in Eq. (11.94) then becomes the Fourier transform of $C(\mathbf{q}\lambda, t)$,

$$W = \frac{n_1(n_2 + 1)}{\hbar^2} \sum_{\mathbf{q}\lambda} |\Gamma(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}\lambda)|^2 C(\mathbf{q}\lambda, \omega). \qquad (11.95)$$

The differential scattering cross-section $d^2\sigma/d\omega d\Omega$ is the number of transitions per unit time per unit solid angle per unit frequency interval per unit incident flux. The number of transitions per unit time into a solid angle $d\Omega$ and a frequency interval $(\omega_2, \omega_2 + d\omega)$ is obtained by multiplying W by the number of photon states, of a given polarization, in the interval $d\omega d\Omega$. The number of such photon states is $(V/8\pi^3)q_2^2 dq d\Omega = (V/8\pi^3 c^3)\omega_2^2 d\omega d\Omega$. The incident flux is the number of photons striking a unit area of the crystal per unit time. During a time interval Δt, the photons in a volume $Ac\Delta t$ strike an area A of the crystal (the incident light is assumed to be normal to the surface of the crystal). Since the number of incident photons per unit volume is n_1/V, the incident flux is $n_1 c/V$. Therefore,

$$\frac{d^2\sigma}{d\omega d\Omega} = \frac{(n_2 + 1)V^2\omega_2^2}{8\pi^3\hbar^2 c^4} \sum_{\mathbf{q}\lambda} |\Gamma(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}\lambda)|^2 C(\mathbf{q}\lambda, \omega).$$

Using the fluctuation–dissipation theorem (see Eq. [6.49]) which relates the correlation function to the imaginary part of the retarded Green's function, our final result is

$$\frac{d^2\sigma}{d\omega d\Omega} = -\frac{(n_\omega + 1)(n_2 + 1)V^2\omega_2^2}{8\pi^3\hbar^2 c^4} \sum_{\mathbf{q}\lambda} |\Gamma(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}\lambda)|^2 Im D^R(\mathbf{q}\lambda, \omega)$$

$$(11.96)$$

where $n_\omega = (e^{\beta\hbar\omega} - 1)^{-1}$ is the Bose–Einstein distribution function. We have managed to express the differential scattering cross-section for light scattering by a crystal in terms of the retarded function of the crystal excitation that participates in the scattering process. This function is obtained by analytic continuation of the corresponding imaginary-time function which, in turn, can be calculated using the Feynman diagram techniques developed in previous chapters.

11.14 Raman scattering in insulators

In a Raman scattering experiment, a photon of frequency ω_1, incident on a crystal, is absorbed, and a photon of frequency ω_2 is created. The process is accompanied by the emission (Stoke's scattering) or the absorption (anti-Stoke's scattering) of an optical phonon. At low temperatures, the optical phonon occupation number is small; hence, Raman scattering processes in which a phonon is created are

generally more important than those in which a phonon is absorbed. Here, we consider Raman scattering with phonon emission.

Our system consists of a crystal (an insulator), the radiation (electromagnetic) field, and lattice vibrations (phonons). The Hamiltonian is

$$H = H_0 + H_{\text{ER}} + H_{\text{EL}} = H_0 + H'. \tag{11.97}$$

H_0 is the sum of the Hamiltonians for the electrons in the crystal, the radiation field, and the lattice vibrations. H_{ER} is the electron–photon interaction, and H_{EL} is the electron–phonon interaction:

$$H_{\text{ER}} = \sum_{ss'} \sum_{\mathbf{k}\sigma} \sum_{\mathbf{q}\lambda} P^{ss'}_{\mathbf{k},\mathbf{k}+\mathbf{q}}(\lambda) c^{\dagger}_{s'\mathbf{k}+\mathbf{q}\sigma} c_{s\mathbf{k}\sigma} (b_{\mathbf{q}\lambda} + b^{\dagger}_{-\mathbf{q}\lambda}) \tag{11.98}$$

$$H_{\text{EL}} = \sum_{ss'} \sum_{\mathbf{k}\sigma} \sum_{\mathbf{q}\lambda} M^{ss'}_{\mathbf{q}\lambda} c^{\dagger}_{s'\mathbf{k}+\mathbf{q}\sigma} c_{s\mathbf{k}\sigma} (a_{\mathbf{q}\lambda} + a^{\dagger}_{-\mathbf{q}\lambda}). \tag{11.99}$$

The process of interest involves the annihilation of a photon, the creation of another photon, and the creation of a phonon. This is a third-order process in which H_{ER} acts twice and H_{EL} acts once. We need to transform the Hamiltonian into a form that contains an effective photon–phonon interaction in which a photon is scattered and a phonon is created. The Hamiltonian, as given above, is written in terms of a certain basis set that spans the Hilbert space of the system (electrons, phonons, and photons). The basis consists of states $|m\rangle = |s\mathbf{k}\sigma\rangle |\mathbf{q}\lambda\rangle_{\text{phonon}} |\mathbf{q}'\lambda'\rangle_{\text{photon}}$. In this basis, H_0 is diagonal. We can transform to a new basis set of states $|\tilde{m}\rangle = U|m\rangle$, where $U^{\dagger}U = 1$. In the new basis, the Hamiltonian matrix elements are $\langle \tilde{m}|H|\tilde{n}\rangle = \langle m|U^{\dagger}HU|n\rangle = \langle m|\tilde{H}|n\rangle$, where $\tilde{H} = U^{\dagger}HU$. In other words, the change of basis is equivalent to applying a similarity transformation to the Hamiltonian. We thus consider the following similarity (canonical) transformation: ($U = e^{-S}$)

$$\tilde{H} = e^S H e^{-S} \tag{11.100}$$

where S is an operator such that $S^{\dagger} = -S$. $\tilde{H}$ has the same eigenvalues as H, and its eigenstates are obtained by the operator e^S acting on the corresponding eigenstates of H. Expanding $e^{\pm S}$, we obtain

$$\tilde{H} = (1 + S + S^2/2! + S^3/3! + \cdots) H (1 - S + S^2/2! - S^3/3! + \cdots)$$

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

$$= H_0 + H' + [S, H_0] + [S, H'] + \frac{1}{2}[S, [S, H_0]] + \frac{1}{2}[S, [S, H']]$$

$$+ \frac{1}{6}[S, [S, [S, H_0]]] + \cdots.$$

The operator S is now chosen such that

$$[S, H_0] = -H'. \tag{11.101}$$

With this choice,

$$\tilde{H} = H_0 + \frac{1}{2}[S, H'] + \frac{1}{3}[S, [S, H']] + \cdots$$
$$= H_0 + H_2 + H_3 + \cdots. \tag{11.102}$$

Consider any two eigenstates $|I\rangle$ and $|F\rangle$ of H_0. Equation (11.101) gives

$$\langle F|SH_0|I\rangle - \langle F|H_0 S|I\rangle = -\langle F|H'|I\rangle \Rightarrow (E_F - E_I)\langle F|S|I\rangle = \langle F|H'|I\rangle$$

$$\Longrightarrow \langle F|S|I\rangle = \frac{\langle F|H'|I\rangle}{E_F - E_I}. \tag{11.103}$$

This shows that S is proportional to H'. Since our interest is in third-order processes, we consider the third term on the RHS of Eq. (11.102):

$$H_3 = \frac{1}{3}[S, [S, H']] = \frac{1}{3}(S^2 H' - 2SH'S + H'S^2).$$

Using Eq. (11.103) and two resolutions of identity, we can write

$$\langle F|H_3|I\rangle = \frac{1}{3}\sum_{m,n} \frac{\langle F|H'|n\rangle\langle n|H'|m\rangle\langle m|H'|I\rangle}{(E_F - E_n)(E_n - E_m)(E_m - E_I)}[E_F - E_I + 3(E_m - E_n)].$$

In Fermi's golden rule, the initial and final states have the same energy; setting $E_F = E_I$, we obtain

$$\langle F|H_3|I\rangle = \sum_{m,n} \frac{\langle F|H'|n\rangle\langle n|H'|m\rangle\langle m|H'|I\rangle}{(E_I - E_n)(E_I - E_m)}. \tag{11.104}$$

In Raman scattering with phonon emission, the initial state $|I\rangle$ consists of an incident photon of coordinates $(\mathbf{q}_1\lambda_1)$ and frequency ω_1, and a crystal (an insulator) in its electronic ground state (all of its valence bands are occupied and all of its conduction bands are empty). The final state $|F\rangle$ consists of a scattered photon of coordinates $(\mathbf{q}_2\lambda_2)$ and frequency ω_2 and a phonon of coordinates $(\mathbf{q}\lambda)$ and frequency $\omega = \omega_1 - \omega_2$. In state $|F\rangle$, the crystal is still in its electronic ground state. For these initial and final states, $\langle F|H_3|I\rangle$ corresponds to the matrix element $\Gamma(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}\lambda)$ in Eq. (11.90).

Replacing H' by $H_{\text{ER}} + H_{\text{EL}}$, the product of the three matrix elements on the RHS of Eq. (11.104) becomes a sum of eight terms, each of which is a product of three matrix elements. Of these eight terms, three are nonzero: $\langle F|H_{\text{EL}}|n\rangle\langle n|H_{\text{ER}}|m\rangle\langle m|H_{\text{ER}}|I\rangle$, $\langle F|H_{\text{ER}}|n\rangle\langle n|H_{\text{EL}}|m\rangle\langle m|H_{\text{ER}}|I\rangle$, and $\langle F|H_{\text{ER}}|n\rangle\langle n|H_{\text{ER}}|m\rangle\langle m|H_{\text{EL}}|I\rangle$; this follows from the definition of $|I\rangle$ and $|F\rangle$.

Furthermore, in H_{ER}, a photon is either emitted or absorbed, so that we can write $H_{ER} = H_{ER}^{em} + H_{ER}^{ab}$, and each of the surviving three terms now becomes a sum of four terms, only two of which are nonzero (the number of photons in $|I\rangle$ and $|F\rangle$ is the same). Therefore, the matrix element for Stoke's Raman scattering (phonon emission) is

$$\langle F|H|I\rangle = \sum_{m,n} \frac{1}{(E_I - E_n)(E_I - E_m)} \Big[\langle F|H_{EL}^{em}|n\rangle \langle n|H_{ER}^{em}|m\rangle \langle m|H_{ER}^{ab}|I\rangle$$

$$+ \langle F|H_{EL}^{em}|n\rangle \langle n|H_{ER}^{ab}|m\rangle \langle m|H_{ER}^{em}|I\rangle + \langle F|H_{ER}^{em}|n\rangle \langle n|H_{EL}^{em}|m\rangle \langle m|H_{ER}^{ab}|I\rangle$$

$$+ \langle F|H_{ER}^{ab}|n\rangle \langle n|H_{EL}^{em}|m\rangle \langle m|H_{ER}^{em}|I\rangle + \langle F|H_{ER}^{ab}|n\rangle \langle n|H_{ER}^{em}|m\rangle \langle m|H_{EL}^{em}|I\rangle$$

$$+ \langle F|H_{ER}^{em}|n\rangle \langle n|H_{ER}^{ab}|m\rangle \langle m|H_{EL}^{em}|I\rangle \Big]. \tag{11.105}$$

The various coupling Hamiltonians appearing in the above equation are

$$H_{EL}^{em} = \sum_{ss'} \sum_{k\sigma} M_{-q\lambda}^{ss'} c_{s'k-q\sigma}^{\dagger} c_{sk\sigma} a_{q\lambda}^{\dagger} \tag{11.106a}$$

$$H_{ER}^{em} = \sum_{ss'} \sum_{k\sigma} P_{k,k-q_2}^{ss'}(\lambda_2) c_{s'k-q_2\sigma}^{\dagger} c_{sk\sigma} b_{q_2\lambda_2}^{\dagger} \tag{11.106b}$$

$$H_{ER}^{ab} = \sum_{ss'} \sum_{k\sigma} P_{k,k+q_1}^{ss'}(\lambda_1) c_{s'k+q_1\sigma}^{\dagger} c_{sk\sigma} b_{q_1\lambda_1}. \tag{11.106c}$$

We have not summed over the wave vectors and polarizations of the photons and phonons since we consider the absorption of a photon of specific coordinates $(q_1\lambda_1)$, the emission of a photon of specific coordinates $(q_2\lambda_2)$, and the emission of a phonon of specific coordinates $(q\lambda)$. As for the insulator (the crystal), we only consider transitions between the highest occupied band and the lowest empty band, and we assume that the energy of the incident photon is lower than the energy gap, so that the transitions are virtual processes. Now we consider the various terms in Eq. (11.105).

The sequence of processes that occur in the first term on the RHS of Eq. (11.105) is illustrated in Figure 11.16. Here, $E_I = \hbar\omega_1$, $E_m = \epsilon_{ck+q_1} - \epsilon_{vk} \simeq \epsilon_{ck} - \epsilon_{vk}$ (since q_1 is much smaller than the width of the Brillouin zone). We also assume that there is little dispersion in the bands such that $\epsilon_{ck} - \epsilon_{vk} \simeq E_g$, where E_g is the energy gap. The first term on the RHS of Eq. (11.105) is thus approximately equal to

$$\delta_{q,q_1-q_2} \sum_{k\sigma} \frac{M_{q\lambda}^{cv} \big[P_{k+q_1,k+q_1-q_2}^{cc}(\lambda_2) + P_{k+q_2,k}^{vv}(\lambda_2) \big] P_{k,k+q_1}^{vc}(\lambda_1)}{(\hbar\omega_1 - \hbar\omega_2 - E_g)(\hbar\omega_1 - E_g)}.$$

We can simplify the notation: since the photon wave vector is very small compared to the extent of the Brillouin zone, we can replace $P_{k+q_1,k+q_1-q_2}^{cc}(\lambda_2)$ with $P_k^{cc}(\lambda_2)$, i.e., we assume that the electron–photon matrix element depends only on k. Similar
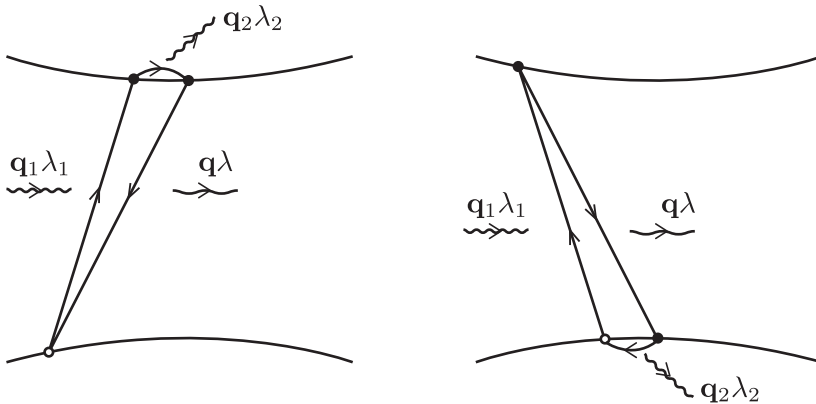
Figure 11.16 The sequence of processes in the first term of Eq. (11.105). A photon $(\mathbf{q}_1\lambda_1)$ is absorbed and an electron is promoted to the conduction band c (the upper band), leaving behind a hole in the valence band v. The next step can proceed in two different ways: in (a), the electron is scattered in the conduction band and a photon $(\mathbf{q}_2\lambda_2)$ is emitted, while in (b) an electron in the valence band is scattered and a photon $(\mathbf{q}_2\lambda_2)$ is emitted (we can also say that the hole is scattered). The third step, common to both, is an electron–hole recombination accompanied by the emission of a phonon $(\mathbf{q}\lambda)$. Note that for this sequence of processes, $\mathbf{q} = \mathbf{q}_1 - \mathbf{q}_2$, which is a statement of wave vector conservation.

replacements are made for other P-matrix elements. The above expression is now written as

$$\delta_{\mathbf{q},\mathbf{q}_1-\mathbf{q}_2} \sum_{\mathbf{k}\sigma} \frac{M_{\mathbf{q}\lambda}^{cv} \left[P_{\mathbf{k}}^{cc}(\lambda_2) + P_{\mathbf{k}}^{vv}(\lambda_2) \right] P_{\mathbf{k}}^{vc}(\lambda_1)}{(\hbar\omega_1 - \hbar\omega_2 - E_g)(\hbar\omega_1 - E_g)}.$$

The remaining five terms are evaluated in a similar way; we obtain

$$\Gamma(\mathbf{q}_1\lambda_1, \mathbf{q}_2\lambda_2, \mathbf{q}\lambda) = \delta_{\mathbf{q},\mathbf{q}_1-\mathbf{q}_2} \sum_{\mathbf{k}\sigma} \left[\frac{M_{\mathbf{q}\lambda}^{cv} \left[P_{\mathbf{k}}^{cc}(\lambda_2) + P_{\mathbf{k}}^{vv}(\lambda_2) \right] P_{\mathbf{k}}^{vc}(\lambda_1)}{(\hbar\omega_1 - \hbar\omega_2 - E_g)(\hbar\omega_1 - E_g)} \right.$$

$$+ \frac{M_{\mathbf{q}\lambda}^{cv} \left[P_{\mathbf{k}}^{cc}(\lambda_1) + P_{\mathbf{k}}^{vv}(\lambda_1) \right] P_{\mathbf{k}}^{vc}(\lambda_2)}{(\hbar\omega_1 - \hbar\omega_2 - E_g)(-\hbar\omega_2 - E_g)} + \frac{P_{\mathbf{k}}^{cv}(\lambda_2) \left[M_{\mathbf{q}\lambda}^{cc} + M_{\mathbf{q}\lambda}^{vv} \right] P_{\mathbf{k}}^{vc}(\lambda_1)}{(\hbar\omega_1 - \hbar\omega_{\mathbf{q}\lambda} - E_g)(\hbar\omega_1 - E_g)}$$

$$+ \frac{P_{\mathbf{k}}^{cv}(\lambda_1) \left[M_{\mathbf{q}\lambda}^{cc} + M_{\mathbf{q}\lambda}^{vv} \right] P_{\mathbf{k}}^{vc}(\lambda_2)}{(\hbar\omega_2 + \hbar\omega_{\mathbf{q}\lambda} + E_g)(\hbar\omega_2 + E_g)} + \frac{P_{\mathbf{k}}^{cv}(\lambda_1) \left[P_{\mathbf{k}}^{cc}(\lambda_2) + P_{\mathbf{k}}^{vv}(\lambda_2) \right] M_{\mathbf{q}\lambda}^{vc}}{(\hbar\omega_2 + \hbar\omega_{\mathbf{q}\lambda} + E_g)(\hbar\omega_{\mathbf{q}\lambda} + E_g)}$$

$$\left. + \frac{P_{\mathbf{k}}^{cv}(\lambda_2) \left[P_{\mathbf{k}}^{cc}(\lambda_1) + P_{\mathbf{k}}^{vv}(\lambda_1) \right] M_{\mathbf{q}\lambda}^{vc}}{(\hbar\omega_1 - \hbar\omega_{\mathbf{q}\lambda} - E_g)(-\hbar\omega_{\mathbf{q}\lambda} - E_g)} \right]. \tag{11.107}$$

The Kronecker delta ensures that momentum is conserved. If the energy of the incident photon is close to the energy gap ($\hbar\omega_1 \lesssim E_g$), then the third term on the

RHS of Eq. (11.107) dominates over the other five terms; this is called resonant Raman scattering.

In obtaining the above result for Γ, we have assumed that the intermediate states consist of an electron in the conduction band and a hole in the valence band. The electron and the hole were treated as independent particles. In insulators, the attraction between electrons and holes may be significant, leading to the formation of excitons, which are bound electron–hole pairs (Kittel, 2005). A description of Raman scattering in insulators which takes exciton formation into account can be formulated (Ganguly and Birman, 1967), but we will stop here and not take that road.

Further reading

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Venkataraman, G., Feldkamp, L.A., and Sahni, V.C. (1975). *Dynamics of Perfect Crystals*. Cambridge, MA: MIT Press.

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Problems

11.1 *Lesser free-phonon Green's function*. Derive Eq. (11.61).

11.2 *Electron self energy*. Using the Feynman diagram rules, derive the expression for the electron self energy, given in Eq. (11.68), due to electron–phonon interaction.

11.3 *Phonon self energy*. Consider a system of electrons and phonons with a Hamiltonian

$$H = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \sum_{\mathbf{q}\lambda} \hbar\omega_{\mathbf{q}\lambda}(a_{\mathbf{q}\lambda}^{\dagger} a_{\mathbf{q}\lambda} + 1/2) + \sum_{\mathbf{k}\sigma} \sum_{\mathbf{q}\lambda} M_{\mathbf{q}\lambda} c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger} c_{\mathbf{k}\sigma} \phi_{\mathbf{q}\lambda}.$$

(a) Write down the perturbation expansion for the phonon Green's function $d(\mathbf{q}\lambda, \tau)$.

(b) Using Wick's theorem, obtain $d(\mathbf{q}\lambda, \tau)$ to second order in the electron–phonon interaction.

(c) Show that, to second order in the electron–phonon interaction,

$$d(\mathbf{q}\lambda, \omega_m) = d^0(\mathbf{q}\lambda, \omega_m) + \frac{V}{\hbar}|M_{\mathbf{q}}\lambda|^2 d^0(\mathbf{q}\lambda, \omega_m)\Pi^0(\mathbf{q}, \omega_m)d^0(\mathbf{q}\lambda, \omega_m),$$

where $\Pi^0(\mathbf{q}, \omega_m)$ is the polarizability of noninteracting electrons.

Figure 11.17 Phonon Green's function in the random phase approximation. The shaded bubble is the polarizability of interacting electrons. The single wavy line represents the bare (noninteracting) phonon Green's function, while the double wavy line represents the dressed (interacting) phonon Green's function.

11.4 *Electron–phonon interaction in the jellium model*. In the jellium model of a metal, the positive ions are replaced by a positive background of constant charge density. The longitudinal phonon frequency reduces to the ionic plasma frequency $\Omega_q = (4\pi Z^2 e^2 n_i/M)^{1/2}$, where M is the ionic mass, Ze is the ionic charge, and $n_i = N/V$ is the number of ions per unit volume. The longitudinal modes are assumed to be dispersionless. In reality, the phonon frequency approaches zero as $q \to 0$. The inclusion of electron–phonon interaction is necessary to produce the correct behavior.

In the jellium model, the electron–phonon interaction is obtained from Eq. (11.40) by the replacements: $\omega_{\mathbf{q}\lambda} \to \Omega$, $\mathbf{G} \to \mathbf{0}$, $V_{\mathbf{q}} \to -4\pi Z e^2/q^2$. Thus,

$$H_{e-\text{phonon}} = \sum_{\mathbf{k}\sigma\mathbf{q}} M_{\mathbf{q}} c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger} c_{\mathbf{k}\sigma} \phi_{\mathbf{q}\lambda}, \quad M_{\mathbf{q}} = i\frac{4\pi Z e^2}{Vq}\sqrt{\frac{N\hbar}{2M\Omega}}\,\hat{\mathbf{q}}.\boldsymbol{\epsilon}_L(\mathbf{q}).$$

In the random phase approximation, the dressed phonon Green's function is depicted in Figure 11.17. It is given by

$$d(\mathbf{q}, \omega_m) = d^0(\mathbf{q}, \omega_m) + \frac{V}{\hbar}|M_{\mathbf{q}}|^2 d^0(\mathbf{q}, \omega_m)\Pi(\mathbf{q}, \omega_m)d(\mathbf{q}, \omega_m),$$

where $\Pi(\mathbf{q}, \omega_m)$ is the polarizability of interacting electrons. Since the phonon frequency is much smaller than the electron plasmon frequency, we are justified in replacing $\Pi(\mathbf{q}, \omega_m)$ with $\Pi(\mathbf{q}, 0)$.

Show that, as $q \to 0$ the renormalized phonon frequency is given by $\omega = vq$. What is the value of v?

11.5 *Electromagnetic field Lagrangian*. Define the 4-vectors

$$\partial^\mu = \left(\frac{1}{c}\frac{\partial}{\partial t}, -\boldsymbol{\nabla}\right), \quad \partial_\mu = \left(\frac{1}{c}\frac{\partial}{\partial t}, \boldsymbol{\nabla}\right), \quad A^\mu = (\phi, \mathbf{A}), \quad A_\mu = (\phi, -\mathbf{A})$$

and the tensors

$$F^{\mu\nu} = \partial^\mu A^\nu - \partial^\nu A^\mu, \quad F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu.$$

Here, the indices μ and ν take the values 0, 1, 2, and 3. The Lagrangian is given by $\int \mathcal{L} d^3 r$ where $\mathcal{L}$ is the Lagrangian density. The Euler–Lagrange
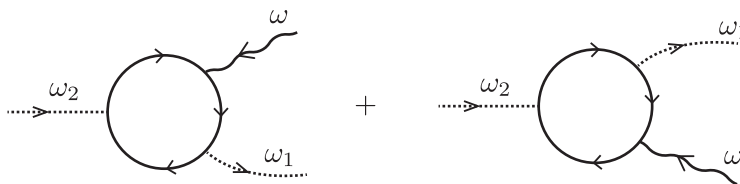
Figure 11.18 The two diagrams that describe Raman scattering in insulators. Solid lines are electron lines, dotted lines are photon lines, and wavy lines are phonon lines.

equations (one for each ν) are

$$\partial^\mu \frac{\partial \mathcal{L}}{\partial(\partial^\mu A_\nu)} = \frac{\partial \mathcal{L}}{\partial A_\nu},$$

where a repeated index (μ in the above equation) is summed over.

(a) Show that the Euler–Lagrange equations yield Maxwell's equations in free space if

$$\mathcal{L} = -\frac{1}{16\pi} F_{\mu\nu} F^{\mu\nu}.$$

(b) Show that

$$\mathcal{L} = \frac{1}{8\pi}(E^2 - B^2).$$

(c) Derive Eq. (11.82).

11.6 *Raman tensor*. Raman scattering in insulators is described by the two Feynman diagrams shown in Figure 11.18. Each diagram represents a process in which a photon of coordinates $(\mathbf{q}_1 \lambda_1)$ is annihilated, a photon of coordinates $(\mathbf{q}_2 \lambda_2)$ is created, and a phonon of coordinates $(\mathbf{q} \lambda)$ is created. In each diagram there are three interactions (one electron–phonon interaction and two electron–photon interactions) occurring at three different times. Use Dzyaloshinski's rules for time-ordered diagrams (there are six time-ordered diagrams corresponding to each of the two Feynman diagrams) to calculate the Raman tensor $\Gamma(\mathbf{q}_1 \lambda_1, \mathbf{q}_2 \lambda_2, \mathbf{q} \lambda)$.