Condensed Matter Physics - II

Chapter 7: Phonons
Electron Phonon Coupling
Superconductivity.

Refs: H. Bruus and K. Flensberg.
P. Phillips.
J. Solom. (Vol 2, chapter 23).

Phonons - the quantized particles of vibrations, here lattice vibrations, is known even before the formulation of the quantum theory. The earliest topic of phonon that we still study is called the Einstein phonon that Einstein considered as collective vibrations of atoms in 1906 (that time it was not called phonon, but only wave) to explain the increase of specific heat with increasing temperature. Looking back from today, the Einstein phonon is analogous to the plasmons that we studies for electron gas, but here for ion gas which is caused by the collective excitation / oscillation of ion density at some characteristic frequency which is determined by coulomb interaction between ions and its density. In 3D this is a finite frequency oscillation, and does not have any dispersion. But a material has continuous values of specific heat as a function of temperature, and hence the question of how does an insulator (ie, no contribution from electrons here) store thermal energy at any energy if there is only one oscillator mode in a material?

In 1912, the Debye model was developed which accurately explained the $C_v \sim T^3$ behavior at low-temperature in an insulator. Deye assumed the ionic gas as collection of simple harmonic oscillators, but they are confined in a box such that it has a highest frequency - called the Debye frequency. According to the Debye model, the ions vibrations produce collective wave with frequencies $W(q) \sim v_s q$, where v_s is the sound velocity. This is like a black body radiation, except here the frequency is cut off below a characteristic frequency, W_D.

called the Debye frequency, which is related to the highest wavelength possible in a box of length L, i.e., $\omega_D \sim v_s \frac{2\pi}{2L}$. Above this temperature, the solid cannot store any further thermal energy and hence specific heat becomes constant in temperature following Dulong-Petit empirical law. For such a dispersion we can simply use equipartition law to compute the internal energy as $E = \sum \varepsilon_i n_i$, where n_i = # of oscillator modes excited at a temperature T, i.e., the degrees of freedom, which is 3 in 3D. So, we have $n_i \sim (k_B T)^3$. Each mode carry energy $\sim k_B T$. Hence $E \sim T^4$ and $c_V = \partial E / \partial T \sim T^3$.

- In addition to specific heat behavior due to phonon modes, specifically in an insulator, phonons also take part in energy transport - called thermal conductivity. They are especially important in systems, such as in computers, to allow heat transport without any electrical current. Electrons carry both electric and thermal conductivity, while phonons only carry heat but no charge. Generally electron's fermi velocity $v_F \gg v_s$, where v_s is the sound velocity of phonons, in a metal. Hence, electrons dominate the thermal conductivity in a metal. The Wiedamann-Franz law is: $\kappa / \sigma = LT$, where κ, σ are thermal and electric conductivity, and L = Lorentz number $= \frac{\pi^2}{3}(k_B/e)^2$ is a universal constant. So, in metals, where phonons are not important, the Wiedamann-Franz law is obeyed.

There is another important materials properties of present interest — called the thermo-electric effect — is, in general, a conversion between the electrical current and temperature gradient. This includes three main effects: Seebeck effect which creates a electrical voltage difference from temperature gradient, Peltier effect which drives thermal current due to an electric current, and Thomson effect which produces reversible heating/cooling within a conductor/metal when both electric current and temperature gradient are applied. To quantify the thermoelectric properties of a material, a figure of merit is defined as (called "Zet-T")

$$Z_T = ZT = \frac{\sigma S^2 T}{\kappa}$$

where σ, κ are electrical and thermal conductivity, S is the Seebeck coefficient, T = temperature.

Thermal conductivity has two contributions from electrons and phonons (also magnons in magnetic ground states), while electric conductivity only comes from electrons (electron-phonon scattering plays an indirect role of reducing electric conductivity). For many purposes, we want to enhance Z_T, i.e., we want to enhance electrical conductivity due to thermal gradient, but at the same time, reduce thermal conductivity. For this purpose we need a metal with phonon degrees of freedom being "frozen" like a glass.

- If the phonon's oscillation amplitude becomes larger than some critical value compared to the lattice constant, the crystal/solid can melts. This is called the Lindemann criterion for melting. On the other hand, the anharmonic effect of phonons can expand the lattice - called the thermal expansion.

- Finally, the electron-phonon coupling gives a lot of interesting properties of materials. Electrons can scatter from one k-state to another, by transfering momentum and/or energy to phonons. Such process cause renormalization to electron's velocity and effective mass - hence the electron's have finite life time and resistivity. As an electron scatters via phonon, it reduces the local charge density to an effective positive charge cloud - which further attracts another electron. This gives an effective attractive electron-electron interaction which gives rise to the superconductivity.
  Finally, strong electron-phonon coupling produces a bound state of electron and phonon - called the polaron. Furthermore, electron-phonon interaction also changes the phonon dispersion. As we integrate the electron's states, we encounter the same $F(q/2k_F)$ function that we saw in the electron-liquid chapter. The singularity of this function at $F(1)$ causes a singularity in the phonon dispersion which can distort the lattice. This effect is called the Kohn Anomaly.

7.1 Einstein Phonon : Density oscillation

Let us now go back to Chapter 1 where we decoupled the nucleus (of charge $+Ze$) or the ion (nucleus and core electrons of charge $+e$) part from the electron's Hamiltonian using the Born-Oppenheimer approximation as.

$$\left[-\frac{\hbar^2}{2M}\sum_I \nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{(Ze)^2}{|R_I - R_J|}\right]\Psi(R_I \cdots R_N) = E\,\Psi(R_I \cdots R_N) \quad \text{--(1)}$$

If we proceed with a Hartree-Fock like state for the ions and assume plane wave solutions for electron liquid, then compute the RPA-based density-density response function, we will get a plasmon oscillation defined similarly as

$$\omega_e = \sqrt{\frac{4\pi (Ze)^2 n}{M}} \quad \text{--(2)}$$

where we have replaced electron's charge e with nucleus charge Ze and electron's mass m with nucleus mass M, and n is the nucleus density $= N/V$ = # of nucleus per unit cell.

The exact result Einstein obtained/assumed in 1906 for his model of solid (which is sometimes called the Einstein solid) but without actually assuming a periodic array of atom, rather that a "liquid" of atoms. Einstein assumed that atoms are independent but collectively vibrate/oscillate with the same frequency ω_e, and the energies are quantized in unit of this frequency $E_n = (n+1/2)\hbar\omega_e$. Einstein, in fact, generalized his idea of quantized energy for electrons to explain the photoelectric effect to explain the specific heat data in a solid. This was Einstein another contribution to quantum mechanics. He eventually did not like the modern quantum mechanics or the wave function based quantum mechanics, but he founded two important quantization formula for energy in atoms and solids.

- The computation of the C_V in this model is standard. The thermal average energy (i.e. the internal energy) is

$$\langle E \rangle = \sum_{n=0}^{\infty} E_n \, n_B(E_n) \,, \quad \text{where } n_B = \text{Bose factor}$$

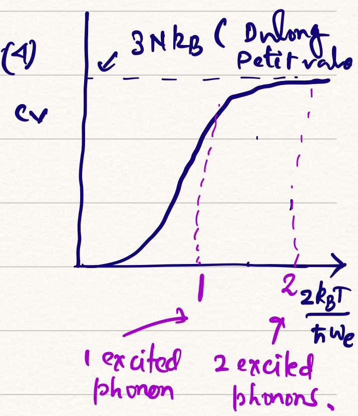
(H. W)

$$= \frac{\omega_e}{2} \coth(\beta \omega_e / 2) \quad \text{--(3a)} \qquad \left[\hbar = 1, \; \beta = \frac{1}{k_B T}\right].$$

This gives the specific heat

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \left(\frac{\beta \omega_e}{2}\right)^2 n_B^2(\omega_e) \, e^{-\beta \omega_e}$$

$$= k_B (\beta \omega)^2 \operatorname{cosech}^2\left(\frac{\beta \omega_e}{2}\right) \quad \text{--(4)}$$



This results gives the exponential rise of C_V with temperature as seen experimentally at intermediate temperature and the Dulong-Petit values at high-T, but completely misses the algebric T-dependence ($\sim T^3$) at low-T region.

(*) So what went right in Einstein's model, despite now we know that its a very poor model of solid?

The reason Einstein's model of independent oscillators at a single frequency worked is the same reason that there is a plasma frequency for electron's liquid which arises from the mean field theory within the RPA method. Within the mean-field theory, the Coulomb interaction decouples into an independent electron model seeing the other electrons providing a mean potential energy to it. In one of the homeworks we also learned that within the mean field approximation, i.e., $\delta(q) \approx \langle \delta(0) \rangle$, the Coulomb interaction exerted on the independent electron appears to give a constant "restoring force", and hence the all electrons, despite being independent to each other, collectively oscillates with the same (plasma) frequency. In what follows, if the Einstein model has to be right at high energy, the Coulomb interaction part in eq(1) should also provide a "restoring" force to the nucleus. Indeed this turns out to be the case as we will show below.

⊛ Then what went wrong in Einstein model that it failed to reproduce low-T behavior of C_V?

Because the Einstein phonon energy is quite high, it takes large temperature to occupy this state. But $C_V \sim T^3$ suggest there must be more states below W_0. The continuous translational invariance of the solid as assumed by Einstein that atoms in a solid are randomly placed without any periodic boundary condition was the problem in the Einstein model. In 1912, Debye generalized Einstein's model to a periodic lattice and obtain a linear dispersion $W(q) = v_s q$, as in photons, but with sound velocity $v_s \ll c$. These are called the acoustic phonons. At high-energy and small q-values, i.e., large distances, the periodic lattice constant is negligible and there one also obtain Einstein phonon like mode, which is called the optical mode.

7.2 Debye model :

Debye model is similar to the blackbody radiation case of photon, but here for sound waves or phonons. As the atoms are in a box of fixed length L, so, the vibrational waves have to have nodes at the boundary. This makes the wavelength to be quantized as $\lambda_n = 2L/n, n \in \mathbb{Z}$. From the de-Broglie relation we have $p_n = h/\lambda_n = \hbar q_n$, where q_n are the quantized wave number. Assuming relativistic relation for massless phonons we get

$$\begin{aligned} E_n &= p_n v_s \qquad\qquad v_s = \text{sound velocity} \\ &= \hbar v_s q_n \\ &= \frac{h v_s}{2L} n \\ &= \hbar \omega n \quad \text{---} (4) \end{aligned}$$

This also gives quantized energy in units of a fixed frequency $\omega = \pi v_s / L$, much like what Einstein assumed. But here the frequency $\omega \ll \omega_E$, so these phonon modes can be excited at a much lower energy than the Einstein modes. Moreover, there is a minimum wavelength possible in this box, which is $\lambda_{min} = 2L/N$, where N is the number of unit cell / atoms in the box. This gives the maximum number of phonon modes that can be excited in a solid of N atom in N (in 3D it will generalize to N_x, N_y, N_z or $\sqrt[3]{N}$ for N atoms). This upper cut off on the frequency for phonon in a solid is called the Debye frequency ω_D, and the corresponding temperature is the Debye temperature T_D, which represents a characteristic temperature by which all possible phonon modes are excited in this system. These two factors make the difference in the Debye model and we have an algebric relation of $C_V \sim T^d$, $d=$ dimension, in a solid.

Proceeding similarly, we have

$$\langle E \rangle = \sum_{n=0}^{N} E_n \, n_B(E_n)$$

Now since the summation truncates at finite N, we cannot do this sum. On the other hand, since n is very small compared to N, we can convert this sum into integration $\sum_n = \int_0^N d^3 n = \frac{V}{(2\pi)^3} \int_0^{q_D} d^3 q$, where the maximum value of q is called the Debye wavenumber, defined as $q_D = 4\pi N/L$. Then we have

$$\langle E \rangle = \int_0^{q_D} \frac{v_s q}{e^{\beta v_s q}-1} 4\pi q^2 dq = 4\pi v_s \int_0^{q_D} \frac{q^3 \, dq}{e^{\beta v_s q}-1}$$

$$= 4\pi v_s \frac{1}{\beta^4 v_s^4} \underbrace{\int_0^{\beta v_s q_D} \frac{x^3}{e^x-1} dx}_{\text{Debye integral } D_3(x)}$$

Define $x = \beta v_s q$.

$x_D = \beta v_s q_D$

Because x is dimensionless parameter, this integral simply gives a number.

We define the Debye temperature as

$$T_D = \hbar \omega_D / k_B$$

$$= \frac{\hbar v_s q_D}{k_B} = \frac{4\pi v_s N}{k_B L}$$

In 3D, q_D is obtained as

$N = \left(\frac{4}{3}\pi q_D^3\right) / \left(\frac{2\pi}{L}\right)^3$

$\Rightarrow q_D = \left(6\pi^2 \frac{N}{V}\right)^{1/3}$

Then we have

$$\langle E \rangle = 9 N k_B T \left(\frac{T}{T_D}\right)^3 \underbrace{\int_0^{T_D/T} \frac{x^3}{(e^x-1)} dx}_{D_3(T_D/T)}.$$

$$= 3T \, D_3(T_D/T) \quad -(5a).$$

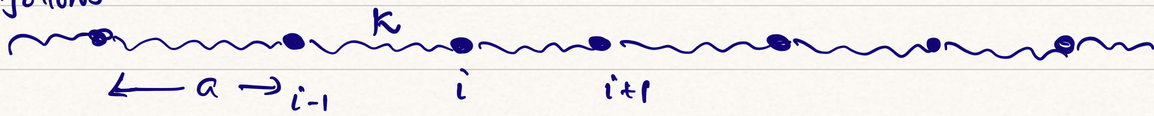
And $\boxed{C_V = 9 N k_B (T/T_D)^3 \, D_3'(T_D/T)}$, $D_D'(T_D/T) = \int_0^{T_D/T} \frac{x^4 e^x}{(e^x-1)^2} dx.$ $-(5b)$

Therefore, Debye model correctly predicts the T^3 dependence of the specific heat upto T_D, and above it, it smoothly becomes exponential to the Einstein result before it saturates to the Dulong-Petit value.

To capture the entire phonon spectrum and the specific heat result, we need a better model which captures the accoustic phonons as obtained by Debye and the optical phonon as assumed by Einstein. What is missing is a periodic boundary condition on the atoms vibration. Then to compute the sound velocity v_s, we, we have to go back to Eq (1) and obtain the restoring force accurately.

7.3 Chain of atoms with periodic boundary condition.

We improve on the Debye model by putting the atoms in a periodic lattice, and allow them to oscillate. Its defined as follows:



The equilibrium positions of atoms are in a periodic lattice of unit cell length "a = 1". Then the atoms oscillates around it which is governed by the Coulomb interaction between them. Now, we will just model this as the oscillators are connected to each other by springs of spring constant K. Therefore, the Hamiltonian is

$$H = \sum_{i=1}^{N}\left[\frac{p_i^2}{2M} + \frac{1}{2}K\left(u_i - u_{i+1}\right)^2 + \frac{1}{2}K\left(u_i - u_{i-1}\right)^2\right] \quad \cdots (6)$$

where u_i are the displacements from the equilibrium position a, $x_i = R_i + u_i$, so, $p_i = -i\frac{\partial}{\partial u_i}$.

In this case, the atoms are not independently vibrating, rather collectively vibrating. The frequencies (or energy in quantum theory) are the collective/normal modes of Hamiltonian, that we also obtained in classical mechanics by solving the equation of motion of the corresponding equation of motion.

One of the frequency we obtained in classical mechanic was $w = 0$. Therefore, there exist an infinite period oscillation, which is like a (permanent) translation of the lattice. This is expected to survive here because a (permanent) translation of all the atoms by a constant value $u_i \to u_i + a$, does not change the Hamiltonian. In other words the Hamiltonian is translationally invariant, and it does not cost any energy to simply move the entire lattice by a constant value. This is the logest wavelength or the shortest wavevector collective oscillation. So, we do expect a $\omega=0$ or $E=0$ phonon mode at $q=0$.

There there will be other shorter wave lengths and larger wave vectors and corresponing frequencies, and hence we obtain a dispersion relation $\omega(q)$. Unlike in the Debye model, where the dispersion relation is sharply cut off at the Debye frequency, ω_D, in a periodic boundary condition, we should have a dispersion relation $\omega(q)$ which should be periodic as $\omega(q+G)=\omega(q)$. A periodic function which should reproduce a linear dispersion at $q\to 0$ should be of $\sin(qa)$ form. Indeed we obtain such a dispersion by Fourier transforming the position and momentum variables to the momentum space.

$$p_j = \frac{1}{\sqrt{N}} \sum_{q\in BZ} p_k e^{iqR_j} \quad , \quad u_j = \frac{1}{\sqrt{N}} \sum_{q\in BZ} e^{iqR_j} \quad , \quad \cdots (7a)$$

$$\Rightarrow \; p_q = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} p_j e^{-iqR_j} \quad ; \quad u_q = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} u_j e^{-iqR_j} \, . \quad --(7b)$$

[This Fourier transformation may sound strange, as we often take a function in position space and Fourier transform to its conjugate momentum space. On the other hand here we seem to be Fourier transforming position & momentum in real space to "position" and "momentum" in the momentum space. In fact, u_j, p_j are considered to be independent "fields" defined in the position space (denoted by j) and Fourier transforming them to the momentum space (denoted by k). In fact, u_i & p_j are not completely independent fields, they are related to each other by the cannonical commutation relation $[u_i, p_j] = i\hbar\delta_{ij}$, $[u_q, p_{q'}] = i\hbar\delta_{q,-q'}$.]

In the Fourier transformations in eqs (7a) & (7b), we note an important factor. p_j, u_j are Hermitial (real) fields, but on the R.H.S in eq (7a), we have the complex functions $e^{iq\cdot R_j}$. Therefore to ensure hermiticity, we impose the constraint $p_q = p^+_{-q}$ and $u_k = u^+_{-k}$ (Sometimes, one write $p_i = \frac{1}{\sqrt{N}} \sum_{q \in BZ} (p_q e^{iqR_j} + p_{-q} e^{-iq\cdot R_j})$ which is to say, include the hermitian conjugate field also).
Then substituting eq (7) in eq (6) we diagonalise the Hamiltonian:

$$H = \sum_q \left[\frac{1}{2M} \underbrace{|p_q|^2}_{p^+_q p_q = p_{-q} p_q} + \frac{1}{2} M \omega_q^2 |u_q|^2\right] \quad \text{--- (8)}$$

where $\omega_q = \sqrt{\frac{K}{M}}\, 2\left|\sin \frac{qa}{2}\right|$

We can define the usual creation and annihilation operators (for phonon) in the momentum space as

$$a_q = \frac{1}{\sqrt{2}\, l_q}\left(u_q + i\frac{l_q^2}{\hbar} p_q\right), \quad \text{where } l_q = \text{oscillator length} = \sqrt{\frac{\hbar}{M\omega_q}}$$

$$a^+_{-q} = \frac{1}{\sqrt{2}\, l_q}\left(u_q - \frac{i\, l_q^2}{\hbar} p_q\right) \quad \text{--- (9a).}$$

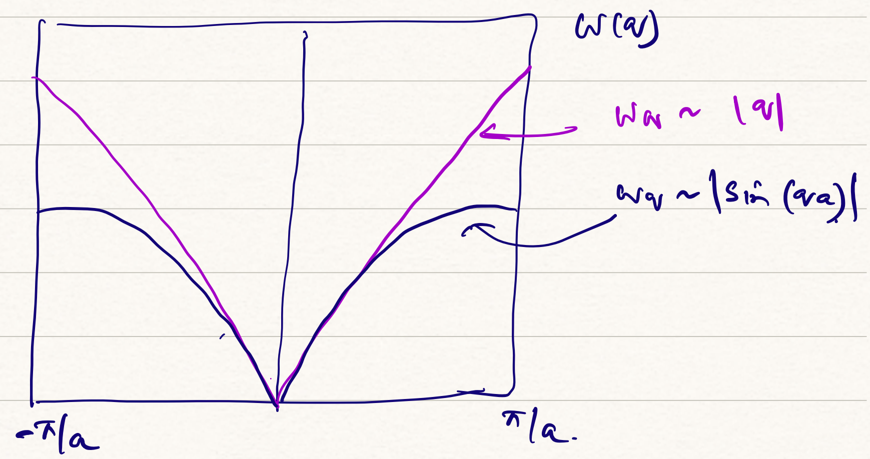
or, $u_q = \frac{l_q}{\sqrt{2}}(a^+_{-q} + a_q)$, $p_q = \frac{i\hbar}{\sqrt{2}\, l_q}(a^+_{-q} - a_q)$ --(9b)

This diagonalise the Hamiltonian as

$$H = \hbar \omega_q \left(a_q^\dagger a_q + \tfrac{1}{2}\right) , \quad \left[a_q, a_{q'}^\dagger\right] = \delta_{qq'} .$$

This is similar to what we said at the introduction of second quantization that we introduce an oscillator for each state $|q\rangle$.

- We recover the Debye result in the long wavelength ($q \to 0$) limit, which gives $\omega_q \approx \hbar v_s |q|$, where $v_s = \frac{1}{\hbar}\sqrt{k/m}$.

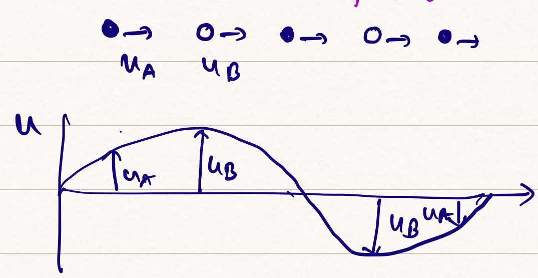


In a lattice, the phonon has a well-defined bandwidth of $\omega_{q=0}$ to $\omega_\pi = 2\sqrt{k/m}$. This contains N-number of phonon modes as possible in a lattice of length L: $N = L/a$. As the temperature $k_B T \sim \omega_\pi$ is reached, there is no other phonon mode to excite, and hence the specific heat becomes constant. In Debye theory the Debye frequency is defined when the linear dispersion accomodate N-modes. clearly $\omega_D > \omega_\pi$ in a solid.

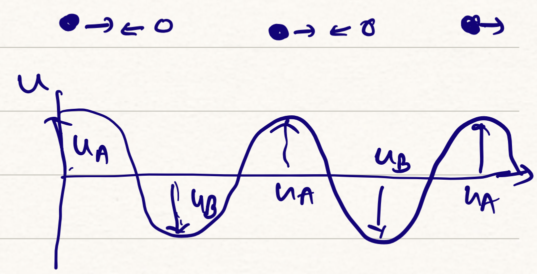
• Accoustic and Optical Phonons:

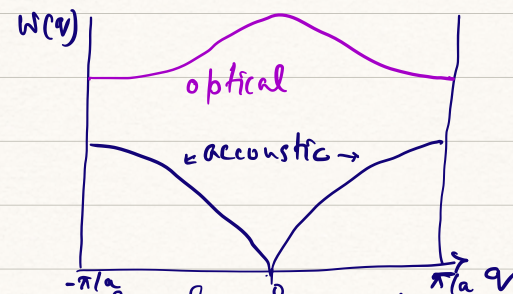
If we have two different atoms, A, B in an unit cell, then there is expected to be two phonon bands, with one of them remaing as gapless accoustic mode and the other one a gapped mode (called the optical mode). The origin of the optical mode is similar to what we saw in classical mechanics that there is one in-phase vibration (accoustic) and another out-of-phase vibration:

Accoustic phonon:



Optical phonon





In an unit cell with n-different atoms (basis), there is always one accoustic mode guaranteed due to the translational invariance (ie, if we move all atoms by a constant value, the system remains invariant). The remaing (n-1) are optical phonons.

The optical phonons are named so because they can be exited optically.

⊛ Higher dimensions:

As we go to higher dimensions, there is a displacement field u_i^μ for each dim $\mu = 1, 2, \cdots \dim$, and at each lattice position $i = 1, 2, \cdots, N_g$ and a corresponding conjugate momentum field p_i^μ. More generally, u_x (displacement field along x) many not a function of x only but x, y etc, especicially in the case of lattices whose primitive directions are not $90°$ to each other. In that case, the spring constant $K_{\mu\nu}$ will also be a tensor and we have to diagonalize it. This gives us eigen modes, called the polarization mode, as in the electromagnetic field. Then one has longitudinal and transverse modes, for vibration along and perpendicular to the direction of propagation. So, there is one longitudinal mode and $(d-1)$ transverse modes in d-dim. All of them are gapless acoustic modes, and they are denoted by LA and TA, for longitudinal and transverse acoustic modes.

If we have n - distinct atoms per unit cell in a d-dimensional lattice, there will be a total of nd - phonon bands. Among which d - acconostic phonons (1 LA & $d-1$ transverse) and $nd-d$ optical modes. optical modes are also distinguished as LO & TO for longitudinal and transverse optical phonons.

7.5 Realistic Model of Phonons:

We can now derive the lattice spring constant from the nucleus-nucleus coulomb repulsion from eqr (1). We denote the lattice equilibrium position as R_i and the displacement from it is u_i, i.e., $\vec{R}_I(t) = \vec{R}_I(0) + \vec{u}_I(t)$ (This is conceptually similar to the mean-field theory)
Now, doing a Taylor expansion of the ion-ion Coulomb interaction, we get

$$V(R_I - R_J(t)) = V(\vec{R}_i - \vec{R}_j(0)) + \sum_{\mu\nu} \left.\frac{\partial^2 V}{\partial u_i^\mu \partial u_j^\nu}\right|_{R_i, R_j(0)} u_i^\mu u_j^\nu + \mathcal{O}(u^3) \quad \text{--(10a)}$$

where we have set the first derivative term to zero, because the potential energy has a minimum at the equilibrium position, by definition of the equilibrium position. From now, $\vec{R}_i$ simply denotes at $t=0$.
The spring constant is a tensor, and denoted by, $D_{\mu\nu}(\vec{R}_i, \vec{R}_j)$

$$D_{\mu\nu}(\vec{R}_i - \vec{R}_j) = \left.\frac{\partial^2 V}{\partial u_i^\mu \partial u_j^\nu}\right|_{\vec{R}_i, \vec{R}_j(0)} \quad \text{--- (10b)}$$

The Fourier component of this spring constant is called the Dynamical matrix,

$$D_{\mu\nu}(\vec{q}) = \sum_{\underbrace{R_i - R_j}_{\vec{R}}} D_{\mu\nu}(\underbrace{\vec{R}_i - \vec{R}_j}_{\vec{R}}) e^{-i\vec{q}\cdot\underbrace{(\vec{R}_i - \vec{R}_j)}_{\vec{R}}} \quad \text{--(11a)}.$$

(Due to lattice translational symmetry, $D_{\mu\nu}$ does not depend on the absolute positions $\vec{R}_i$, $\vec{R}_j$ but their difference $\vec{R} = \vec{R}_i - \vec{R}_j$. So, its Fourier component only has one wavevector $\vec{q}$.)

$D_{\mu\nu}$ is a symmetric tensor $D_{\mu\nu} = D_{\nu\mu}$, and is even function of $|\vec{R}_i - \vec{R}_j|$.

- Eq (11a) is like a "tight binding model" in the sense that $D_{\mu\nu}$ is like the "tunneling" between the sites at $\vec{R}_i$ & $\vec{R}_j$. We have to sum over all equivalent nearest neighbors which depends on the specific symmetry of the lattice. Finally we have to subtract off the contributions from the same site ($\bar{R}_i = \bar{R}_j$). This gives

$$D_{\mu\nu}(q) = \frac{1}{2} \sum_{\bar{R}} D_{\mu\nu}(\vec{R}) \left[e^{-i\bar{q}\cdot\vec{R}} + e^{i\bar{q}\cdot\vec{R}} - 2 \right]$$

$$= \sum_{\bar{R}} D_{\mu\nu}(\bar{R}) \left[\cos(q\cdot R) - 1 \right]$$

$$= -2 \sum_{R} D_{\mu\nu}(\bar{R}) \sin^2\left(\frac{q\cdot R}{2}\right) \quad --- (11b)$$

So, we get a linear in q term from the sin function.

[To see this more clearly, one should go to back to the Hamiltonian and drive equation of motion:

$$H = \sum_I \frac{P_I^2}{2M} + \sum_{I,J} V_0(\bar{R}_I - \bar{R}_J) + \frac{1}{2} \sum_{IJ} D_{\mu\nu}(R_I - R_J)\, u_\mu(R_I)\, u_\nu(R_J).$$

Then define the Heisenberg eq of motion.

$$i\hbar\, \dot{u}_\mu(R_I) = [u_\mu(R_I), H] = 2\sum_J \frac{1}{2M} P_J [u_\mu(R_I), P_J]$$

$$= i\hbar P_J / M.$$

$$i\hbar\, \dot{P}_J = [P_J, H] = \sum_J D_{\mu\nu}(R_I - R_J) [P_J, u_\mu(R_J)]\, u_\nu(R_J)$$

$$= -i\hbar \sum_J D_{\mu\nu}(R_I - R_J)\, u_\nu(R_I)$$

$$\therefore \quad \ddot{u}_\mu(R_I) = -\frac{1}{M} \sum_J D_{\mu\nu}(R_I - R_J)\, u_\nu(R_J) \quad --(11c)$$

$$= -\frac{1}{M} D_{\mu\nu}(R_I) \left[u_\nu(R_J + 1) + u_\nu(R_J - 1) - 2u_\nu(R_J) \right]$$

If we fourier transform on both sides, we get eq(11b)]

- $D_{\mu\nu}$ is a tensor and u_μ are components of the displacement vector. Therefore, the equation of motion is an eigenvalue equation among the three directions of vibrations. Generally, the eigen-directions of vibrations may not be aligned along the cartesian coordinates of the reference of frame, or even the bond directions. There are also point group symmetry (rotation, reflection) symmetry which the eigen directions have to respect. Considerations of such point group symmetry dictates the irreducible representations of the eigendirections and one has A_{1g}, A_{2g}, B_{1g}, B_{2g}; etc modes which are used in the Raman scattering data. I

- These eigen directions are called Polarization directions, as in the electromagnetic fields, and we denote them as $\vec{\varepsilon}_s(\vec{q})$ where $s = 1, 2, 3$ are three eigendirections, written as a linear combinations of $u_\mu(\vec{q})$. Since $D_{\mu\nu}(q)$ is a real, symmetric tensor, we can diagonalize it by an orthogonal matrix, say O, and the eigenvectors u_s are obtained using O:

$$O \overleftrightarrow{D}(q) O^T = K(q) \quad \text{-- (12a)}$$

$$u_\mu(q) = \sum_\mu O_{s\mu} u_s(q) \quad \text{-- (12b).}$$

Each column $\hat{\varepsilon}_s$ corresponds to the polarization unit vectors.

$K(q)$ is a diagonal matrix, whose components K_s gives the spring constants for the vibrations along the polarization direction. and obey:

$$\overleftrightarrow{D}(q) u_s(q) = K_s(q) u_s(q). \quad \text{-- (12c).}$$

ε_s are orthonormalised as $\sum_q \hat{\varepsilon}_s(q) \hat{\varepsilon}_{s'}(q) = \delta_{s,s'}$, $s, s' = 1, 2, 3$.
unit and $\hat{\varepsilon}_s(q) = \hat{\varepsilon}_s^*(-q)$.

- In this eigen directions notation, one would have a longitudinal accoustic (LA) mode and two transverse accoustic (TA) modes. The frequency of phonons are polarization dependent:

$$\omega_s(q) = \sqrt{\frac{K_s(q)}{M}} = ()_s \left|\sin\left(\frac{qa}{2}\right)\right| \quad \text{---(13)}$$

$$\approx \hbar v_s q. \qquad \text{for } qa \ll 1$$

where v_s are the sound velocity for each eigendirection. Its value depends on the orthogonal matrix $\hat{O}$ and hence the details of the crystal symmetry.

- As we have 2 or more distinct atoms per unit cell, the dynamical matrix becomes $D^{nm}_{\mu\nu}(\bar{R}_i - \bar{R}_j)$, where n, m stands for atoms and μ, ν for spatial dimensions. One can then define a $N \times d$-dimensional vector space for u^n_μ where N stands for total number of distinct atoms and d = dimension. This gives $Nd \times Nd$-dimensional dynamical matrix which can can be decomposed according to the corresponding Point group and space group symmetry of the lattice. We will eventually have d-acoustic branch of polarization and $(N-1)d$ transverse branch. Those who work on Raman and neutron scattering experiments need to know all these modes and symmetry in details. We will not go into details of such multi-atomic phonon case. Now, density functional theory (DFT) codes can compute these phonon dispersions quite accurately.

- The after Fourier transforming the nucleus Hamiltonian to the momentum space, we have

$$H = \sum_{q,\mu} \frac{P_\mu(q) P_\mu(-q)}{2M} + \sum_{q,\mu,\nu} D_{\mu\nu}(q)\, u_\mu(q)\, u_\nu(-q) + \sum_{i \neq j} V_{ion}(R_i - R_j). \quad \text{--- (14a)}$$

and acting the orthogonal rotation $\hat{O}$ in the entire Hamiltonian we obtain

$$H = \sum_{q,s} \frac{P_s(q) P_s(-q)}{2M} + \frac{1}{2}\sum_{q,s} M\omega_s^2(q)\, u_s(q)\, u_s(-q) + \text{constant} \quad \text{--- (14b)}$$

where the polarization vectors are the displacement field and p_s are the corresponding cannonical momentum.
By defining phonon creation and annihilation operators for these directions as

$$u_s(q) = \frac{l_s(q)}{\sqrt{2}} \left(a_s(q) + a_s^\dagger(-q) \right) \hat{\varepsilon}_s \; ; \; l_s(q) = \sqrt{\frac{\hbar}{M\omega_s(q)}}$$

$$p_s(q) = i \frac{\hbar}{\sqrt{2}\, l_s(q)} \left(a_s^\dagger(-q) - a_s(q) \right) \hat{\varepsilon}_s , \quad \text{-- (15)}$$

we obtain a diagonal Hamiltonian

$$H = \sum_{q,s} \hbar\omega_s(q) \left(\underbrace{a_{qs}^\dagger a_{-qs}}_{n_{qs} = \text{number operator.}} + \frac{1}{2} \right). \quad \text{--- (16)}$$

- $\varepsilon_s(q)$ are called the "normal modes", they are the "extendended" or "collective" vibrations of all atoms in a solid.

- The $E_0 = \frac{1}{2}\sum_{s,q} \hbar\omega_s(q)$ is called the zero point (quantum) energy of the lattice while $\sum_{i \neq j} V_{ion}(R_i - R_j)$ gives the classical energy.

- The calculation of thermodynamic quantities (specific heat) follows the same as in the Debye model, except here the momentum integration is done for a periodic function of $\omega_s(q)$ for $q \in FBZ$, rather than a linear function $\omega_q \sim v_s q$ and putting an artificial cutoff (Debye frequency / temperature).

7.6 Electron - Phonon Coupling

Next we consider one of the most important interaction, i.e, the electron phonon coupling of a lattice. The electron-phonon coupling causes many properties of a material such as band renormalization of electrons, transport phenomena, charge density wave and superconductivity.

The electron and nucleons interact with each other via attractive coulomb interaction, which we generically write as

$$V_{eI} = \sum_{i,I} V_{eI}(\vec{r_i} - \vec{R_I}) .$$

Now, again expand $\vec{R_I}(t) = \vec{R_I}(0) + \vec{u_I}(t)$ in a mean field like theory, and keep only the first term in the Taylor expansion:

$$V_{eI} = \sum_{i,I} V_{eI}(\vec{r_i} - \vec{R_I}(0)) - \sum_{i,I} \underbrace{(\nabla V_{eI})\Big|_{R_I} \cdot \vec{u}(R_I)}_{V_{ep}(r_i)} + \mathcal{O}(u^2) \quad \text{--- (17a)}$$

The first term gives the static coulomb repulsion between electron with the nucleons and is already modelled as a background (uniform) potential in the Jellium model or as a periodic potential in the band structure / tight binding model. The second term corresponds to the electron-phonon coupling of our present interest. We only focus on the electron phonon part at r_i (we drop the index 'i' and pretend its a continuous value and put it back when its not obvious)

$$V_{ep}(\vec{r}) = -\sum_I \vec{u}\,(\vec{R}_I)\,.\,\vec{\nabla}\,V_{eI}(\vec{r}-\vec{R}) \quad --- (17b)$$

The Fourier transformation of $V_{eI}(\vec{r})$ is

$$V_{eI}(\vec{r}) = \frac{1}{N}\sum_q V_{eI}(q)\, e^{i\vec{q}.\vec{r}} \quad --- (18a)$$

Then $$\nabla V_{eI} = \frac{i}{N}\sum_q \vec{q}\, V_{eI}(q)\, e^{i\vec{q}.\vec{r}} \quad -(18b)$$

$N =$ total number of q-values.

Now, we see that q is not restricted to the Brillouin zone because $V_{eI}(\vec{r})$ is not a periodic function of the lattice. Therefore, we have to split the q-summation to a periodic one $q \in$ First BZ and on all possible values of G (we keep the same notation q for both cases) :

$$\sum_q f(\vec{q}) = \sum_{G \in \text{all RLC}} \; \sum_{q \in FBZ} f(q+G).$$

Then plugging eq (18b) in eq (17b), we get

$$V_{ep}(\vec{r}) = -\frac{i}{N}\sum_G \sum_q \sum_I \vec{u}(R_I).(\vec{q}+\vec{G})\, e^{i(q+G).\vec{r}}\, \underbrace{e^{-i(q+\vec{G}).\vec{R}}}_{\substack{= e^{-i\vec{q}.\vec{R}} \\ \because\, e^{i\vec{G}'.\vec{R}} = 1}} \times V_{eI}(\vec{q}+\vec{G})$$

$$= -\frac{i}{N}\sum_G \sum_q e^{i(q+\vec{G}).\vec{r}}\,(\vec{q}+\vec{G})\,.\,\underbrace{\sum_I \vec{u}(\vec{R}_I)\, e^{-i\vec{q}.\vec{R}}}_{\vec{u}(q)}\, V_{eI}(q+G)$$

$$= -\frac{i}{N}\sum_G \sum_q e^{i(q+\vec{G}).\vec{r}}\;\vec{u}(q)\,.\,(\vec{q}+\vec{G}) \times V_{eI}(\vec{q}+\vec{G}) \quad --(18c)$$

Next we express $u_{\mu l}(\vec{r})$ in terms of its eigen directions $u_s(q)$ and the polarization unit vector $\varepsilon_s^{\mu}(q)$, and express u_s in terms of the creation/annihilation operators (eq 15) as

$$u_{\mu}(q) = \sum_s \epsilon_{\mu}^{s}\, u_s(q)$$

$$= \sum_s \epsilon_s^{\mu} \frac{l_s(q)}{\sqrt{2}}\left(a_s(q) + a_s^{\dagger}(-q)\right) \quad \cdots (18d)$$

and substitute in eq (18c) to get

$$V_{ep}(\vec{r}) = -\frac{i}{N}\sum_G \sum_q \sum_s \underset{\substack{\uparrow \\ V_{eI}(\vec{q}+\vec{G})}}{} e^{i(\vec{q}+\vec{G})\cdot\vec{r}} \left[\hat{\epsilon}_s(q)\cdot(\vec{q}+\vec{G})\right] \frac{l_s(q)}{\sqrt{2}}\left(a_s(q) + a_s^{\dagger}(-q)\right) \quad (18e)$$

Then the electron-phonon coupling Hamiltonian is obtained as

$$H_{ep} = \sum_i V_{ep}(r_i)$$

$$= -\frac{i}{N}\sum_G \sum_q \sum_s \underbrace{\sum_{r_i} e^{i(\vec{q}+\vec{G})\cdot\vec{r}_i}}_{=\ \rho_{\vec{q}+\vec{G}}\ =\ \text{electrons density}} \left[\text{rest of the terms}\right]$$

Actually we have already used the plane wave basis in the above Fourier transformation and now retrieving the electron density from here. Recall the electron density $\rho(r) = \sum_i \delta(r - r_i)$, so that $\rho(q) = \sum_i e^{i\vec{q}\cdot\vec{r}}$. Then expressing the density in terms of the field operator $\rho(r) = \psi^{\dagger}(r)\psi(r)$ and doing a Fourier-transformation of the field operator to the momentum space we get $\psi(r) = \int e^{ik\cdot r} dr\, c_k$. This way we write $\rho_{q+G} = \sum_{k,\sigma} c^{\dagger}_{k+q+G,\sigma} c_{k\sigma}$, including spin $\sigma = \uparrow, \downarrow$.

Then we get

$$H_{ep} = -\frac{i}{N} \sum_{G} \sum_{q} \sum_{s} \underbrace{\left[V_{eI}(\vec{q}+\vec{G}) (\vec{q}+\vec{G}) \cdot \hat{\epsilon}_s(q) \frac{l_s(q)}{\sqrt{2}} \right]}_{g_s(q+G)} \rho_{q+G} \left[a_s(q) + a_s^{\dagger}(-q) \right] \quad \text{--(19)}$$

$g_s(q+G)$ Electron-phonon Matrix element or Electron-phonon Coupling constant. Remember that the E.P. coupling constant depends on the phonon frequency via $l_s(q) = \sqrt{\hbar / M\omega_s(q)}$.

→ $g_s(q)$ remains Hermitian since $\omega_s(q) = \omega_s(-q)$, and $l_s(q) = l_s(-q)$, $V_{eI}(q) = V_{eI}(-q)$ and $\epsilon_s^*(q) = \epsilon_s(-q)$. [H.W.]

→ $\hat{\epsilon}_s(q)$, $\omega_s(q)$, $l_s(q)$, $a_s(q)$ are all defined within the first BZ, while $g_s(\vec{q}+\vec{G}) \neq g_s(\vec{q})$, because $V_{eI}(q) \neq V_{eI}(q+G)$. So, all BZs contribute to the e-p coupling. Typically one has a long-range interaction $V_{eI}(q) = \frac{4\pi e^2}{\epsilon_0} \frac{1}{q^2}$, or take a screened Coulomb interaction (Yukawa potential): $V_{eI}(q) = \frac{4\pi e^2}{\epsilon_0} \frac{1}{q^2 + q_{TF}^2}$. Then the e-p coupling is

$$g_s(q) = -i\, V_{eI}\, q \sqrt{\frac{\hbar}{2M\omega_s(q)}} = i \frac{Ze^2}{\epsilon_0} \frac{q}{q^2 + q_{TF}^2} \sqrt{\frac{\hbar}{2M\omega_s(q)}} \approx i \frac{Ze^2}{\epsilon_0 q} \sqrt{\frac{\hbar}{2M\omega_s(q)}}$$

→ The scattering to $q+G$, i.e., outside the first BZ is called the Umklapp scattering. They are generally small and one often neglects. Often we simply set $G=0$.

→ Another important thing to notice in the e-p coupling is the term $\vec{q} \cdot \vec{\epsilon}_s(\vec{q})$. $\vec{q}$ vector gives the direction of propagation of the phonon while $\vec{\epsilon}_s$ gives its polarization. So, due to the dot product, only longitudinal component contributes (or dominate) in the electron phonon coupling.

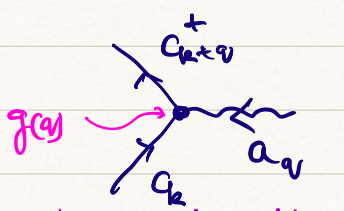
→ Therefore, neglecting the sum over G, and s, we simply write H_{ep} as.

$$H_{ep} = \frac{1}{N}\sum_{G}\sum_{q}\sum_{s} g_s(q+G)\, \underbrace{\rho_{q+G}}\left(a_s(q) + a_s^{\dagger}(-q)\right)$$

$$\Rightarrow \boxed{H_{ep} = \frac{1}{N}\sum_{k,q} g(q)\, c^{\dagger}_{k+q_\sigma} c_{k\sigma}\left(a_q + a^{\dagger}_{-q}\right) \quad --- \quad (20)}$$

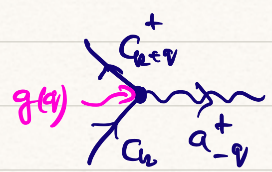
- This is like a single electron scattered (annihilated) from its initial state $|k\rangle$ and goes to another state $|k+q\rangle$, via interacting with a phonon and the scattering amplitude is $g(q)$. The phonon part is not written as a phonon density $a^{\dagger}_q a_q$ as we saw in the electron-electron interaction part, rather its $a^{\dagger}+a$ which is the displacement vector of the lattice. The electrons momentum is absorbed / gained by displacing the nucleons and vice versa. In this scattering process the electron number remains unchanged, but phonon number changes. This is all right as phonons are bosons and hence its number is not conserved. In the electron scattering process, it can create or destroy a phonon of opposite momentum, so, its a coherent superposition of the two cases.

With feynmann diagram, we often define is scattering process as follows



Phonon Absorption

+



Phonon emission.

Its obvious that the above process is possible if $|k\rangle$ state lies below the Fermi level and $|k+q\rangle$ state above it.

- The Full tight binding Hamiltonian for electrons and phonon in a lattice is

$$H = \underbrace{\sum_{k,\sigma} \varepsilon(k)\, c^{\dagger}_{k\sigma} c_{k\sigma}}_{H_0} + \underbrace{\sum_{q,\sigma,\sigma'} v(q)\, c^{\dagger}_{k+q\sigma} c^{\dagger}_{k'-q\sigma'} c_{k'\sigma'} c_{k\sigma}}_{H_{int}}$$

$$+ \underbrace{\sum_{q} \hbar\omega(q)\, a^{\dagger}_{q} a_{-q}}_{H_p} + \underbrace{\sum_{q,k,\sigma} g(q)\, c^{\dagger}_{k+q\sigma} c_{k\sigma} (a_q + a^{\dagger}_{-q})}_{H_{ep}} + \underbrace{\sum_{I} V_{ion}(R_I)}_{\text{constant.}} \quad — (21)$$

where a summation over the phonon polarizations are kept implicit.

→ The H_{int} is the electron-electron coulomb interaction, which we often approximate by the Hubbard model. Hubbard model with electron-phonon coupling term together is often called the Hubbard-Holstein model. In this chapter, we will mainly ignore the electron-electron interaction term.

Frölich Hamiltonian:

Therefore, the problem we set out to solve in the reminder of this chapter is

$$H = \underbrace{\sum_{k,\sigma} \varepsilon(k)\, c^{\dagger}_{k\sigma} c_{k\sigma}}_{H_0} + \underbrace{\sum_{q} \hbar\omega(q)\, a^{\dagger}_{q} a_{-q}}_{H_p}$$

$$\underbrace{+ \sum_{q,k,\sigma} g(q)\, c^{\dagger}_{k+q\sigma} c_{k\sigma}\left(a_q + a^{\dagger}_{-q}\right)}_{H_{ep}} \quad --- \quad (22).$$

The first two terms are individual non-interacting terms, while the last term corresponds to the electron-phonon coupling which makes the problem not exactly solvable. We will try to solve it in the usual methods we have learned so far, i.e., mean-field theory, and perturbation theory. We obtain a gamut of interesting phases and properties that we will discuss now.

Mean field theory: There are two mean field average we can define here. For electrons we define mean field of binear operators, $c^{\dagger}c$, because in the ground state the number of electron remains conserved, as electrons can not be created / destroyed in vacuum. So, the mean field average of electron density operator $\langle c^{\dagger}_{k+q\sigma} c_{k\sigma}\rangle$ gives a number, which does not affect the electronic spectrum. It only changes the phonon spectrum as

$$\sum_{q}\left[W(q)\, \underbrace{a^{\dagger}_{q} a_{q}}_{p^2+x^2} + g(q)\langle S_q\rangle \underbrace{(a_q + a^{\dagger}_{-q})}_{x}\right].$$

Now recall that the first term comes from p^2+x^2 and 2nd term from x. Hence this mean field theory only shifts the equilibrium positions of ion. At $q=0$, this is just a constant shift, which does not change the system due to translational invariance. For $q \neq 0$ one would get position dependent shift of atoms. Of course they are higher energy states as a periodic lattice always has lower energy, at least at low temperature.

Another interesting mean-field theory for phonon that we have not talked about in this course. Because, phonons are bosons and boson number is not conserved in any state, so, one can have mean field values of

$$\langle a_q \rangle = \sqrt{n_q}\, e^{i\theta_q}$$
$$\langle a_q^{+} \rangle = \sqrt{n_q}\, e^{-i\theta_q}.$$

where n_q = number of bosons in the ground state and θ_q is the phase coherence. As we know that the number of particles (probability density) and the phase are canonically conjugate variables and have an uncertainty relation $\Delta n \, \Delta \theta \geq \hbar/2$. So, if we have a state with number of particles completely arbitrary, its phase is completely known. This is what happens in the Bose-Einstein condensate state (and also in superconductivity). Sometimes Bose-Einstein condensate state is also called the superfluid state (where the name came from the liquid He context which goes to a superfluid state at zero temperature instead of a solid).

Coming back to the phonon condensate case, the condensation happens at the lowest possible state which is $q=0$ for the accoustic phonon (for optical phonon, the lower energy state happens at finite q and something interesting can happen). So, the phonon part becomes zero as $\omega_q \to 0$. The electron-phonon part decouples as

$$H_{ep} = \sum_{k,\sigma} g(0) \sqrt{n_0}\, 2\cos\theta_0\, c^{\dagger}_{k\sigma} c_{k\sigma}$$

Therefore, this simply gets absorbed into the chemical potential of the electrons.

Therefore, nothing interesting happens in the mean-field theory for the electron-phonon coupling case. We have to go to the perturbation theory.

Perturbation Theory: A lot of interesting physics happens in the 2nd order perturbation term that we now embark to study. As usual, for a perturbation theory, we need a small parameter.

→ **Weak Electron-Phonon Coupling:** For $|g(q)| \ll |\varepsilon_k|$ and $|g(q)| \ll |\omega(q)|$, we have the electron-phonon coupling term treated as perturbation. Here the first order perturbation term may vanish as will be discussed below. But in the 2nd order perturbation theory, we will obtain corrections to the electronic spectrum $\varepsilon_k \to \varepsilon_k + \Sigma_k^{(e)}$ and also to the phonon spectrum $\omega(q) \to \omega(q) + \Sigma_q^{(b)}$, which includes shift in energies due to real parts of the self-energy as well as life-time / brodening of states due to scattering. Such life-time is used in the calculation of the conductivity in the Drude / Boltzmann transport calculation in the next chapter.

More interestingly, we will see that the 2nd order perturbation theory generates terms which can be singular, causing instabilities such as deformation, Peierls distortion, Jahn-Teller Distortion, Ultrasound attenuation, Kohn anomaly, CDW, superconductivity and many more.

→ Strong electron-phonon coupling: $|g(q)| >> |\varepsilon(k)|$ and/or $|g(q)| >> |\omega(q)|$.

Such a strong electron-phonon coupling limit is rarely happens, especially having a coupling larger than electronic bandwidth is very rare. But mathematically we can solve this problem perturbatively by treating the electronic and phonon parts are perturbation. One of the interesting phenomena that happens in a bound state of electron and phonon - which is called the Polaron.

7.7 Weak Coupling Theory:

In the case of weak electron-phonon coupling, we have the non-interacting Hamiltonian $H = H_e + H_p$, in which the electron and hole parts decoupled. So, the total wavefunction is a product state of the electron's part, which is a Fermi sea, and the phonon part, :

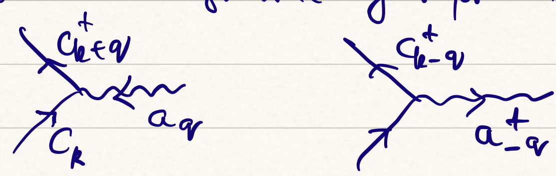
$$|\Psi^{(0)}_{ep}\rangle = \underbrace{\Big(\overbrace{\prod_{k\le k_{F},\sigma} c^{\dagger}_{k\sigma}|0\rangle}^{|k\rangle}\Big)}_{\text{Hartree Fock state (Fermi sea) for fermions}} \otimes \underbrace{\Big(\overbrace{\sum_{\{n_q\}}\prod_{q}(a^{\dagger}_{q})^{n_q}|0\rangle}^{|n_q\rangle}\Big)}_{\text{Hartree Fock state for bosons.}} , \quad \cdots (23)$$

$$= \sum_{\{n_q\}} \prod_{\substack{k\le k_F \\ q\in BZ}} |k, n_q\rangle$$

First order term: The first order correction to this ground state vanishes. Because, Hep term destroys an electron in the Fermi sea and put it outside the Fermi sea, by either absorbing or emitting a phonon. Therefore, it gives an particle hole excited state, and the inner product of the excited state with the ground state is zero.

$$E^{(1)} = \langle\Psi^{(0)}_{ep}|\underbrace{H_{ep}|\Psi^{(0)}_{ep}\rangle}_{|\Psi^{(eh)}_{ep}\rangle\,\text{excited state.}} = 0.$$

This process is diagrammatically represented as



Second order terms!

For simplicity we denote the electron-phonon product state as $|k\, n_q\rangle$ as follows: $|k, n_q\rangle = c_k^{+}(a_q^{+})^{n_q}|0\rangle$ [An electron for in the Fermi sea $k \leq k_F$ and n_q phonon in its $|q\rangle$ state.

$|k \pm q, \bar{n}_q\rangle = c_{k-q}^{+}(a_q^{+})^{n_q \pm 1}|0\rangle$ [An electron is excited from $k \leq k_F$ to above the fermi level to $k \pm q > k_F$ by creating/destroying a phonon for $\bar{n}_q = n_q + 1$ or $n_q - 1$ in the $|q\rangle$ state.

→ we ignore the electron spin σ and the phonon polarization s for simplicity, and we can insert them back in equations when required by demanding spin conservation in a scattering process)

→ we will ignore the Umklapp process and only consider $q \in BZ$, $w_q < w_D$

(A) Then the 2nd order perturbation term becomes:

$$E_k^{(2)} = \sum_{\substack{q \in BZ \\ (w_q \leq w_D \\ k \pm q > k_F)}} \frac{\langle k, n_q | H_{ep} | k \pm q, \bar{n}_q\rangle \langle k \pm q, \bar{n}_q | H_{ep} | k, n_q\rangle}{(\varepsilon_k + w_q n_q) - (\varepsilon_{k \pm q} + w_q \bar{n}_q)}, \quad \forall\, k \leq k_F. \qquad \text{--- (24a)}$$

$k \leq k_F$ $\qquad$ where $n_q - \bar{n}_q = \pm 1$ $\qquad$ $k \pm q$

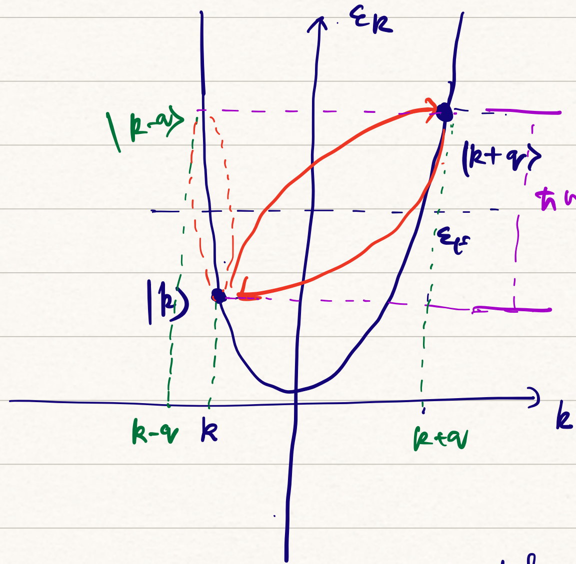
Now, with the modified perturbation theory we learned, we can even obtain off diagonal term as.

(B)
$$\left(H_{eff}^{(2)}\right)_{k, k'} = \frac{1}{2} \sum_{\substack{q, q' \in BZ \\ (k-q,\, k' \pm q' > k_F)}} \langle k, n_q | H_{ep} | k \pm q, \bar{n}_q\rangle \langle k' \pm q', \bar{n}_{q'} | H_{ep} | k', n_{q'}\rangle$$

$k, k' \leq k_F.$

$$\times \left[\frac{1}{(\varepsilon_k + w_q n_q) - (\varepsilon_{k \pm q} + w_q \bar{n}_q)} - \frac{1}{(\varepsilon_{k' \pm q'} + w_q \bar{n}_{q'}) - (\varepsilon_{k'} + w_{q'} n_{q'})} \right] \qquad \text{--- (24b)}.$$

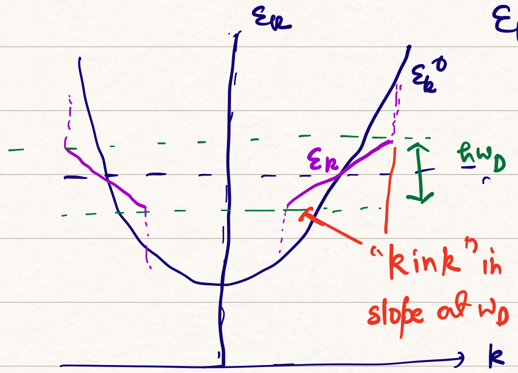
A



(for single phonon absorption, the particle hole excitations occurs within the phonon frequency ω_q, where q corresponds to k to $k \pm q$.).

Here we create a particle-hole excitation by absorbing/emiting a phonon

There are two processes here, phonon absorption/distraction, causing momentum gain to $|k+q\rangle$ and phonon emission/creation, causing momentum loss to $|k-q\rangle$. We have to sum over both such process. This gives an energy correction to the electronic band structure at the same momentum. In analogy with the Fermi liquid theory, we will denote this 2nd order energy correction as "self-energy" correction $\Sigma_k = E_k^{(2)}$. Therefore, after the scattering with phonon, the electronic band structure is renormalized as

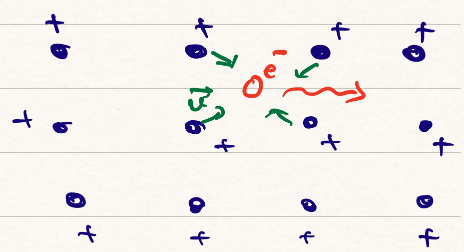


$$\varepsilon_k = \varepsilon_k^0 + \Sigma_k$$
$$\approx Z\,\varepsilon_k^0 \,, \quad \text{where } Z = 1 + \left.\frac{\partial \Sigma}{\partial \varepsilon_k}\right|_{k_F} < 1$$

is the renormalization due to electron-phonon coupling.

- The phonon renormalized electrons are called polarons. Polaron energies are renormalized from the bare electrons with its fermi velocity $v_F \to Z v_F^0$ and effective mass $m^* \to m^* = m_0^*/Z$. The electron–phonon coupling is active for the electrons near the Fermi level with energy $|\varepsilon_k - \varepsilon_F| \leq \hbar\omega_D$. Hence at $|\varepsilon_k - \varepsilon_F| \sim \hbar\omega_D$, on both sides of the Fermi level, the electronic dispersion changes abruptly from the polaron dispersion to the bare electron, and hence shows a "kink" or break in slope in the dispersion. This "kink" is directly observed in angle-dependent photoemission spectroscopy (ARPES) and also in the density of states measured in Scanning Tunneling Microscopy (STM) experiments.

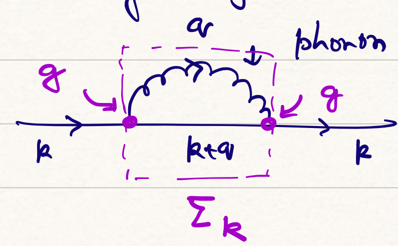
- So polaron is a type of quasiparticle, except here it is accompanied by a cloud of positive ions around it.
As an electron moves, the nearby positive ions are attracted towards, and the entire charge cloud moves together. Because, this charge cloud results in an instantaneous polarization of the lattice (locally), this quasiparticle is called Polaron. This is a fermion.



- The wavefunction of a polaron can be obtained as the first order correction to the Bloch state as

$$|k\rangle^{(1)} = |k\rangle + \sum_q \frac{\langle k\pm q\ \bar{n}_q | H_{ep} | k\ n_q\rangle}{\varepsilon_k - \varepsilon_{k\pm q} - \hbar\omega_q(\bar{n}_q - n_q)} |k\pm q, \bar{n}_q\rangle.$$

• The Feynmann diagram for this 2nd order term is



we can now calculate this self-energy term, by summing over both the phonon emission and absorption terms as

$$\Sigma_k = \sum_q \left[\frac{\left|\langle k-q, n_q+1 | H_{ep} | k, n_q\rangle\right|^2}{\varepsilon_k - \varepsilon_{k-q} - \hbar\omega_q + i\eta} + \frac{\left|\langle k+q, n_q^{-1} | H_{ep} | k, n_q\rangle\right|^2}{\varepsilon_k - \varepsilon_{k+q} - \hbar\omega_q + i\eta} \right] \quad \text{--- (25).}$$

(since Σ_k is a correction to ε_k, the $\langle k| x |k\rangle$ expectation to be omitted above)

As we did for the response function in the linear response theory, for the integral ω_q to converse, we add a complex decay term $i\eta$. This makes the self-energy complex, with its imaginary part corresponding to the inverse of the life time of the electron in its state $|k\rangle$. Using the formula

$$\lim_{\eta\to 0} \frac{1}{x+i\eta} = \mathcal{P}\left(\frac{1}{x}\right) - i\pi\,\delta(x),$$

we obtain the life time of the "quasiparticle" as

$$\frac{1}{\tau_k} = -\,\mathrm{Im}\,\Sigma_k = \frac{\pi}{\hbar}\sum_q \Big[\left|\langle k-q, n_q+1 | H_{ep} | k, n_q\rangle\right|^2 \delta(\varepsilon_k - \varepsilon_{k-q} - \hbar\omega_q) + (q\to -q)\Big]. \quad \text{--- (26).}$$

(The same expression can also be obtained from the Fermi Golden rule).

- The numerator in the self-energy

$$\left| \langle k-q \; n_q+1 \, | H_{ep} | \, k \; n_q \rangle \right|^2 = |g_q|^2 f(\varepsilon_k) \left(1 - f(\varepsilon_{k-q})\right) n_B(\omega_q) \quad \text{--- (27)}$$

implying that the initial state $|k\rangle$ must be filled and the final state $|k-q\rangle$ must be above the Fermi level. The scattering strength is proportional to $|g_q|^2$ as also obtained from the Fermi-Golden rule.

Then, plugging this in eq(25), we obtain terms like $f(\varepsilon_k)\left(\left(1-f(\varepsilon_{k+q})\right) n_B(\omega_q) / (\varepsilon_k - \varepsilon_{k-q} + \hbar\omega_q) + (q \to -q)\right]$. This is expected because particle-hole continuum in the excitation spectrum of a non-interacting electron gas.

- The denominator can be expanded in the small-q region as

$$\varepsilon_{k-q} - \varepsilon_k \approx -\left.\frac{\partial \varepsilon_{k+q}}{\partial k}\right|_{k_F} q \approx -\hbar v_F q.$$

Then the resonance condition yields

$$\varepsilon_k - \varepsilon_{k-q} - \hbar\omega_q \approx \hbar(v_F - v_s) q.$$

Therefore, in metals, where the fermi velocity $v_F \gg v_s$, the renormalization due to electron-phonon coupling is strongly suppressed.

- In the low temperature region, $T \ll T_D$, the lifetime of electrons due to electron-phonon coupling scales as $1/\tau \sim T^3$, which essentially depends on the number of phonon modes excited at a given temperature. This temperature dependence is slower than the electron-electron scattering one $1/\tau \sim T^2$, which eventually dominates at low-temperatures.

- At $T \gg T_D$, when all phonon modes are excited, we get $1/\tau \sim T$. These results are reflected in the resistivity vs. temperature behavior as we will see in next chapter.

- ## Kohn Anomaly, Peierls instability:

In eq (24a), we computed the correction to electron's energy by summing over all the intermediate states produced by the phonon momentum. Now, we want to compute an energy correction to the phonon dispersion by integrating over the electron's states, i.e., integrating out all the intermediate $|k\rangle$ states. Exploiting eq (24a) we get

$$\hbar \omega_q^{(2)} = \Sigma_q^{(\text{phonon})} =$$

$$= \sum_{\substack{k \leq k_F \\ k \pm q \geq k_F}} \frac{\langle k, n_q | H_{ep} | k \pm q, \bar{n}_q \rangle \langle k \pm q, \bar{n}_q | H_{ep} | k, n_q \rangle}{(\varepsilon_k + \omega_q n_q) - (\varepsilon_{k \pm q} + \omega_q \bar{n}_q) + i\eta}$$

$$= |g_q|^2 \sum_k \frac{f(\varepsilon_k)\,(1 - f(\varepsilon_{k+q}))}{\hbar \omega_q + \varepsilon_k - \varepsilon_{k+q} + i\eta} = |g_q|^2 \chi(q, \omega_q). \quad \text{--- (28)}$$

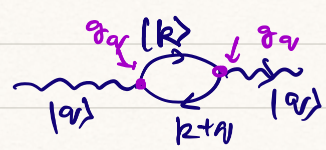
where $\chi(q, \omega_q)$ is the Lindhard susceptibility we defined before.

This gives a complex phonon self-energy to the phonon dispersion as

$$\hbar \omega_p = \hbar \omega_p^{(0)} + |g_q|^2 \chi(q, \omega_q) \quad \text{--- (29)}$$

→ we see that a phonon spectrum creates and destroys particle-hole excitation in the electronic spectrum.

Feynman Diagram is



$\Sigma_p \sim |g_q|^2 \chi(q, \omega_q)$

→ The life time of phonons is obtained by the imaginary part of the self energy

$$\frac{1}{\tau_{ph}} = -\Sigma''_q = \pi |g_q|^2 \chi''(q,\omega), \quad \text{---} (30)$$

which is directly obtained by the particle-hole continuum. Therefore a phonon state can decay into creating a particle-hole continuum and vice versa. The decay of the phonon is called the Ultrasound attenuation.

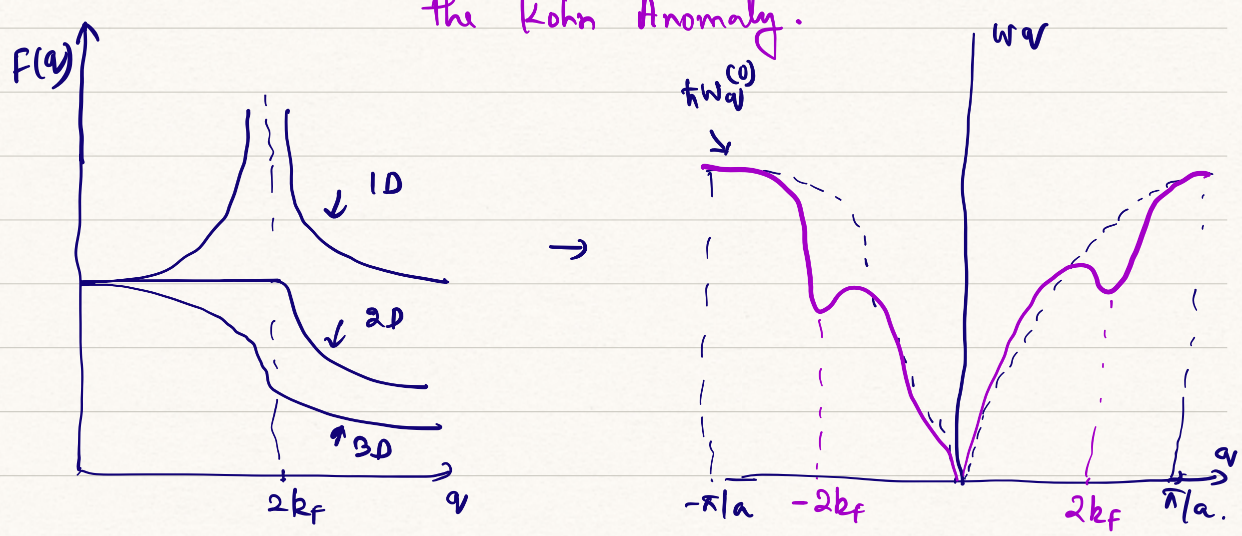
→ Generally, the phonon frequency $\hbar\omega_q << |\varepsilon_{k+q} - \varepsilon_k|$. In the low phonon frequency limit, the Lindhard susceptibility becomes

$$\chi(q, \omega_q \to 0) = -d(0)\, F(q/2k_F) \quad \text{---} (31).$$

where the F-function was introduced earlier:

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \frac{1+x}{1-x} \quad ; \text{ for } x = q/2k_F.$$

This function has a log-singularity at $q = 2k_F$. This singularity translates into a singularity in the phonon dispersion which is called the Kohn Anomaly.



This anomaly is very strong in 1D due to log-divergence in f and causes a distraction or melting of the lattice. In fact, when $2k_F = G/2$, ie, the Kohn anomaly occurs exactly at half of the reciprocal lattice vector (or any integer divison of the reciprocal lattice vector per se), the original peridic lattice becomes doubled in real space (ie, become halved in the momentum space). The new doubled unit cell now contain two atomic sites - One has a Charge Density wave (CDW).

In the reduced Brillouin zone, we can fold the phonon dispersion, which now split into two component (in 1D), and open a gap at the zone boundary $\sim |g_{2k_F}|^2 d(0)$.

The new gapped mode in the phonon spectrum is the optical mode, which is expected as now we have two sublattices in a unit cell.

A similar band gap also opens in the electronic structure at the reduced BZ boundary due to the formation of the CDW state.

In polyacetelene, which is a 1D chain of C-atoms, has such a CDW instability, giving two sublattices in a unit cell - with slightly different bond length. This lattice gives the famous

Su-Schrieffer-Heeger (SSH) model.

- The corresponding CDW instability is called the Peierls instability. To see that we go back to eq (29):

$$\hbar \omega_q = \hbar \omega_q^{(0)} - |g(q)|^2 d(0)\, F(q/2k_F)$$

Now, we see that the RHS vanishes at a critical condition

$$\hbar \omega_q^{(0)} = |g(q)|^2 d(0)\, F(q/2k_F) \quad \text{--- (30)}$$

above which the phonon frequency becomes negative. Negative phonon frequency suggests that the excited states (lattice displacement here) have a lower energy than the original lattice. This means, the lattice structure is unstable to a different lattice where phonon modes will be positive. This is the Peierls instability of a CDW state. (This instability looks very similar to the SDW instability for antiferromagnet obtained for the Hubbard model).

We can in fact obtain a critical temperature for the Peierls instability from eq (30) in 1D. In 1D, the f-function has a logarithmic instability obtained to be

$$F(1) = \log\left(2.28\, \frac{T_F}{T_{CDW}}\right), \quad T_F = \text{Fermi temp.}$$

Substituting this in eq (30) gives

$$\boxed{T_{CDW} = 2.28\, T_F\, e^{-\hbar \omega(2k_F)/|g(2k_F)|^2 d(0)}} \quad \text{--- (32)}$$

(B) Effective electron-electron interaction Hamiltonian $(H_{eff})_{kk'}$

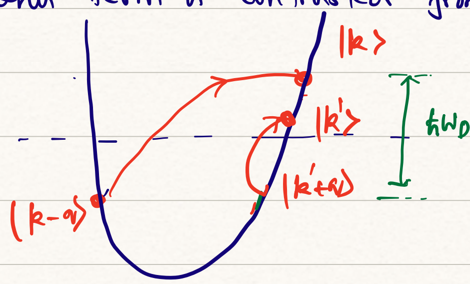
Now we consider the effective Hamiltonian in eq (24b) as

$$\left(H^{(2)}_{eff}\right)_{k,k'} = \frac{1}{2} \sum_{\substack{q,q' \in BZ \\ (k-q,\, k'\pm q' >, k_F)}} \langle k, n_q | H_{ep} | k\pm q, \bar{n}_q \rangle \langle k'\pm q', \bar{n}_{q'} | H_{ep} | k', n_{q'} \rangle$$

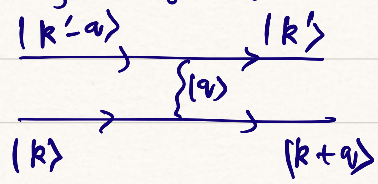
$k, k' \leq k_F.$

$$\times \left[\frac{1}{(\varepsilon_k + \omega_q n_q) - (\varepsilon_{k\pm q} + \omega_q \bar{n}_q)} - \frac{1}{(\varepsilon_{k'\pm q'} + \omega_{q'} \bar{n}_{q'}) - (\varepsilon_{k'} + \omega_{q'} n_{q'})} \right] \quad \text{---(24b)}$$

This term is contrasted from the diagonal term (eq 24a) as



The corresponding Feynman diagram



- In the first process, we have

$$\langle k, n_q | H_{ep} | k\pm q, \bar{n}_q \rangle = \sum_{k_1 q_1} g(q_1) \left[\langle k\, n_q | c^\dagger_{k_1+q} c_{k_1} (a_{q_1} + a^\dagger_{-q_1}) | k\pm q\, \bar{n}_q \rangle \right]$$

In the first case, we have $\bar{n}_q = n_q + 1$, $q_1 = q$, $k_1 = k - q$, giving us a term $\langle k | c^\dagger_k c_{k-q} | k-q \rangle$ after taking the expectation value of the phonon part. In the second term, we get $\bar{n}_q = n_q - 1$, $q_1 = -q$, $k_1 = k + q$, giving us a term $\langle k | c^\dagger_k c_{k+q} | k+q \rangle$. Both terms are related to each other by $q \to -q$, and since $g(-q) = g(q)$, they both correspond to the same term.

The 2nd process works similarly. To have the phonon momentum to be conserved, if the first process corresponds to phonon emission, i.e. $k_1 = k-q$, the 2nd process should be phonon absorption and hence the final state should be $k'+q$.

The product of the two terms gives the matrix element as.

$$\sum_q g(q)\, g(-q) \langle k | c_k^\dagger c_{k-q} | k-q\rangle \langle k-q | c^\dagger_{k'-q} c_{k'} | k'\rangle + h.c.$$

Change of dummy variable $k'-q \to k'$

$$= \sum_q g(q)\, g(-q) \langle k, k' | c_k^\dagger c_{k-q} c_{k'}^\dagger c_{k'+q} | \underbrace{k-q, k'+q}_{|k-q\rangle \otimes |k'+q\rangle} \rangle$$

This is actually a two-body interaction term.

Now, we insert the spin index as $k \to k,\sigma$, $k' \to k'\sigma'$ and do the normal order to obtain

$$= \sum_{q,\sigma,\sigma'} |g(q)|^2 \langle k\sigma, k'\sigma' | c^\dagger_{k\sigma} c^\dagger_{k'\sigma'} c_{k'+q\sigma'} c_{k-q\sigma} | k-q\sigma, k'+q\sigma' \rangle$$

- The electron-phonon propagator is $D_{kk'}(\hbar\omega_q)$

$$\frac{1}{\epsilon_k - \epsilon_{k-q} - \hbar\omega_q} - \frac{1}{\epsilon_{k'} - \epsilon_{k'+q} + \hbar\omega_q} = \frac{2\hbar\omega_q + (\epsilon_{k'} - \epsilon_k) + (\epsilon_{k-q} - \epsilon_{k'+q})}{(\epsilon_k - \epsilon_{k-q} - \hbar\omega_q)(\epsilon_{k'} - \epsilon_{k'+q} + \hbar\omega_q)}.$$

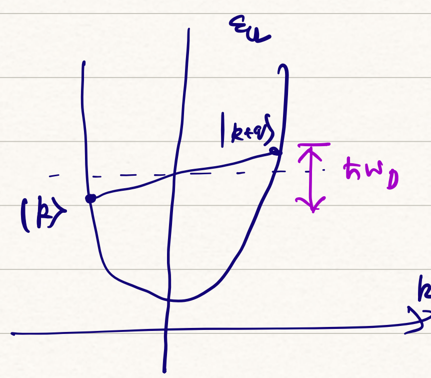
• Combining them together we ~~write~~ obtain a two-body interacting Hamiltonian (without the matrix element):

$$H_{eff} = \sum_{\substack{kk'q \\ \sigma\sigma'}} \underbrace{|g(q)|^2 D_{kk'}(q)}_{V_{kk'}(q) \,=\, \text{interaction strength.}} c^{\dagger}_{k\sigma} c^{\dagger}_{k'\sigma'} c_{k'+q\sigma'} c_{k-q} \quad \text{--}(33).$$

$$+ \sum_{k} \varepsilon_k c^{\dagger}_{k\sigma} c_{k\sigma} + (\text{Phonon part which is now decoupled})$$

This is a generic two-electron interaction mediated by the electron-phonon coupling. There is a special case of $k' = -k$, which is of our interest for superconductivity. Since $\varepsilon_k = \varepsilon_{-k}$, we get

$$\boxed{V_{k,-k}(q) = |g(q)|^2 \frac{2\hbar\omega_q}{(\varepsilon_k - \varepsilon_{k+q})^2 - (\hbar\omega_q)^2}} \quad \text{--}(34).$$



The important property of this interaction term is that for the electrons near the Fermi level, and for $(\varepsilon_k - \varepsilon_{k+q}) \leq \hbar\omega_D$, the above potential becomes Attractive. This attractive potential between electrons produces a two-electron bound state which gives superconductivity.

H.W. (i) Derive the two-body interaction term by the unitary matrix procedure we described in the previous chapter. Here assume the S-operator to be

$$S = \sum_{k,q} g(q)\, c^{+}_{k+q} c_k \left[A_{k,q}\, a_q + B_{k,q}\, a^{+}_{-q} \right]$$

[Determine $A_{k,q}$ & $B_{k,q}$ by requiring that $i[S, H_0] + V = 0$ where $H_0 = H_e + H_p$ and $V = H_{ep}$].

(ii) For the electron-phonon problem, there exist a unitary transformation, which makes $H_{eff} = \tilde{H}_e + H_p + \text{constant}$, where $\tilde{H}_e$ is the non-interacting electron Hamiltonian but for renormalized electrons - called Polarons.

[H.W. Search for 'S' such that $[S, H_{ep}] = \text{constant}$.

(iii) Derive the same eq (33) for the optical phonon (similar for the Einstein phonon).