

TA1 THEORETICAL SOLID STATE PHYSICS WS2016-17

These notes are based on TA 1 Theoretical Solid State Physics at the LMU Munich in Wintersemester 2016-17. A section header with AM-xx indicates that it is based on Ashcroft-Mermin [1] Chapter xx. Warning: unfortunately not everything written is (mathematically) rigorous, and there are incomplete sections.

1. CRYSTAL LATTICES

Definition 1. A *lattice* is a subgroup of \mathbb{R}^d isomorphic to \mathbb{Z}^d and whose \mathbb{R} -span is \mathbb{R}^d . If $d = 3$, a lattice is called a *Bravais lattice*.

Equivalently, a lattice is a set of points

$$\{R\} = \{n_1 a_1 + \dots + n_d a_d\}, \quad a_i \in \mathbb{R}^d \text{ linearly independent (basis) vectors, } n_i \in \mathbb{Z}.$$

The vectors a_i are called *primitive vectors*. A lattice looks the same from any point in the lattice, i.e. all points are equivalent.

Examples.

(1) Simple cubic lattice: \mathbb{Z}^d or $(a\mathbb{Z})^d$, $a > 0$.

(2) Body-centered cubic (BCC): Add to the simple cubic lattice a point in the center of each little cube.

(3) Face-centered cubic (FCC): Add to the simple cubic lattice a point in the face of each little cube. BCC and FCC are more common in nature than the simple cubic.

Definition 2. The *coordination number* of a lattice point is the number of *nearest neighbors* (which are the lattice points closest to the given point) of the point.

For example, the coordination for the simple cubic is 6, for BCC it is 8, and for FCC it is 12.

Remark. We idealize crystals as being infinite, i.e. we ignore surface/boundary effects. Sometimes we will instead deal with a finite subset of a lattice and enforce periodic boundary conditions on everything.

Definition 3. A *primitive unit cell* is a fundamental domain for the action of \mathbb{Z}^d on \mathbb{R}^d , i.e. it is a set of representatives for the orbits, usually required to be connected with some sort of regularity on the boundary. Equivalently, it is a minimum volume cell S such that

$$\bigcup_{n_i \in \mathbb{Z}} (S + n_1 a_1 + \dots + n_d a_d) = \mathbb{R}^d.$$

Note that a primitive unit cell can only contain one lattice point in its interior.

1.1. How to choose a primitive unit cell. Easy method: Simply take $r = t_1 a_1 + \dots + t_d a_d$, $t_i \in [0, 1)$. But this doesn't display the symmetry of the lattice. To fix this, we define the *Wigner-Seitz primitive cell*.

Definition 4. Let $\{R\}$ be a lattice. The *Wigner-Seitz primitive cell* at a lattice point x is

$$WS := \{y \in \mathbb{R}^d : |y - x| \leq |y - \ell| \forall \ell \in \{R\}\},$$

i.e. it is the region closer to x than to any other lattice point. More generally (including non-Bravais), this is called a *Voronoi diagram*.

Construction of the Wigner-Seitz primitive cell in 2 or 3 dimensions is easy: Draw line segments connecting x to its nearest neighbors. Then draw the perpendicular line (or plane in 3D) bisecting each segment. The enclosed region is the Wigner-Seitz cell.

Remark. Physical crystal structure is called *crystal structure* or *lattice with a basis*. Usually this is $\{a_1, \dots, a_n\} + R$, where $\{a_1, \dots, a_n\}$ is the basis with each a_i representing an atom at position a_i , and R is a Bravais lattice. We need lattice with a basis and not just a Bravais lattice if we have two or more different types of atoms. Some other lattices in nature are also lattices with a basis but not Bravais lattices, such as diamond and hexagonal close-packed (hcp). Hcp is one way to close-pack spheres. Fcc

is another way. If we start packing spheres one layer at a time, the difference is in the 3rd and higher layers – whether we place the spheres directly above spheres in the first level (hcp), or directly above gaps in the first level (fcc). At each level 3 or higher we can make a choice, so hcp and fcc are by no means the only possible ways (and other close-packed structures show up in nature).

2. THE RECIPROCAL LATTICE OR FOURIER TRANSFORM OF A LATTICE

Definition 5. Let $\{R\}$ be a (Bravais) lattice. A vector K is in the *reciprocal lattice* $\{K\}$ iff

$$e^{iK \cdot R} = 1, \quad \forall R \in \{R\},$$

i.e. $K \cdot R \in 2\pi\mathbb{Z}$ for all $R \in \{R\}$. In this context, the original lattice $\{R\}$ is called the *direct lattice*.

Proposition 1. *The reciprocal lattice is a (Bravais) lattice.*

Proof. We can construct primitive vectors $\{b_i\}$ for $\{K\}$ such that $b_i \cdot a_j = 2\pi\delta_{ij}$. Take nonzero $b_i \in \text{span}_{\mathbb{R}}(\{a_j\} \setminus a_i)^\perp \simeq \mathbb{R}$, then scale it so that $b_i \cdot a_i = 2\pi$, e.g. $2\pi \cdot \frac{b_i}{|b_i \cdot a_i|}$. Then $\text{span}_{\mathbb{Z}}(b_i) \subseteq \{K\}$, and for any $K \in \{K\}$, we can write

$$K = \sum_{i=1}^d \frac{K \cdot a_i}{2\pi} b_i \in \text{span}_{\mathbb{Z}}(b_i).$$

□

Proposition 2. *The reciprocal of the reciprocal lattice is the direct lattice.*

Proof. We write K' to be the reciprocal of the reciprocal lattice $\{K\}$. Then $\{K'\} \supseteq \{R\}$ by the definition of reciprocal lattice. If $x \notin \{R\}$, then write $x = y a_1 + n_2 a_2 + \dots + n_d a_d$, wlog $y \notin \mathbb{Z}$. But then $b_1 \in K$ and $x \cdot b_1 \notin 2\pi\mathbb{Z}$, so $x \notin \{K'\}$. □

Examples.

- (1) simple cubic with side length a : reciprocal is simple cubic with cell length $\frac{2\pi}{a}$.
- (2) fcc with conventional cubic cell length a : reciprocal is bcc with cell length $\frac{4\pi}{a}$.
- (3) simple hexagonal Bravais lattice: reciprocal also same type (different length)

Proposition 3. *Letting V be the volume of a primitive unit cell in the direct lattice, then $\frac{(2\pi)^d}{V}$ is the volume of a primitive unit cell in the reciprocal lattice.*

Proof. We use the “easy” construction of the primitive unit cell, $\sum t_i a_i$ where $t_i \in [0, 1)$. For d vectors $\{a_i\}$ in \mathbb{R}^d , the volume of the parallelepiped (convex hull) spanned by them is $V = |\det(A^T A)|^{1/2}$, where $A = (a_1 \dots a_d) \in M_{d \times d}$. Let $A = (a_1 \dots a_d)$ be the matrix of primitive vectors of the direct lattice and $B = (b_1 \dots b_d)$ be the matrix of primitive vectors of the reciprocal lattice. Then

$$\text{Vol}(A)^2 \text{Vol}(B)^2 = \det(AA^T BB^T) = (2\pi)^d \det(AB^T) = (2\pi)^{2d},$$

using that $A^T B = 2\pi = B^T A$ since $b_i \cdot a_j = 2\pi\delta_{ij}$. □

Definition 6. The *first Brillouin zone* (1BZ) is the Wigner-Seitz primitive cell of the reciprocal lattice.

In 3D, a *lattice plane* is a plane containing 3 noncollinear lattice points. A *family of lattice planes* is a set of parallel, equally spaced lattice planes whose union covers $\{R\}$.

The reciprocal lattice lets us classify all possible families of lattice planes.

Proposition 4. *There is a bijection between $\{K\}$ and families of lattice planes, such that each K is normal to the family and has magnitude $\frac{2\pi}{d}$, where d is the separation distance between lattice planes.*

Proof. The proof is straightforward. □

Miller indices of lattice planes let us identify a lattice plane by the shortest normal vector in the reciprocal lattice. The notation (hkl) denotes the lattice plane orthogonal to (h, k, ℓ) . Negative numbers sometimes are written with an overbar instead of a negative sign, so we can write e.g. $(4\bar{2}1)$ for the $(4, -2, 1)$ plane.

2.1. Application: X-ray diffraction. TODO

3. NONINTERACTING ELECTRONS IN A PERIODIC LATTICE: BLOCH'S THEOREM

We consider periodic potentials U such that $U(r + R) = U(r)$ for all $R \in \{R\}$. In the independent electron approximation, we look at an effective one electron potential U , so the Schrödinger equation is

$$H\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(r)\right)\psi = E\psi.$$

We call these independent electrons in a periodic potential *Bloch electrons*.

Theorem 1 (Bloch). *Let $H = -\frac{\hbar^2}{2m}\nabla^2 + U(r)$, with $U(r + R) = U(r)$ for all $R \in \{R\}$. Restrict to periodic boundary conditions (called Born-von Karmen boundary conditions),*

$$\psi(r + N_i a_i) = \psi(r), \quad a_i \in \{R\} \text{ primitive vectors}, \quad \prod N_i = N,$$

where N is the number of primitive cells in the crystal. Then the eigenstates ψ_{nk} of H can be chosen to be of the form

$$(3.1) \quad \psi_{nk}(r) = e^{ik \cdot r} u_{nk}(r), \quad u_{nk}(r + R) = u_{nk}(r) \quad \forall R \in \{R\}$$

where $k = \sum \frac{m_i}{N_i} b_i$, $m_i \in \mathbb{Z}$ and b_i the primitive vectors for the reciprocal lattice.

Definition 7. The number $n \in \mathbb{N}$ is called the *band index*. A function of the form (3.1) for any $k \in \mathbb{R}^d$ is called a *Bloch wave*.

Remark. The 1D case is an ODE problem and was proved first by Floquet; it is sometimes called Floquet's theorem.

Theorem 2 (Bloch, alternate form). *An equivalent statement of Bloch's theorem is that the eigenstates can be chosen to satisfy*

$$(3.2) \quad \psi(r + R) = e^{ik \cdot R} \psi(r), \quad \forall R \in \{R\}.$$

Proof (first version, operators). Define the translation operator $T_R f(r) := f(r + R)$. Since H is periodic in $\{R\}$, we have $T_R H = H T_R$. Since $T_R T_{R'} = T_{R+R'}$ commute, then $\{H, T_R\}_{R \in \{R\}}$ all commute. Thus by (TODO simultaneous eigenbasis?? for unbounded...) there is a common eigenbasis for all of them. We are almost done then if we prove the following lemma:

Lemma. *An eigenvector of all the T_R s, $R \in \{R\}$, must be a Bloch wave, i.e. of the form (3.1) or (3.2).*

If ψ is an eigenvector of all the T_R , then write $T_R \psi = \lambda(R) \psi$. The T_R s are unitary so $|\lambda(R)| = 1$. Since $T_R T_{R'} = T_{R+R'}$, then $\lambda(R + R') = \lambda(R) \lambda(R')$. Thus there is some $k \in \mathbb{R}^d$ such that $\lambda(R) = e^{ik \cdot R}$ (for example, write $\lambda(a_i) = e^{2\pi i x_i}$ for the primitive vectors a_i , then compute $\lambda(R)$). Thus

$$\psi(r + R) = e^{ik \cdot R} \psi(r),$$

so the lemma is proven and all that remains to prove the theorem is to show the form of k .

Using (3.2) with the Born-von Karmen boundary conditions yields,

$$\psi_{nk}(r) = \psi_{nk}(r + N_i a_i) = e^{i N_i k \cdot a_i} \psi_{nk}(r),$$

so $e^{N_i k \cdot a_i} = 1$. Writing $k = \sum x_i b_i$ for primitive RL vectors b_i , we need $N_i x_i \in \mathbb{Z}$, so k must be of the form

$$k = \sum_i \frac{m_i}{N_i} b_i, \quad m_i \in \mathbb{Z}.$$

□

Proof (second version, Fourier series). Translation operators take a nice form in Fourier space, which suggests using the Fourier transform. Expand ψ satisfying the Born-von Karmen boundary conditions using Fourier series:

$$\psi(r) = \sum_q c_q e^{iq \cdot r}, \quad q = \sum_i \frac{m_i}{N_i} b_i, \quad m_i \in \mathbb{Z}.$$

The potential is periodic in the direct lattice, so it has Fourier series expansion

$$U(r) = \sum_{K \in \text{RL}} U_K e^{iK \cdot r}, \quad U_K = \frac{1}{|\text{cell}|} \int_{\text{cell}} dr e^{-iK \cdot r} U(r).$$

Now plug the Fourier series into the (time-independent) Schrödinger equation to obtain the Schrödinger equation for a periodic potential in momentum space:

$$\boxed{\text{tise-fourier}} \quad (3.3) \quad \sum_q \frac{\hbar^2 |q|^2}{2m} e^{iq \cdot r} c_q + \sum_{q, K'} c_q U_{K'} e^{i(q+K') \cdot r} = \mathcal{E} \sum_q c_q e^{iq \cdot r}.$$

The potential term can be rewritten by shifting indices as

$$\sum_{q, K'} c_q U_{K'} e^{i(q+K') \cdot r} = \sum_{q, K'} c_{q-K'} U_{K'} e^{iq \cdot r}.$$

Now using orthogonality of $e^{iq \cdot r}$ for different q , we see ^{eqn:tise-fourier} (3.3) holds for each separate q -term, i.e.

$$\boxed{\text{eqn:q}} \quad (3.4) \quad \left(\frac{\hbar^2 |q|^2}{2m} - \mathcal{E} \right) c_q + \sum_{K'} c_{q-K'} U_{K'} = 0.$$

For convenience, we choose a $K \in \text{RL}$ so that $q = k - K$ and $k \in 1\text{BZ}$. Then to make things prettier, we also shift the summation over K' via $K' \mapsto K' - K$. Then ^{eqn:q} (3.4) becomes

$$\boxed{\text{eqn:q2}} \quad (3.5) \quad \left(\frac{\hbar^2 |k - K|^2}{2m} - \mathcal{E} \right) c_{k-K} + \sum_{K'} c_{k-K'} U_{K'-K} = 0.$$

The key point: Given ^{eqn:q2} (3.5) containing a particular c_q , the only other c_q 's involved are $c_{k-K'}, c_{k-K''}, \dots$, i.e. $c_{q'}$ with $q' - k \in \text{RL}$. So for each $k \in 1\text{BZ}$, we can solve the system ^{eqn:q2} (3.5) by setting $c_q = 0$ for $q - k \notin \text{RL}$, and then solving the system ^{eqn:q2} (3.5) for a particular k with K ranging. In general there are an infinite number of solutions, which corresponds to the band index n . These solutions ψ_k are thus Bloch waves,

$$\psi_k(r) = \sum_K c_{k-K} e^{i(k-K) \cdot r} = e^{ik \cdot r} \sum_K c_{k-K} e^{-iK \cdot r}.$$

□

Remark. TODO We never showed H was self-adjoint or had a complete eigenbasis. In the operator proof we need to justify the “simultaneous diagonalization”. In the Fourier series proof we never showed the solutions ψ_k form a basis. A rigorous version can be stated using the “direct integral decomposition” described in ^{RedSimon, GrafETH} [4, 2].

3.1. Fermi surface and density of states.

Definition 8. The *Fermi energy* is the energy of the highest occupied level at absolute zero. When $T = 0$, fermions stack, starting at the lowest energy state and obeying the Pauli exclusion principle.

When the Fermi energy lies at the top of a filled band, we say it lies in the gap, and may draw it in the gap rather than at the top of the band.

Definition 9. A substance is a *insulator* if all bands are either full or empty at $T = 0$; equivalently, if the Fermi energy lies in a gap. A substance is a *metal* if it has a partially filled band; equivalently, if the Fermi energy lies within a band.

Definition 10. Three equivalent definitions of the *density of states* (DOS):

- (1) The DOS is the number of available states per energy interval per volume, i.e.

$$g(E) := \frac{1}{V_0} \frac{dN(E)}{dE},$$

where $N(E)$ is the number of states with energy $\leq E$, and V is the total volume of the system. In other words,

$$(3.6) \quad g(E) dE = \frac{1}{V} \cdot \{\text{number of states with energy in } (E, E + dE)\},$$

where V is the total volume of the system.

- (2) The DOS $g(E)$ is the function that satisfies

$$(3.7) \quad \int_{1\text{BZ}} \frac{d^3 k}{4\pi^3} F(\mathcal{E}(k)) = \int_{\mathbb{R}} d\mathcal{E} g(\mathcal{E}) F(\mathcal{E}).$$

More generally the k -integral normalization is $\frac{q d^d k}{(2\pi)^d}$, where q is the spin.

(3) The DOS is

$$(3.8) \quad g(E) = q \int_{1BZ} \frac{dk}{(2\pi)^d} \delta(E - E(k)),$$

where q is the spin.

TODO proof, spherical coordinates and change of var, $E(k) = E(|k|)$ helps

4. WEAK POTENTIAL

We have the free Hamiltonian $H_0 = -i\hbar\nabla^2$ and consider a weak periodic potential U . Then we do perturbation theory on $H = H_0 + U$. Let $\mathcal{E}_q^0 := \frac{\hbar^2|q|^2}{2m}$. The starting point is [\(3.4\)](#),

$$(4.1) \quad (\mathcal{E}_q^0 - \mathcal{E}) c_q + \sum_{K'} c_{q-K'} U_{K'} = 0, \quad q = \sum_i \frac{m_i}{N_i} b_i, \quad m_i \in \mathbb{Z}.$$

We assume there exists perturbation expansions $c_q = c_q^{(0)} + c_q^{(1)}\varepsilon + \dots$ and $\mathcal{E} = \mathcal{E}^{(0)} + \mathcal{E}^{(1)}\varepsilon + \mathcal{E}^{(2)}\varepsilon^2 + \dots$. Because $U = \sum_K U_K e^{iK \cdot r}$ is small, write $U_K =: \varepsilon W_K$. For the good way to actually compute the energy corrections, see Section [4.3](#). Below we first derive things from perturbation series expansion.

4.1. Nondegenerate perturbation theory. We are able to use nondegenerate perturbation theory *away* from the first Brillouin zone boundary. At the boundary of the first Brillouin zone, we obtain degeneracies.

Plug the perturbation series into [\(4.1\)](#):

$$(\mathcal{E}_q^0 - (\mathcal{E}^{(0)} + \mathcal{E}^{(1)}\varepsilon + \dots)) + \sum_K \varepsilon W_K (c_{q-k}^{(0)} + c_{q-k}^{(1)}\varepsilon + \dots) = 0,$$

and collect terms by power of ε to obtain the energy corrections.

* 0th order:

$$(4.2) \quad (\mathcal{E}_q^0 - \mathcal{E}^{(0)})c_q^{(0)} = 0.$$

So either $c_q^{(0)} = 0$ or $\mathcal{E}^{(0)} = \mathcal{E}_q^0$. For non-degenerate perturbation theory, pick some $q = k$ and assume this is the only q with $\mathcal{E}_q^0 = \mathcal{E}_k^0$. Thus $c_q^{(0)} = 0$ for all $q \neq k$, and we can take $c_k^{(0)} = 1$ which corresponds to the plane wave solution $e^{ik \cdot r}$. Thus this is the same as the free electron case to 0th order as expected. By choosing k we pick which energy and eigenfunction we perturb.

* 1st order:

$$(4.3) \quad (\mathcal{E}_q^0 - \mathcal{E}_k^0)c_q^{(1)} - \mathcal{E}^{(1)}c_q^{(0)} + \sum_K W_K c_{q-K}^{(0)} = 0.$$

By setting $q = k$ and using $c_q^{(0)} = \delta_{qk}$, we obtain

$$\mathcal{E}^{(1)} = W_0.$$

Thus [\(4.3\)](#) becomes

$$(\mathcal{E}_q^0 - \mathcal{E}_k^0)c_q^{(1)} + \sum_{K \neq 0} W_K c_{q-K}^{(0)} = 0,$$

and so

$$c_q^{(1)} = \sum_{K \neq 0} W_K \frac{\delta_{k, q-K}}{\mathcal{E}_k^0 - \mathcal{E}_q^0}.$$

and

$$c_q = \delta_{q,k} + \sum_{K \neq 0} U_K \frac{\delta_{k, q-K}}{\mathcal{E}_k^0 - \mathcal{E}_q^0} + \mathcal{O}(\varepsilon^2).$$

* 2nd order (energy only):

$$(4.4) \quad \text{TODO}$$

By setting $q = k$, we obtain

$$\begin{aligned} \mathcal{E}^{(2)} &= \sum_K W_K c_{q-K}^{(1)} = \sum_K W_K \sum_{K' \neq 0} W_{K'} \frac{\delta_{k, q-K-K'}}{\mathcal{E}_k^0 - \mathcal{E}_{q-K}^0} \\ &= \sum_{K \neq 0} \frac{W_K W_{-K}}{\mathcal{E}_k^0 - \mathcal{E}_{q-K}^0} \end{aligned}$$

and thus

$$(4.5) \quad \mathcal{E} = \mathcal{E}_k^0 + U_0 + \sum_{K \neq 0} \frac{U_K U_{-K}}{\mathcal{E}_k^0 - \mathcal{E}_{q-K}^0} + \mathcal{O}(\varepsilon^3).$$

4.2. **Degenerate perturbation theory.** $\mathcal{E}_{k+K_1}^{(0)} = \dots = \mathcal{E}_{k+K_M}^{(0)}$.

* 0th order: We have $\mathcal{E}^{(0)} = \mathcal{E}_k^0$, but the eigenfunctions are superpositions of $\delta_{k+K_j, q}$, $j = 1, \dots, M$.

* 1st order: We still have (4.3), but to obtain $\mathcal{E}^{(1)}$ we have to solve a system of equations for the coefficients c_{k+K_j} . By setting $q = k + K_j$, we obtain

$$\boxed{\text{eqn:deg1}} \quad (4.6) \quad \underbrace{(\mathcal{E}_{k+K_j}^0 - \mathcal{E}_k^0)}_{=0} c_{k+K_j}^{(0)} - \mathcal{E}^{(1)} c_{k+K_j}^{(0)} + \sum_K W_K c_{k+K_j-K}^{(0)} = 0.$$

This has a nonzero solution for the $c_{k+K_j}^{(0)}$ iff the system matrix

$$(4.7) \quad \begin{pmatrix} \mathcal{E}^{(1)} - W_0 & -W_{K_1-K_2} & \dots & -W_{K_1-K_M} \\ -W_{K_2-K_1} & \mathcal{E}^{(1)} - W_0 & \dots & -W_{K_2-K_M} \\ \vdots & \vdots & \ddots & \vdots \\ -W_{K_M-K_1} & \dots & \dots & \mathcal{E}^{(1)} - W_0 \end{pmatrix}$$

has determinant zero. By multiplying through by $-\varepsilon$, the condition becomes

$$(4.8) \quad \begin{vmatrix} \mathcal{E}_k^0 + U_0 - \mathcal{E} & U_{K_1-K_2} & \dots & U_{K_1-K_M} \\ U_{K_2-K_1} & \mathcal{E}_k^0 + U_0 - \mathcal{E} & \dots & U_{K_2-K_M} \\ \vdots & \vdots & \ddots & \vdots \\ U_{K_M-K_1} & \dots & \dots & \mathcal{E}_k^0 + U_0 - \mathcal{E} \end{vmatrix} = 0.$$

subsec:fast

4.3. **Fast way.**

ak-potential

$$(4.9) \quad H = \sum_q |q\rangle \mathcal{E}_q^0 \langle q| + \sum_{q,k} |q\rangle U_K \langle q-K|.$$

For nondegenerate perturbation theory, the first order energy correction is

$$(4.10) \quad \Delta E_1 = \langle \psi_0 | H - \mathcal{E}_0 | \psi_0 \rangle = U_0,$$

where $\psi_0 = |q\rangle$ forces $K = 0$ hence the U_0 .

For degenerate states $|\psi_1\rangle, \dots, |\psi_m\rangle$, form the matrix

$$(4.11) \quad \begin{pmatrix} \langle \psi_1 | H - \mathcal{E} | \psi_1 \rangle & \langle \psi_1 | H - \mathcal{E} | \psi_2 \rangle & \dots & \langle \psi_1 | H - \mathcal{E} | \psi_M \rangle \\ \langle \psi_2 | H - \mathcal{E} | \psi_1 \rangle & \langle \psi_2 | H - \mathcal{E} | \psi_2 \rangle & \dots & \langle \psi_2 | H - \mathcal{E} | \psi_M \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \psi_M | H - \mathcal{E} | \psi_1 \rangle & \langle \psi_M | H - \mathcal{E} | \psi_2 \rangle & \dots & \langle \psi_M | H - \mathcal{E} | \psi_M \rangle \end{pmatrix}$$

The eigenvalues are the energy corrections, and the eigenvectors are the ‘‘correct’’ initial states to start with.

4.3.1. *Higher degenerate perturbation theory.* For higher orders, simply use the nondegenerate perturbation theory formulas, except in the summations, exclude the unperturbed kets in the same degenerate subspace.

However, if first order degenerate perturbation theory still does not split the degeneracies, then we must do perturbation theory again. We form the matrix

$$\langle \psi | H_{\text{pert}} | \psi' \rangle := \sum_m \frac{\langle \psi | U | \psi_m \rangle \langle \psi_m | U | \psi' \rangle}{E^0 - E_m},$$

and compute eigenvalues and eigenvectors. For example, see Sheet 3 Exercise 2 ($k \cdot p$ theory).

5. TIGHT BINDING MODEL

In the tight-binding model, most of the electrons are held tightly in closed shells. The wavefunctions decay exponentially away from the nucleus sitting at the Bravais lattice vector. We then use atomic wave functions to build our solution.

Our Hamiltonian is

$$(5.1) \quad H = -\frac{\hbar^2}{2m}\Delta + \sum_R U^{\text{at}}(r - R),$$

where U^{at} is the potential for an atom, and we put one atom at each of the N lattice points R .

Let a_n^{at} be the atomic wavefunction for an electron near an isolated atom. Like the hydrogen electrons this decays exponentially. We form *trial wave functions* from a_n^{at} that satisfy Bloch's theorem:

$$(5.2) \quad \Phi_{nk}(r) = \frac{1}{\sqrt{N}} \sum_R e^{ik \cdot R} a_n^{\text{at}}(r - R).$$

But these are not normalized and don't solve the Schrödinger equation. So we take a superposition of these trial states,

$$(5.3) \quad \psi_{nk}(r) = \sum_{n'} C_{nn'} \Phi_{n'k}(r),$$

with $C_{nn'}$ unknown. For ψ_{nk} to be an eigenfunction of H , we need

$$(5.4) \quad \begin{aligned} 0 &= \langle \psi_{nk} | H - \mathcal{E} | \psi_{nk} \rangle \\ \Rightarrow 0 &= \sum_{n'} C_{nn'} \langle \Phi_{n'k} | H - \mathcal{E} | \Phi_{n'k} \rangle \\ \Rightarrow 0 &= \sum_{n'} C_{nn'} (\mathcal{H}_{n'n'} - \mathcal{E}_n \mathcal{S}_{n'n'}), \end{aligned}$$

where

$$\mathcal{H}_{nn'} := \langle \Phi_{nk} | H | \Phi_{n'k} \rangle, \quad \mathcal{S}_{nn'} := \langle \Phi_{nk} | \Phi_{n'k} \rangle.$$

The matrix $\mathcal{S}_{nn'}$ is the *overlap matrix*.

In general, solving (5.4) with m orbitals (i.e. $\psi_{nk} = \sum_{n'=1}^m C_{nn'} \Phi_{n'k}$, an m -fold degeneracy) involves solving a system of m equations, i.e. a $m \times m$ matrix. For example, an orbital is non-degenerate so there is only a single equation, while there are 3 p -orbitals which leads to a 3×3 system. For the transition metals, people in practice solve a 6×6 system for the s and d levels together (“ s - d mixing” or “hybridization”).

5.1. Example: single s orbital and nice lattice. Here we only have a single (spherically-symmetric) atomic wave function $a^{\text{at}}(r)$. TODO

5.2. Lattice with basis.

5.3. Wannier functions. Note that an eigenfunction ψ_{nk} of H is periodic in k in the reciprocal lattice (cf Bloch theorem). Thus if we have all the eigenfunctions (“Bloch functions”) of H , then we can define the *Wannier function* for band n at lattice site R as the (discrete) Fourier transform of $\psi_{nk}(r)$ in variable k , i.e.

$$(5.5) \quad w_n(R, r) := \frac{1}{\sqrt{N}} \sum_{k \in \text{1BZ}} e^{-ik \cdot R} \psi_{nk}(r).$$

There is also Fourier inversion,

$$\frac{1}{\sqrt{N}} \sum_R w_n(R, r) e^{ik \cdot R} = \psi_{nk}(r).$$

The Wannier functions are orthogonal in n and R unlike the atomic functions Φ_{nk} , which makes them a nice orthogonal basis.

6. FREE FERMI GAS AND SOMMERFELD EXPANSION (AM-2)

Apply Pauli exclusion principle \Rightarrow replace Maxwell-Boltzmann distribution with the Fermi-Dirac distribution for electron occupation number,

$$f(v) := \frac{m^3}{\hbar^3} \frac{1}{4\pi^2} \cdot \frac{1}{e^{(\frac{1}{2}mv^2 - k_B T_0)/(k_B T)} + 1}$$

$$n \equiv \frac{N}{V} = \int dv f(v).$$

6.1. Ground state of electron gas at zero temperature. Independent electron approximation, solve particle in a box $[0, L]^d$ of volume $V = L^d$:

$$-\frac{\hbar^2}{2m} \Delta \psi(r) = \mathcal{E} \psi(r),$$

with periodic boundary conditions $\psi(r + L\hat{r}) = \psi(r)$, $\hat{r} \in \{\hat{x}, \hat{y}, \hat{z}\}$. Results:

$$(6.1) \quad \psi_k(r) = \frac{1}{\sqrt{V}} e^{ik \cdot r}$$

$$(6.2) \quad \mathcal{E}(k) = \frac{\hbar^2 k^2}{2m}, \quad k \in \frac{2\pi}{L} \mathbb{Z}^d$$

Other important results:

* k -space volume Ω contains $\frac{\Omega}{(2\pi/L)^d} = \frac{\Omega V}{(2\pi)^d}$ allowed values of k ,

$$\Delta k = \frac{V}{(2\pi)^d}.$$

* Build ground state of N electrons by putting electrons in lowest free state, with spin. Fermi sphere: filled states, radius k_F .

$$N = 2 \cdot \frac{V}{(2\pi)^d} \cdot \nu_d k_F^d, \quad \nu_d := \text{volume of unit ball in } \mathbb{R}^d.$$

In \mathbb{R}^3 , determine k_F by

$$(6.3) \quad \frac{N}{V} \equiv n = \frac{k_F^3}{3\pi^2}.$$

* Fermi momentum $p_F := \hbar k_F$, Fermi energy $\mathcal{E}_F := \hbar^2 k_F^2 / (2m)$, Fermi velocity $v_F := p_F / m$.

* Using $E = \frac{\hbar^2 k^2}{2m}$, DoS is

$$(6.4) \quad g(E) = \begin{cases} \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2mE}{\hbar^2}}, & E > 0 \\ 0, & E < 0 \end{cases}.$$

* Total energy of ground state

$$E = 2 \sum_{k < k_F} \frac{\hbar^2 k^2}{2m}$$

Approximate by integral: Use $\Delta k = (2\pi)^d / V$ volume per allowed k :

$$(6.5) \quad \lim_{V \rightarrow \infty} \frac{1}{V} \sum_k F(k) = \lim_{V \rightarrow \infty} \frac{1}{(2\pi)^d} \sum_k F(k) \Delta k = \int \frac{dk}{(2\pi)^d} F(k).$$

The domain of integration is the range of k in the original \sum_k , as $V \rightarrow \infty$. Thus

$$(6.6) \quad \frac{E}{V} = \frac{2}{(2\pi)^d} \int_{k < k_F} d^d k \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \kappa_d}{(2\pi)^d m} \frac{k_F^{d+2}}{(d+2)}, \quad \kappa_d := \text{surface area of } \mathbb{S}^{d-1} \subset \mathbb{R}^d$$

$$(6.7) \quad \stackrel{\mathbb{R}^3}{=} \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m}$$

* In \mathbb{R}^3 : Since $\frac{N}{V} = \frac{k_F^3}{3\pi^2}$, obtain

$$(6.8) \quad \frac{E}{N} = \frac{3}{5} \mathcal{E}_F = \frac{3}{5} k_B T_F, \quad T_F := \frac{\mathcal{E}_F}{k_B}.$$

Compare with classical gas $\frac{3}{2} k_B T$. Also compute pressure $P := -(\partial E / \partial V)_N = \frac{2}{3} \frac{E}{V}$ and compressibility K via $\frac{1}{K} := -V \frac{\partial P}{\partial V} = \frac{2}{3} n \mathcal{E}_F$.

6.2. Fermi-Dirac distribution: nonzero temperature. Statistical mechanics: N particle system in thermal equilibrium at temperature T ,

$$\Pr(E) = \frac{e^{-E/(k_B T)}}{\sum e^{-E_\alpha/(k_B T)}} = \frac{e^{-E/(k_B T)}}{\mathcal{Z}}$$

$$f_i^N = \sum_{\substack{\alpha \text{ s.t.} \\ e^- \text{ in } i}} \Pr(E_\alpha) \quad (\text{probability that 1-electron state } i \text{ is filled})$$

Turns out

$$(6.9) \quad f_i^N = \frac{1}{e^{(\mathcal{E}_i - \mu)/(k_B T)} + 1}.$$

Define the *Fermi function*

$$(6.10) \quad f(\varepsilon) := \frac{1}{e^{(\varepsilon - \mu)/(k_B T)} + 1}.$$

To agree with $T = 0$ results from before, need

$$(6.11) \quad \lim_{T \rightarrow 0} \mu = \mathcal{E}_F.$$

In fact for metals, $\mu \approx \mathcal{E}_F$ up to at least room temperature.

6.2.1. *Computing specific heat.*

$$(6.12) \quad C_V := \frac{T}{V} \left(\frac{\partial S}{\partial T} \right)_V \equiv \frac{1}{V} \left(\frac{\partial U}{\partial T} \right)_V$$

Use $U = 2 \sum_k \mathcal{E}(k) f(\mathcal{E}(k))$, so

$$(6.13) \quad u := \frac{U}{V} = \int \frac{dk}{4\pi^3} \mathcal{E}(k) f(\mathcal{E}(k)) = \int_{\mathbb{R}} d\mathcal{E} g(\mathcal{E}) \mathcal{E} f(\mathcal{E})$$

$$(6.14) \quad n := \frac{N}{V} = \int \frac{dk}{4\pi^3} f(\mathcal{E}(k)) = \int_{\mathbb{R}} d\mathcal{E} g(\mathcal{E}) f(\mathcal{E}),$$

where $g(\mathcal{E})$ is the density of states.

6.3. Sommerfeld expansion. For metals usually any temperatures we care about satisfy $T \ll T_F$, where T_F is the Fermi temperature $T_F := \mathcal{E}_F/k_B$. In this regime, for H smooth at μ with $H \rightarrow 0$ as $\mathcal{E} \rightarrow -\infty$ and polynomially bounded as $\mathcal{E} \rightarrow \infty$, we have the *Sommerfeld expansion*,

$$(6.15) \quad \int_{-\infty}^{\infty} H(\mathcal{E}) f(\mathcal{E}) d\mathcal{E} = \int_{-\infty}^{\mu} H(\mathcal{E}) d\mathcal{E} + \frac{\pi^2}{6} (k_B T)^2 H'(\mu) + \frac{7\pi^4}{360} (k_B T)^4 H'''(\mu) + O(k_B T/\mu)^6,$$

where $f(\mathcal{E}) = \frac{1}{e^{(\mathcal{E} - \mu)/(k_B T)} + 1}$ the Fermi function.

Proof. First integrate by parts to obtain

$$\int_{-\infty}^{\infty} H(\mathcal{E}) f(\mathcal{E}) d\mathcal{E} = \int_{-\infty}^{\infty} K(\mathcal{E}) \left(-\frac{\partial f}{\partial \mathcal{E}} \right) d\mathcal{E},$$

where $K(\mathcal{E}) := \int_{-\infty}^{\mathcal{E}} d\mathcal{E}' H(\mathcal{E}')$. Then Taylor expand $K(\mathcal{E})$ at $\mathcal{E} = \mu$ and note that f is even to obtain [\(6.15\)](#). □

To calculate C_V , we apply the Sommerfeld expansion to [\(6.13\)](#) and [\(6.14\)](#): Up to order T^2 , $\mu \approx \mathcal{E}_F$ so we replace μ by \mathcal{E}_F in terms $\mathcal{O}(T^2)$ and eventually¹ obtain

$$(6.16) \quad C_V \equiv \left(\frac{\partial u}{\partial T} \right)_n = \frac{\pi^2}{3} k_B^2 T g(\mathcal{E}_F)$$

$$(6.17) \quad \stackrel{\text{free } e^-}{=} \frac{\pi^2}{2} \frac{k_B T}{\mathcal{E}_F} n k_B$$

6.4. **Sommerfeld conduction in metals.**

¹[\[1\]](#) pg. 46

7. CLASSICAL LATTICE DYNAMICS (AM, MARDER)

Phonons are traveling waves in a crystal that help describe the vibrating modes.

We pretend a crystal lattice is a bunch of masses connected by springs. So instead of having atoms fixed at points of a Bravais lattice, we now allow the atoms to vary from their equilibrium positions a little.

TODO Harmonic approximation to potential, what is phonon

7.1. One dimension. Recall springs in 1D: We have a chain of N ions each of mass M , equilibrium distance a , connected by springs with spring constant K , and periodic boundary conditions.

- * Let u^ℓ be the displacement of the ℓ th ion, $\ell \in [0, \dots, N-1]$.
- * System of equations:

$$M\ddot{u}^\ell = K(u^{\ell+1} - u^\ell) + K(u^{\ell-1} - u^\ell)$$

- * Ansatz

$$u^\ell = \varepsilon e^{ik\ell a - i\omega t}$$

- * Periodic boundary condition $u^N = u^0$ implies

$$k \in \frac{2\pi}{Na} \mathbb{Z} =: \frac{2\pi}{L} \mathbb{Z}.$$

- * Plug in ansatz and solve for ω to get dispersion relation

$$\omega = 2\sqrt{\frac{K}{M}} |\sin(ka/2)|.$$

Remark. For small k , ω is roughly linear. The solution is periodic with period $\frac{2\pi}{a}$ as expected since the physical space is periodic with period a , and $[-\frac{\pi}{a}, \frac{\pi}{a}]$ is called the Brillouin zone.

7.2. One dimension: lattice with basis. Now there is a chain with alternating atoms of mass M_1 and M_2 .

- * System of equations:

$$\begin{aligned} M_1 \ddot{u}_1^\ell &= K(u_2^\ell - 2u_1^\ell + u_2^{\ell-1}) \\ M_2 \ddot{u}_2^\ell &= K(u_1^{\ell+1} - 2u_2^\ell + u_1^\ell) \end{aligned}$$

- * Ansatz

$$u_j^\ell = \varepsilon_j e^{ik\ell a - i\omega t}$$

- * Periodic boundary condition $u_2^N = u_1^0$ implies as before

$$k \in \frac{2\pi}{Na} \mathbb{Z} =: \frac{2\pi}{L} \mathbb{Z}.$$

- * Plug in ansatz to get

$$\begin{pmatrix} \omega^2 M_1 - 2K & K + K e^{-ika} \\ K + K e^{ika} & \omega^2 M_2 - 2K \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \end{pmatrix} = 0$$

Set determinant equal to zero and solve for ω . There are two solutions, called *branches*:

$$\omega = \sqrt{K} \sqrt{\frac{M_1 + M_2 \pm \sqrt{M_1^2 + 2M_1 M_2 \cos(ka) + M_2^2}}{M_1 M_2}}.$$

- * Once branch is linear near $k = 0$: *acoustic branch* (atoms move together), the other is higher frequencies: *optical branch* (atoms vibrate out of phase).

TODO picture

7.3. Three dimensions. Setting: We have a crystal lattice with equilibrium positions of ions $R = (R^1, \dots, R^N)$ and displacement vectors $u = (u^1, \dots, u^N)$. We expand the energy $\mathcal{E} = \mathcal{E}(u^1, \dots, u^N)$ in a Taylor series, remembering that each u^j is $(u_\alpha^j)_{\alpha=1}^3$.

$$(7.1) \quad \mathcal{E}(u) = \sum_{|\gamma| \leq k} \frac{\partial^\gamma \mathcal{E}(0)}{\gamma!} u^\gamma = \mathcal{E}_C + \sum_{\alpha, \ell} \frac{\partial \mathcal{E}}{\partial u_\alpha^\ell}(0) u_\alpha^\ell + \frac{1}{2} \sum_{\substack{\alpha, \beta \\ \ell, \ell'}} u_\alpha^\ell \Phi_{\alpha\beta}^{\ell\ell'}(0) u_\beta^{\ell'} + O(u^3)$$

$$(7.2) \quad = \mathcal{E}_C + u \cdot \nabla_u \mathcal{E}(0) + u \cdot \Phi(0) \cdot u + O(u^3),$$

where

$$(7.3) \quad \Phi_{\alpha\beta}^{\ell\ell'} = \frac{\partial^2 \mathcal{E}}{\partial u_\alpha^\ell \partial u_\beta^{\ell'}}$$

is the $3N \times 3N$ Hessian matrix. But in fact $\nabla_u \mathcal{E}(0) = 0$ since this is the equilibrium state. In the harmonic or quadratic approximation, we drop all terms higher than quadratic, so ignoring the constant \mathcal{E}_C , we use

$$(7.4) \quad \mathcal{E}(u) = u \cdot \Phi(0) \cdot u = \frac{1}{2} \sum_{\substack{\alpha, \beta \\ \ell, \ell'}} u_\alpha^\ell \Phi_{\alpha\beta}^{\ell\ell'}(0) u_\beta^{\ell'}.$$

The force on ion ℓ is conservative and given by the negative gradient of the potential, $-\frac{\partial \mathcal{E}}{\partial u^\ell} = -\nabla_{u^\ell} \mathcal{E}(u)$. Thus we obtain

* System of $3N$ equations:

$$M\ddot{u}^\ell = -\sum_{\ell'} \Phi^{\ell\ell'}(0) u^{\ell'},$$

where $\Phi^{\ell\ell'} = (\Phi^{\ell\ell'})_{\alpha\beta}$ is the 3×3 matrix for u^ℓ and $u^{\ell'}$ contained in the Hessian.

* Ansatz:

$$u^\ell = \varepsilon e^{ik \cdot R^\ell - i\omega t}, \quad \varepsilon \in \mathbb{R}^3 \text{ (the polarization)}$$

* Periodic boundary conditions ???

$$k = \frac{n_1}{N_1} b_1 + \frac{n_2}{N_2} b_2 + \frac{n_3}{N_3} b_3, \quad n_1, n_2, n_3 \in \mathbb{Z}.$$

* Plug in ansatz:

$$\begin{aligned} M\omega^2 \varepsilon &= \sum_{\ell'} \Phi^{\ell\ell'} e^{ik(R^\ell - R^{\ell'})} \varepsilon \\ &= D(k) \varepsilon, \quad D(k) := \sum_{\ell'} e^{ik(R^\ell - R^{\ell'})} \Phi^{\ell\ell'}. \end{aligned}$$

The 3×3 matrix $D(k)$ is called the *dynamical matrix*. It is independent of ℓ because of Bravais lattice structure and periodic boundary conditions: everything just depends on the difference $R^\ell - R^{\ell'}$.

* More dynamical matrix: Because $D(k)$ is independent of ℓ , we can take $R^\ell = 0$. Additionally, we have symmetry conditions: $D(0) = \sum_{\ell'} \Phi^{\ell\ell'} = 0$, and $D(k) = D(-k)$. Thus

$$\begin{aligned} D(k) &= \sum_{\ell'} \Phi^{\ell\ell'}(0) e^{-ikR^{\ell'}} \\ &= \frac{1}{2} \sum_{\ell'} \Phi^{\ell\ell'}(0) (e^{-ikR^{\ell'}} + e^{ikR^{\ell'}} - 2) = \sum_{\ell'} \Phi^{\ell\ell'}(0) [\cos(k \cdot R^{\ell'}) - 1] \\ &= -2 \sum_{\ell'} \Phi^{\ell\ell'} \sin^2\left(\frac{1}{2} k \cdot R^{\ell'}\right). \end{aligned}$$

* Since $D(k)$ is real and symmetric, it has a complete ON eigenbasis. Let $\varepsilon_{k\nu}$, $\nu = 1, 2, 3$ be the ON eigenvectors and λ_ν the corresponding eigenvalues. Then

$$(7.5) \quad \omega_\nu^2(k) = \frac{\lambda_\nu(k)}{M}.$$

If we had a perfect crystal invariant under all rotations, then the three polarization vectors $\varepsilon_{k\nu}$ would split into one longitudinal mode (ε parallel to k) and two transverse (ε orthogonal to k). But roughly, the idea is one longitudinal and two transverse modes.

* Can always take k in 1BZ.

* All modes are acoustic: Approximate $\sin^2(\frac{1}{2} k \cdot R^{\ell'}) \approx (\frac{1}{2} k \cdot R^{\ell'})^2$, so that

$$D(k) \approx -\frac{k^2}{2} \sum_{\ell'} (\hat{k} \cdot R^{\ell'})^2 \Phi^{\ell\ell'}, \quad \hat{k} := \frac{k}{|k|},$$

and then $\omega_\nu(k) = c_\nu(\hat{k})k$.

Remark. Letting k range in the Brillouin zone exhausts all normal modes. This differs from the electron case where there were infinitely many possible normal modes.

7.4. **3D lattice with basis.** As in the 1D case, adding a lattice with basis allows for optical modes. The mathematical formulation gets a bit complicated because of the indexing. For each k , there are $3p$ normal modes, where p is the number of ions in the basis: 3 are acoustic and $3(p-1)$ are optical.

8. QUANTUM LATTICE DYNAMICS (AM-23)

The *specific heat* c is the heat required per mass to raise the temperature by 1 Celsius (Kelvin), i.e.

$$\Delta Q = cm\Delta T.$$

For us we follow [1] and normalize by the volume (e.g. of a primitive cell) instead,

$$c_v := \frac{1}{V} \left(\frac{dQ}{dT} \right)_V,$$

where $dQ := dU - dW$ is the heat intake of the system. (Both dQ and dW depend on more than just final states, hence the different d symbol.) For constant volume $dW = 0$, and we are just left with internal energy term², thus obtaining

$$(8.1) \quad c_v = \frac{\partial u}{\partial T} \equiv \frac{1}{V} \frac{\partial U}{\partial T},$$

where $u := U/V$ is the energy density.

The specific heat (at constant volume) of solids at room temperature and higher is generally well-described by the classical *Dulong-Petit law* from 1819,

$$(8.2) \quad c_v = 3nk_B,$$

which is *independent* of temperature T . We will derive this law from lattice vibrations in the high temperature limit. For low temperature, quantum statistics are required and the specific heat depends on T .

8.1. Phonon specific heat.

eqn:cv

$$(8.3) \quad c_v = \left(\frac{\partial u}{\partial T} \right)_V = \frac{1}{V} \sum_{k,s} \frac{\partial}{\partial T} \frac{\hbar\omega_s(k)}{e^{\beta\hbar\omega_s(k)} - 1},$$

where the sum is over k in the Brillouin zone, and branches s .

* High temperature: $k_B T / \hbar \gg \omega$, recover classical Dulong and Petit law. Then $\beta\hbar\omega_s(k) \ll 1$, so

$$c_v \approx \frac{1}{V} \sum_{k,s} \frac{\partial}{\partial T} \frac{\hbar\omega_s(k)}{\beta\hbar\omega_s(k)} = \frac{3Nk_B}{V},$$

where $3N$ is the number of normal modes. (3 dimensions: $s = 1, 2, 3$ and k ranges through N points in the Brillouin zone)

* Low temperature: First for a large crystal, rewrite c_v as an integral:

$$(8.4) \quad c_v = \frac{\partial}{\partial T} \sum_s \int_{1BZ} \frac{dk}{(2\pi)^3} \frac{\hbar\omega_s(k)}{e^{\beta\hbar\omega_s(k)} - 1}.$$

If $k_B T / \hbar \ll \omega$, i.e. $\hbar\omega_s(k) \gg k_B T$ then the integrand decays exponentially. But for the acoustic branches with $\omega_s(k) \rightarrow 0$ as $k \rightarrow 0$ this is never satisfied. Thus we can assume:

- Ignore optical modes.
- Assume k is very small (else exponential). In this regime $\omega = c_s(\hat{k})k$.
- Integrate over \mathbb{R}^d instead of just $1BZ$. (Exponential decay for k away from zero.)

Result:

$$(8.5) \quad c_v = \frac{\partial}{\partial T} \sum_{s \text{ acoustic}} \int_{\mathbb{R}^3} \frac{dk}{(2\pi)^3} \frac{\hbar c_s(\hat{k})k}{e^{\hbar c_s(\hat{k})k / (k_B T)} - 1}.$$

Can evaluate this in polar coordinates $dk = k^2 dk d\Omega$ to obtain

$$c_v \approx \frac{2\pi^2}{5} k_B \left(\frac{k_B T}{\hbar c} \right)^3.$$

In fact

$$\lim_{T \searrow 0} \frac{c_v}{T^3} = \frac{2\pi^2}{5} \frac{k_B^4}{\hbar^3 c^3}$$

* Key: Low T : specific heat from lattice vibrations $\sim T^3$.

²See Kardar Statistical Physics of Particles pg.8

Remark. At low T , the *electronic* contribution to c_V is proportional to T , dominating the behavior of c_V there. We derive this heuristically by applying Dulong-Petit but noting that *only a small fraction of the electrons can contribute to specific heat*.

In other words, most of the electrons don't change energy as the temperature changes in $\frac{\partial U}{\partial T}$.

$$k_B T \ll \mathcal{E}_F.$$

The only electrons that can contribute are those in which has width $\approx k_B T$ and contains $\approx k_B T / \mu$???. Thus we obtain

$$(8.6) \quad c_V^{\text{el}} \approx k_B T \cdot (3nk_B) = ?3nk_B^2 \frac{T}{\mathcal{E}_F}.$$

More rigorously, the number of particles in an interval $\Delta \mathcal{E}$ is

$$2g(\mathcal{E})f(\mathcal{E})\Delta \mathcal{E}$$

8.2. Debye and Einstein models. Need intermediate-temperature range: Dulong and Petit bad below room temperature, but low-temperature limit needs very low T .

(1) Debye: There are only 3 branches and they are all the same $\omega = ck$.

- * \int_{1BZ} in (8.4) now $\int_{|k| < k_D}$, where k_D chosen so ball contains N (number of ions in crystal) wavevectors k
- * $4\pi k_D^3 / 3 = (2\pi)^3 / V \cdot N$, so

$$n \equiv \frac{N}{V} = \frac{k_D^3}{6\pi^2}.$$

- * From (8.4) obtain (like in low T limit but simpler)

$$(8.7) \quad c_v = \frac{\partial}{\partial T} \frac{3\hbar c}{2\pi^2} \int_0^{k_D} \frac{k^3}{e^{\beta\hbar ck} - 1} dk$$

$$(8.8) \quad c_v = 9nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad x = \hbar ck / (k_B T).$$

- * Density n in Debye (8.8) is number of primitive cells per unit volume (i.e. just ignore that there are p things in each cell and count the cells as usual)
- * Define *Debye frequency* $\omega_D = k_D c$ and *Debye temperature* Θ_D by $k_B \Theta_D = \hbar \omega_D = \hbar ck_D$. Can rewrite (8.8) in terms of Θ_D only, then match Θ_D to experiments. For agreeing at low T , get

$$c_v = \frac{12\pi^4}{5} nk_B \left(\frac{T}{\Theta_D} \right)^3 \approx 234 \left(\frac{T}{\Theta_D} \right)^3 nk_B.$$

- * For $T \gg \Theta_D$, let x be small and get Dulong and Petit result. So Θ_D can separate quantum from classical regime in some sense.

(2) Einstein: Polyatomic basis. The 3 acoustic branches are all the same $\omega = ck$, and the $3(p-1)$ optical branches are constant $\omega = \omega_E$.

- * (8.8) is the contribution from acoustic branches
- * Each optical branch contributes to thermal energy density (just plug into (8.3) before the $\partial/\partial T$)

$$\frac{n\hbar\omega_E}{e^{\hbar\omega_E/(k_B T)} - 1}$$

so letting $\eta = 3(p-1)$ the number of optical branches,

$$(8.9) \quad c_v^{\text{optical}} = \eta nk_B \frac{\left(\frac{\hbar\omega_E}{k_B T} \right)^2 e^{\hbar\omega_E/(k_B T)}}{(e^{\hbar\omega_E/(k_B T)} - 1)^2}$$

- * For $T \gg \Theta_E = \hbar\omega_E/k_B$, then this is just ηnk_B , or k_B/V per optical mode as in Dulong and Petit.
- * For $T \ll \Theta_E$, optical modes don't contribute much. Difficult to excite optical modes at low T .

(3) Actual heat capacity

- * For metals $\approx c_v^{\text{phonon}} + c_v^{\text{elec}} = AT^3 + \gamma T$. For low T (like 10K), linear term dominates.
- * For thermal insulators $\approx c_v^{\text{phonon}} \sim T^3$.

8.3. Phonon density of states. Just like electronic density of states, but ω instead of E , no q for spin, and we sum over s the branches,

$$(8.10) \quad g(\omega) = \sum_s \int \frac{d^3k}{(2\pi)^3} \delta(\omega - \omega_s(k))$$

* Debye:

$$(8.11) \quad g_D(\omega) = \begin{cases} \frac{3}{2\pi^2} \frac{\omega^2}{c^3}, & \omega < \omega_D = k_D c \\ 0, & \omega > \omega_D \end{cases}.$$

Ok for $\omega \approx 0$ so low T ok. Debye frequency ω_D chosen so $\int g_D(\omega)$ is correct so recover Dulong and Petit at high T .

* Einstein: For an optical branch, get contribution

$$(8.12) \quad g_E^{\text{op}}(\omega) = n \delta(\omega - \omega_E).$$

8.4. Second quantization of phonons.

8.5. Anharmonic effects. Anharmonic effects are the higher than quadratic terms. They account for:

- * high temperature specific heat does not follow the Dulong-Petit law
- * thermal expansion
- * finite thermal conductivity

Usually we only keep cubic and sometimes quartic terms.

8.5.1. Thermal expansion, Grüneisen parameter. The *coefficient of thermal expansion*, which is the amount of expansion per temperature, satisfies

$$(8.13) \quad \alpha = \frac{\gamma c_v}{3B},$$

where γ is the *Grüneisen parameter* and B is the Bulk modulus,

$$\gamma := \frac{\sum_{k,s} \gamma_{ks} c_{vs}(k)}{\sum_{k,s} c_{vs}(k)}, \quad c_{vs}(k) := \frac{\hbar \omega_s(k)}{V} \frac{\partial}{\partial T} n_s(k)$$

$$B := -V \left(\frac{\partial P}{\partial V} \right)_T$$

Each γ_{ks} is called the *Grüneisen parameter* for the mode ks and is defined by

$$(8.14) \quad \gamma_{ks} := -\frac{V}{\omega_s(k)} \frac{\partial \omega_s(k)}{\partial V} = -\frac{\partial(\log \omega_s(k))}{\partial(\log V)}.$$

The quantity $c_{vs}(k)$ is just the contribution of the mode indexed by k, s to the specific heat.

We can see γ tends to different constants as $T \rightarrow 0$ and $T \gg \Theta_D$, and so α behaves like c_v , i.e.

$$(8.15) \quad \alpha^{\text{ph}} \sim \begin{cases} T^3, & T \rightarrow 0 \\ \text{constant}, & T \gg \Theta_D \end{cases}.$$

For metals,

$$\alpha = \frac{1}{3B} (\gamma c_v^{\text{ph}} + \frac{2}{3} c_v^{\text{el}}),$$

where c_v^{el} is the electronic contribution to specific heat and goes like T as $T \rightarrow 0$. Thus as $T \rightarrow 0$, for metals $\alpha \sim T$, while for insulators $\alpha \sim T^3$.

8.6. Anharmonic transitions, lattice thermal conductivity (AM-25). Thermal energy can be stored in the vibrational modes of the crystal. In a perfectly harmonic crystal, the thermal conductivity is infinite (the stationary modes don't change in time). However, these stationary states are only approximate stationary states of the full Hamiltonian.

Typically we write $H = H_{\text{harm}} + H_1$ and view H_1 as perturbations that cause transitions between harmonic eigenstates (creation, destruction, scattering of phonons). In lowest-order perturbation theory, a term of order $n \geq 3$ causes transitions where n of the phonon occupation numbers differ. Such a term contains the composition of n different creation or annihilation operators $a_{ks}^\dagger, a_{k's'}$.

These processes (“collisions”) must conserve energy and crystal momentum:

$$(8.16) \quad \sum \hbar \omega_s(k) n_{ks} = \sum \hbar \omega_s(k) n'_{k's'} \quad (\text{Energy})$$

$$(8.17) \quad \sum k n_{ks} = \sum k n'_{k's'} + K, \quad \text{some } K \in RL$$

This prohibits the processes that create n phonons or destroy n phonons.

TODO picture

8.6.1. Umklapp scattering.

- * Normal processes: conserve crystal momenta exactly
- * Umklapp processes: differ by nonzero reciprocal lattice vector

At low temperature, umklapp processes are “frozen out”; essentially the only scattering that occurs are normal processes.

This occurs because only few phonons are involved in the collision. At low T the participating phonons satisfy (TODO why????) $\omega_s(k) \ll \omega_D$ and the change in crystal momenta must be $\sim \sum_{\text{a few}} |k| \ll k_D$ (Debye), and $k_D \sim |K|$.

9. CLASSICAL TRANSPORT: DRUDE THEORY OF METALS (AM-1)

Assumptions:

- * Solid core of nucleus and inner electrons. conduction electrons free to wander around (following kinetic theory).
- * Independent electron approximation (no electron-electron interaction, reasonable) and free electron approximation (no electron-ion approximation, not so reasonable)
- * Relaxation time τ : Electron collides in time length dt with probability $\text{Pr}(dt) = \frac{dt}{\tau}$. So on average travel for time τ between collisions. Assume τ independent of position, velocity (mostly ok).
- * After collision: new v random direction, speed proportional to temperature at collision place

9.1. Equation of motion and DC conductivity.

$$(9.1) \quad m\dot{v} = -eE - e\frac{v}{c} \times B - m\frac{v}{\tau},$$

τ is the *relaxation time* and describes damping. If electron has initial velocity v_0 and $E = B = 0$, then

$$v(t) = v_0 e^{-t/\tau},$$

so τ describes the time for fluctuations to decay.

With electric field E , instead guess $v(t) = A + B e^{-t/\tau}$ and obtain

$$v(t) = -\frac{\tau e}{m} E + [v_0 + \frac{\tau e}{m} E] e^{-t/\tau}.$$

For $t \gg \tau$, can see from equation of motion or solution above that

$$(9.2) \quad v = -\frac{\tau e}{m} E$$

Thus letting n be the density of electrons, the current density induced by E is

$$(9.3) \quad \begin{aligned} j &= -nev = \frac{ne^2\tau}{m} E \\ \implies \sigma &= \frac{ne^2\tau}{m} \quad \text{conductivity.} \end{aligned}$$

Here is a more physics-y heuristic approach from [\[1\]](#):

- * Define σ via $\mathbf{j} = \sigma \mathbf{E}$ (parallel vectors).
- * The *current density* j points in the direction of flow of charge and has magnitude the flux of the flow.
- * For a wire of length L with cross-sectional area A : density n of electrons each of charge $-e$ with velocity vector v implies

$$j = -nev$$

- * Between collisions, electrons pick up velocity $-eEt/m$ from E -field. Velocity from collision is random (assume average zero). Average of t is τ , thus

$$v_{\text{avg}} = -\frac{eE\tau}{m} \implies j = \left(\frac{ne^2\tau}{m} \right) E.$$

9.2. Applications of Drude theory.

9.2.1. *DC electrical conductivity.* oops just did that above

9.2.2. *Hall effect, magnetoresistance.*

9.2.3. *AC electrical conductivity.* There is a time-dependent electric field

$$E(t) = \Re(E(\omega)e^{-i\omega t}).$$

The current density is

$$j(t) = \Re(j(\omega)e^{-i\omega t}), \quad j(\omega) = \frac{(ne^2/m)E(\omega)}{(1/\tau) - i\omega},$$

written

$$j(\omega) = \sigma(\omega)E(\omega),$$

so that

$$(9.4) \quad \sigma(\omega) = \frac{ne^2\tau/m}{1 - i\omega\tau}.$$

(Note this reduces to the DC at zero frequency as it should.)

9.2.4. *Propagation of electromagnetic waves, plasma oscillations.*

9.2.5. *Thermal conductivity.* The thermal conductivity is

$$\kappa := \frac{1}{3}v^2\tau c_v.$$

Applying ideal gas kinetic laws at $T \gg T_F$, $\langle v^2 \rangle = \frac{2}{m}\frac{3}{2}k_B T$, to the electron gas, we obtain

$$\frac{\kappa}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T.$$

This recovers the empirical *Wiedemann-Franz law*: Let κ be the thermal conductivity and σ the electrical conductivity. Then

$$\frac{\kappa}{\sigma} \propto T,$$

with proportionality constant similar for all metals. The Drude proportionality constant is roughly $\frac{1}{2}$ the experimental value. It turns out that while Drude theory is fairly accurate (up to a factor of 2) at room temperature, this is a result of two errors of around 100 that cancel.

where thermal current for small ∇T (Fourier's law)

$$j^q = -\kappa \nabla T$$

10. SEMICLASSICAL TRANSPORT: BOLTZMANN EQUATION (AM-13)

Electrons moving in a lattice with a weak external field. (Weak field \Rightarrow stay in same energy band.)

- * Electric field \Rightarrow Bloch oscillation
- * Magnetic field \Rightarrow cyclotron motion
- * Electric and magnetic field \Rightarrow Hall effect

Semiclassical equations of motion: Band index does not change, electron in band n stays in band n , so we omit the band index. Then

$$(10.1) \quad v \equiv \dot{r} = \frac{1}{\hbar} \nabla_k \mathcal{E}(k)$$

$$(10.2) \quad \hbar \dot{k} = -eE - \frac{e}{c} \dot{r} \times B.$$

10.1. **Boltzmann equation.** Competition: E field force, dissipating effect from scattering (impurities, phonons)

Denote by $g(r, k, t)$ the density of electrons at position r with wavevector k at time t . The *Boltzmann equation* is

$$(10.3) \quad \frac{\partial g}{\partial t} = -\dot{r} \cdot \nabla_r g - \dot{k} \cdot \nabla_k g + \left. \frac{dg}{dt} \right|_{\text{coll}}.$$

The term $\left. \frac{dg}{dt} \right|_{\text{coll}}$ is the *collision term* and represents contribution from impurities, thermal fluctuations, collisions, etc. This term pushes g back towards thermal equilibrium. A mnemonic for remembering (10.3), is to pretend that $\left. \frac{dg}{dt} \right|_{\text{coll}}$ is a total derivative and $g = g(r, k)$.

10.2. **Relaxation time approximation.** The relaxation time approximation is the assertion

$$(10.4) \quad \left. \frac{dg}{dt} \right|_{\text{coll}} = -\frac{1}{\tau} [g(r, k, t) - f(r, k, t)],$$

where f is the Fermi function for the density and temperature at r (i.e. $\beta = \beta(r)$ and $\mu = \mu(r)$). This is essentially the simplest form we could take that causes g to relax back towards thermal equilibrium.

$$(10.5) \quad g = f - \int_{-\infty}^t dt' e^{-(t-t')/\tau(\mathcal{E})} v(k) \cdot \left[eE + \nabla\mu + \frac{\mathcal{E}(k) - \mu}{T} \nabla T \right] \frac{\partial f(t')}{\partial \mu}$$

If we can assume that ...

$$(10.6) \quad g = f - \tau(\mathcal{E}) v(k) \cdot \left[eE + \nabla\mu + \frac{\mathcal{E}(k) - \mu}{T} \nabla T \right] \frac{\partial f}{\partial \mu}.$$

11. THERMOELECTRIC PHENOMENA (AM-13)

The Boltzmann equation allows one to calculate the response of solids to electrical, magnetic, and thermal fields.

11.0.1. *Electrical current: uniform electrical field.* The *conductivity tensor* is

$$(11.1) \quad \sigma_{\alpha\beta} := \frac{\partial j_\alpha}{\partial E_\beta} = e^2 \int \frac{dk}{4\pi^3} \tau(\mathcal{E}(k)) v_\alpha(k) \cdot v_\beta(k) \frac{\partial f}{\partial \mu}.$$

The *effective mass tensor* M is defined by

$$(11.2) \quad (M^{-1})_{\alpha\beta} := \frac{1}{\hbar^2} \frac{\partial^2 \mathcal{E}_{nk}}{\partial k_\alpha \partial k_\beta}.$$

Filled bands do not conduct current.

Holes.

11.0.2. *Transport coefficients.* Here we have both electrical and thermal gradients. Let $G := E + \frac{\nabla\mu}{e}$ the electrochemical force. Recall

$$j = -e \int \frac{dk}{4\pi^3} v(k) g(k) \quad \text{electrical current density}$$

$$j^q = \int \frac{dk}{4\pi^3} (\mathcal{E}(k) - \mu) v(k) g(k) \quad \text{thermal current density}$$

The dependence on G and ∇T can be expressed in the matrix relations

$$(11.3) \quad j = L^{11} G + L^{12} (-\nabla T)$$

$$(11.4) \quad j^q = L^{21} G + L^{22} (-\nabla T),$$

where the matrices (“transport coefficients”) L^{ij} are defined by

$$(11.5) \quad L^{11} = \mathcal{L}^{(0)}$$

$$(11.6) \quad L^{21} = T L^{12} = -\frac{1}{e} \mathcal{L}^{(1)}$$

$$(11.7) \quad L^{22} = \frac{1}{e^2 T} \mathcal{L}^{(2)}$$

and

$$(11.8) \quad \mathcal{L}^{(\alpha)} := e^2 \int \frac{dk}{4\pi^3} \left(-\frac{\partial f}{\partial \mathcal{E}} \right) \tau(\mathcal{E}(k)) v(k) \cdot v(k) (\mathcal{E}(k) - \mu)^\alpha$$

$$(11.9) \quad = \int d\mathcal{E} \left(-\frac{\partial f}{\partial \mathcal{E}} \right) (\mathcal{E} - \mu)^\alpha \sigma(\mathcal{E}),$$

with

$$\sigma(\mathcal{E}) = e^2 \tau(\mathcal{E}) \int \frac{dk}{4\pi^3} \delta(\mathcal{E} - \mathcal{E}(k)) v(k) v(k).$$

time-approx

eqn:L-sigma

Using the Sommerfeld expansion on ^{eqn:L-sigma}(11.9) (first integrate by parts) and keeping only the first temperature correction, yields

$$(11.10) \quad L^{11} = \sigma(\mathcal{E}_F)$$

$$(11.11) \quad L^{21} = TL^{12} = -\frac{\pi^2}{3e}(k_B T)^2 \sigma'(\mathcal{E}_F)$$

$$(11.12) \quad L^{22} = \frac{\pi^2}{3} \frac{k_B^2 T}{e^2} \sigma(\mathcal{E}_F).$$

Additionally, for metals, $\frac{\sigma'}{\sigma} \approx \mathcal{E}_F$, which can be used to simplify ratios involving L^{21} or L^{12} .

The *thermoelectric power* or *thermopower* Q of a metal is defined by

$$(11.13) \quad G = Q \nabla T.$$

TODO in terms of L

11.0.3. *Wiedemann-Franz law revisited.* We have both thermal and electrical gradients.

Recall thermal conductivity κ is defined by

$$j_Q = \kappa(-\nabla T) = \frac{L^{12}}{L^{11}} = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \frac{\sigma'}{\sigma}.$$

under zero current flow.

Wiedemann-Franz law

$$(11.14) \quad \kappa_{\alpha\beta} = \frac{\pi^2}{3} \frac{k_B^2 T}{e^2} \sigma_{\alpha\beta}$$

TODO finish

11.0.4. *Thermopower: Seebeck effect.* The Seebeck effect is the conversion of heat into electric current. In the 1820s, Thomas Seebeck found that two different metals at different temperatures at a junction in a circuit deflect a compass magnet. The voltage difference is proportional to the temperature difference, with constant (tensor) of proportionality the *thermopower* or *Seebeck coefficient* α defined by

$$(11.15) \quad G = \alpha \nabla T.$$

11.0.5. *Peltier effect.* The Peltier effect is the observation that an electrical current causes heating or cooling at the junction of two different metals. The heat change is proportional to the current, with proportionality constant (tensor) the *Peltier coefficient* Π defined by

$$(11.16) \quad j^q = \Pi j.$$

$$(11.17) \quad \Pi = \frac{L^{21}}{L^{11}}$$

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