Lecture 2 - 436

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Next:

Drude Model for Solids

To first approximation we keep the atoms fixed and only the electrons move.

Assumptions:

1. Neglect Coulomb interaction between electrons.

2. Electrons and ions only interact via collisions.

3. Electron-ion collisions are instantaneous

τ is the average time between two collisions. We take the probability of an electron having a collision in time dt to be dt/τ.

Electrical Conductivity

From Ohm's law $V = IR$, we can write $\vec{E} = \rho\vec{j}$, and invert that to get $\vec{j} = \sigma\vec{E}$ (the linear response approximation).

Number density of electrons → $n = N/V$.

Current density → $j = I/A = N(-e)/tA = n(vdtA)(-e)/dtA = -nev$.

The battery is providing an external force $\vec{F}(t)$, while the electron is also having collisions. We assume that an electron loses all average momentum after a collision. Then the average momentum changes to

$$\langle \vec{p}(t+dt) \rangle = \left(1 - \frac{dt}{\tau}\right)\left(\langle \vec{p}(t) \rangle + \vec{F}(t)dt + \dots\right)$$
$$\frac{\vec{p}(t+dt) - \vec{p}(t)}{dt} = -\frac{1}{\tau}\vec{p}(t) + \vec{F}(t)$$
$$\frac{d\vec{p}}{dt} = -\frac{1}{\tau}\vec{p}(t) + \vec{F}(t)$$

I have dropped the $\langle \rangle$ for convenience but we are talking about averages. We'll utilise this formula often by setting the momentum's derivative to 0 to work in the steady state.

Note that a lot of questions and considerations are swept under the rug in this calculation, because it is genuinely difficult to take them into account.

DC Conductivity

$\vec{F} = -e\vec{E}$, then in the steady state,

$$\frac{d\langle \vec{p} \rangle}{dt} = 0 \implies \langle \vec{p} \rangle = \tau \vec{F}$$
$$\implies \langle \vec{p} \rangle = -e\vec{E}\tau \implies \langle \vec{v} \rangle = \frac{-e\tau\vec{E}}{m}$$
$$\vec{j} = -ne\vec{v} \implies \langle \vec{j} \rangle = \underbrace{\frac{ne^2\tau}{m}}_{\sigma}\vec{E}$$

The highlighted is known as Drude's formula.

Hall Effect

Applying a magnetic field on a current-carrying material causes a voltage difference to develop perpendicular to the current and the field.

Assume $\vec{B} = B\hat{k}$. Steady state, and working in average $\vec{p}, \vec{v}$,

$$\vec{F} = -e(\vec{E} + \vec{v} \times \vec{B})$$
$$\implies \vec{p} = -e\tau(\vec{E} + \vec{v} \times \vec{B})$$
$$\implies e\tau E_x = e\tau v_y B + m v_x$$
$$\& \ \ e\tau E_y = e\tau v_x B - m v_y$$

Rewrite in terms of $\vec{j}$, and note that in the steady state there cannot be j_y because there is no closed circuit, hence (using $\sigma_0 = ne^2\tau/m$, and $\omega_C = eB/m$ is the cyclotron frequency).

$$\sigma_0 E_y = -\omega_C \tau j_x + \cancel{j_y}$$
$$\implies E_y = -\underbrace{\frac{B}{ne}}_{(\sigma^{-1})_{yx}} j_x$$

Divide this by the magnetic field to get the **hall coefficient**, $R_H = \frac{-1}{ne}$.

Hence we've eleminated τ and can now determine n.

Thermal Conductivity

We make a linear response approximation, $\vec{j}^q = -\kappa \nabla T$ is the thermal current. We call κ the thermal conductivity.

Since there is no drive, so it might initially seem like the average velocity should be zero and lead to no thermal conductance. To counter that in the Drude model, he brought in the 4th approximation:

The average velocity is proportional to the temperature.

Then we play with a 1D model for thermal conductivity. Write the current:

$$j^q = \frac{n}{2} v \left[\varepsilon(T(x - v\tau)) - \varepsilon(T(x + v\tau)) \right]$$

$\varepsilon(T)$ is the energy an electron has (obtains after a collision with atom at T). On average an electron moves $v\tau$, so it starts from $x - v\tau$ and takes energy to x, or starts from $x + v\tau$ and steals energy at x.

$$j^q \approx \frac{n}{2} v \left[\varepsilon \left(T - v\tau \frac{dT}{dx} \right) - \varepsilon \left(T + v\tau \frac{dT}{dx} \right) \right]$$
$$\approx \frac{n}{2} v \left[\varepsilon(T) - v\tau \frac{dT}{dx} \frac{d\varepsilon}{dT} - \varepsilon(T) - v\tau \frac{dT}{dx} \frac{d\varepsilon}{dT} \right]$$
$$= nv^2 \tau \frac{d\varepsilon}{dT} \left(-\frac{dT}{dx} \right)$$
$$n\frac{d\varepsilon}{dT} = \frac{N}{V} \frac{d\varepsilon}{dT} = \frac{1}{V} \frac{dE}{dT} = C_V$$
$$\implies \kappa = v^2 \tau C_V$$

Note that this is for the one-dimensional case. For 3-D, we have to carefully realise that the collisions happen in any one direction, but $\langle \vec{v}^2 \rangle = 3 \langle v_x^2 \rangle$, and so the velocity ('s square) in one direction that we use has to be written in terms of the total's square, as a third of it. Hence

$$\kappa = \frac{1}{3} v^2 \tau C_V$$

While this is lovely in its own right, there is another fantastical result to be obtained. We can employ classical ideal gas laws to the electrons and write $\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T, C_V = \frac{3}{2} n k_B$. Then we get

$$\kappa = \frac{1}{3} \cdot \frac{3}{2} k_B T \cdot \frac{2}{m} \cdot \tau \cdot \frac{3}{2} n k_B$$
$$= \frac{3}{2m} n k_B^2 T \tau$$

And then we use our previous result to write

$$\frac{\kappa}{\sigma T} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 \approx 1.11 * 10^{-8} \text{ watt-ohm/K}^2$$

It is quite something that the ratio of these two slightly related quantities should be predicted to be a universal constant for solids by this theory.

Lecture 3 - 436

Course	PH 436 - CMP
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Next: Lecture 4 - 436

Sommerfeld Theory of Metals

Fermi-Dirac statistics

The first correction to the Drude theory is to use Fermi-Dirac statistics instead of Maxwell-Boltzmann for electrons.

Both are represented as the number of electrons per unit volume having velocities in range dv about v as being $f(v)dv$, and hence $n = \int f(v)dv$.

$$\text{M-B Stats}: f_B(v) = n\left(\frac{m}{2nk_BT}\right)^{3/2} e^{-mv^2/2k_BT}$$

$$\text{F-D Stats}: f(v) = \frac{m^3}{4\pi^3\hbar^3}\frac{1}{\exp[(\frac{1}{2}mv^2 - k_BT_0)/k_BT] + 1}$$

Where T_0 is determined by the normalisation condition $n = \int f(v)dv$ (something which is pre-implemented in the MB stats). T_0 is generally of the order of 10^5 degrees.

In most cases, applying the FD stats to the Drude model suffices as an implementation of Sommerfeld's theory. But to justify that, we must look into the quantum theory of electron gas.

Quantum Electron Gas

Due to the independent electron approximation (they don't interact), we can solve for the energy levels of a single electron and fill those up.

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

The ionic attraction is represented as a particle-in-a-box situation, confining the electron to a volume V - for simplicity, we set it to a cube for now, $L^3 = V$.

We dispose of the surface effects by having the boundary condition be that of periodicity at the boundaries, instead of a node (which leads to standing wave solutions):

$$\psi(x + aL, y + bL, z + cL) = \psi(x, y, z)$$
$$a, b, c \in \mathbb{Z}$$

This is the **Born-von Karman** boundary condition.

The solution to the DE (before boundary conditions) is:

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}$$
$$\varepsilon(\vec{k}) = \frac{\hbar^2|\vec{k}|^2}{2m}$$

This is normalised.

The boundary condition implies

$$k_i = \frac{2\pi n_i}{L}, n_i \in \mathbb{Z}, i = x, y, z$$

The **density of states** is the number of k points per unit volume in k space, it's $2 \cdot \frac{L^3}{(2\pi)^3}$, the 2 for spin states. We'll often write $L^3 = V$.

ε_F is the **Fermi energy**, the energy of the highest occupied state, at $T = 0K$.

$$N = 2 \sum_E \Theta(\varepsilon_F - \varepsilon(k))$$

$$\rightarrow \frac{2V}{(2\pi)^3} \int \Theta(\varepsilon_F - \varepsilon(k)) d^3k$$

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m}, \text{Let } \frac{\hbar^2 k_F^2}{2m} = \varepsilon_F,$$

$$N = \frac{2V}{8\pi^3} 4\pi \int_0^{k_F} k^2 dk$$

$$\implies n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$$

Using this, we can write other relations such as $\varepsilon_F = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m}, v_F = \frac{\hbar k_F}{m}, T_f = \frac{\varepsilon_F}{k_B}$ (fermi velocity and temperature). The fermi temp is the temperature a classical gas needs to be to have the energy of a $T = 0$ quantum gas.

Lecture 4 - 436

☰ Course	PH 436 - CMP
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Next: <u>Lecture 5 - 436</u>

Total Energy

$$
\begin{aligned}
E &= \frac{2V}{8\pi^3} \int d^3k \frac{\hbar^2 k^2}{2m} \\
&= \frac{V}{\pi^2} \frac{\hbar^2}{2m} \int_0^{k_F} k^4 dk \\
&\implies \frac{E}{N} = \frac{3}{5} \varepsilon_F
\end{aligned}
$$

Typical Values

Theoretically obtain n by $\frac{\rho}{A}$, where ρ is the mass density and A the atomic mass.

Or by molar density into N_A.

Experimentally, it is obtained often from the hall experiment.

Typical values:

$$
\begin{aligned}
n &\sim 10^{28}/m^3 \\
k_F &\sim 10^{10}/m \\
\varepsilon_F &\sim 1 - 10eV \\
v_F &\sim 10^{-2}c \\
E/N &\sim 1 - 10eV \\
T_F &\sim 10^4 - 10^5 K
\end{aligned}
$$

When a perturbation is applied, only those electrons which can be excited to above ε_F can participate, so only the top few energy levels do participate.

Non-zero Temperature

Classical Statistics

$$f_v(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}}$$

$$f_\varepsilon(\varepsilon) = 2\sqrt{\frac{E}{\pi}} \left(\frac{1}{k_B T}\right)^{3/2} e^{-ik_B T}$$

The above are known as the Maxell-Boltzmann statistics

Quantum (FD) Statistics

$$f_v(\vec{v}) = \frac{m^3}{(4\pi\hbar)^3} \frac{1}{\exp(\frac{1}{2}\frac{mv^2-\mu}{k_B T}) + 1}$$

$$f_\varepsilon(\varepsilon) = \frac{1}{\exp(\frac{\varepsilon-\mu}{k_B T}) + 1}$$

Where μ is the chemical potential $\frac{dE}{dN}$.

Justification - It fits the probability distribution curve we know to be true for small temperatures. We do not discuss any derivation of these statistics.

Note that for $T \to 0$, $f(\varepsilon)$ goes to 1 for $\varepsilon < \mu$ and goes to 0 for $\varepsilon > \mu$. This is exactly the behaviour we expect about ε_F at $T = 0$, so we claim that $\mu(T = 0) = \varepsilon_F$.

Also note that for small T, $f(\varepsilon)$ has a slight curve between the plateaus of $f(\varepsilon) = 1$ and $f(\varepsilon) = 0$ (instead of a discontinuous drop) with a width of order $k_B T$.

We calculate u, n at $T \neq 0$:

$$E = 2 \sum_{\vec{k}} \varepsilon(\vec{k}) f(\varepsilon(\vec{k})) \to \frac{2V}{8\pi^3} \int \varepsilon(\vec{k}) f(\varepsilon(\vec{k})) d^3\vec{k}$$

$$\implies u = \frac{E}{V} = \frac{2}{8\pi^3} \int \varepsilon(\vec{k}) f(\varepsilon(\vec{k})) d^3\vec{k}$$

$$\&\ n = \frac{N}{V} = \frac{2}{8\pi^3} \int f(\varepsilon(\vec{k})) d^3\vec{k}$$

Both these expressions can be written as $\int H(\varepsilon(\vec{k})) d^3\vec{k} = \int g(\varepsilon) H(\varepsilon) d\varepsilon.\ \varepsilon = \hbar^2 k^2 / 2m \implies d\varepsilon = \frac{\hbar^2 k}{m} dk \implies dk = \frac{m}{\hbar\sqrt{2m\varepsilon}} d\varepsilon$

$$\frac{1}{4\pi^3} \int d^3\vec{k}\, H(\varepsilon) = \frac{1}{4\pi^3} \int_0^\infty 4\pi k^2 dk\, H(\varepsilon)$$

$$= \int_0^\infty \frac{\sqrt{2m^3\varepsilon}}{\hbar^3\pi^2} H(\varepsilon) d\varepsilon$$

$$= \int_{-\infty}^\infty g(\varepsilon) H(\varepsilon) d\varepsilon,\ g(\varepsilon) := \begin{cases} \frac{m}{\hbar^2\pi^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}} & \varepsilon \geq 0 \\ 0 & \varepsilon < 0 \end{cases}$$

$g(\varepsilon)$ is known as the **density of states**, depending on the relation between ε, k and other dimensions of the system.

$$g(\varepsilon) = \frac{3}{2} \frac{n}{\varepsilon_F} \sqrt{\frac{\varepsilon}{\varepsilon_F}} \text{ for } \varepsilon \geq 0$$

Calculating Temperature Dependence

In this lecture, we only state the results, and derive them the next lecture.

$$u = u_0 + \frac{\pi^2 (k_B T)^2}{6} g(\varepsilon_F) + \Theta(T^4)$$

$$= u_0 + \frac{\pi^2 (k_B T)^2}{6} \frac{3}{2} \frac{n}{\varepsilon_F} + \Theta(T^4)$$

$$= \frac{3}{5} n\varepsilon_F + \frac{\pi^2}{4} n\varepsilon_F \left(\frac{k_B T}{\varepsilon_F} \right)^2 + \Theta(T^4)$$

$$C_V = \frac{\partial u}{\partial T} \bigg|_n = \frac{\pi^2 k_B^2}{2\varepsilon_F} nT$$

Classically, $C_V = \frac{3}{2} n k_B$.

Classical	Quantum

Classical	Quantum
$\frac{1}{2}mu^2 \sim \frac{3}{2}k_B T$	$v \sim v_F \sqrt{\frac{2\varepsilon_F}{m}}$
nk_B	$nk_B \left(\frac{k_B T}{\varepsilon_F} \right)$
$\frac{1}{3}v^2\tau C_V$	$Q = -\frac{C_v}{3ne} = -\frac{\pi^2}{6}\frac{k_B^2 T}{e\varepsilon_F}$

The last one is the Seebeck coefficient, the derivation of which we saw earlier. The first and second terms are used in the evaluation of the Seebeck coefficient, and we can see that factors of ε_F cancel which is why the classical expression is close to accurate despite the first and second terms being way off in the classical picture.

Lecture 5 - 436

☰ Course	PH 436 - CMP
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Next:

The energy density and number density are:

$$u = \int_{\mathbb{R}} \varepsilon g(\varepsilon) f(\varepsilon) d\varepsilon$$
$$n = \int_{\mathbb{R}} g(\varepsilon) f(\varepsilon) d\varepsilon$$

$f(\varepsilon)$ are the FD statistics.

Sommerfeld expansion

Both integrals are of the following form, which the Sommerfeld expansion helps us evaluate:

$$\int_{\mathbb{R}} H(\varepsilon) f(\varepsilon) d\varepsilon = ?$$

Before we perform the expansion, the final answer is spoiled for us:

$$= \int_{\mathbb{R}} H(\varepsilon) d\varepsilon + \sum_{n=1}^{\infty} (k_B T)^{2n} a_n \left. \frac{d^{2n-1}}{d\varepsilon^{2n-1}} H(\varepsilon) \right|_{\varepsilon=\mu}$$

$$a_n = \int_{\mathbb{R}} \frac{x^{2n}}{(2n)!} \left(-\frac{d}{dx} \frac{1}{e^x + 1} \right) dx = \left(2 - \frac{1}{2^{2(n-1)}} \right) \zeta(2n)$$

$$\zeta(n) = 1 + \frac{1}{2^n} + \frac{1}{3^n} + \dots$$

Now we derive this. Integration by parts,

$$\int_{\mathbb{R}} H(\varepsilon)f(\varepsilon)d\varepsilon = \cancel{f(\varepsilon)\int_{-\infty}^{\varepsilon}\cancel{H(\varepsilon')d\varepsilon'}\Big|_{-\infty}^{\infty}} + \int_{\mathbb{R}}\underbrace{\left(\int_{-\infty}^{\varepsilon}H(\varepsilon')d\varepsilon'\right)}_{K(\varepsilon)}\left(-\frac{\partial f}{\partial \varepsilon}\right)d\varepsilon$$

The first term cancels because the integral is 0 at $-\infty$, and $f(\varepsilon)$ is 0 at ∞. **why?**

$$f(\varepsilon) = \frac{1}{e^{\frac{\varepsilon-\mu}{k_B T}}+1}$$

So $-\frac{df}{d\varepsilon}$ is very sharply peaked at μ and negligible otherwise, and $K(\varepsilon)$ is a smoothly-varying function, so a taylor expansion around μ should give an excellent approximation for the integral.

▼ Justify that $K(\varepsilon)$ is smooth and has a longer energy scale.

   complete

$$K(\varepsilon) = K(\mu) + \sum_{n=1}^{\infty}\frac{(\varepsilon-\mu)^n}{n!}\frac{d^n K}{d\varepsilon^n}\Big|_{\varepsilon=\mu}$$
$$K^{(n)}(\varepsilon)|_{\mu} = H^{(n-1)}(\varepsilon)|_{\mu}$$
$$\int_{\mathbb{R}}-\frac{\partial f}{\partial \varepsilon}K(\varepsilon)d\varepsilon =$$

Complete the integral yourself, the final answer is provided already. Perform a variable sub and notice that the odd n terms disappear because the integral is over $\mathbb{R}$.

Now we evaluate u and n:

$$u = \int_0^{\mu}\varepsilon g(\varepsilon)d\varepsilon + \frac{\pi^2}{6}(k_B T)^2[\mu g'(\mu)+g(\mu)] + \Theta(T^4)$$
$$n = \int_0^{\mu}g(\varepsilon)d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 g'(\mu) + \Theta(T^4)$$

Now the number density should not be changing without an external source of electrons, so how do we see a T^2 dependence? Something hidden must be cancelling this, and the only possible culprit is μ and its T dependence.

Assuming that $\mu(T)$ is possibly slightly different from $\mu(0) = \varepsilon_F$, and taylor-expanding, we write:

$$\int_0^\mu g(\varepsilon)d\varepsilon = \int_0^{\varepsilon_F} g(\varepsilon)d\varepsilon + (\mu - \varepsilon_F)g(\varepsilon_F)$$

We demand that $\int_0^{\varepsilon_F} g(\varepsilon)d\varepsilon = n(T=0) = n(T)$, and hence the other two terms must cancel :

$$\therefore \mu = \varepsilon_F - \frac{\pi^2}{6}(k_B T^2)\frac{g'(\varepsilon_F)}{g(\varepsilon_F)} + \Theta(T^4)$$

Now we can perform the same expansion of μ in the expression for u and obtain

$$u = u_0 + \frac{\pi^2}{6}(k_B T)^2 g(\varepsilon_F)$$

When calling things small, we need a reference. It only makes sense to say $k_B T$ is small wrt ε_F if we can write the expression as $1 + c(\frac{k_B T}{\varepsilon_F})^2$. For that, we need to explicitly write u_0 and $g(\varepsilon_F)$ in terms of ε_F and take factors common.

Issues this model does not solve

Theoretical

- What even is τ? It's not a very satisfactory or macroscopically-connected model for the collisions, it's like sweeping a lot of issues under the rug.

- We've yet to take into account the electron-electron interaction.

Experimental

- $l_{\mathrm{mean}} = v_F \tau \sim 10^6 * 10^{-14} = 10^{-8} = 100\dot{A}$

  - Typical atomic spacing is $1\dot{A}$, so this feels likely to be at least an order of magnitude wrong.

- Experimentally, $c_v = \gamma T + \gamma' T^3$, but γ' is not predicted.

- Nothing said about transport

So what next? All that remains is to attack the scattering model.

What we study now is what arose after diffraction patterns revealed the crystal (periodic) structure of metals. So we'll delve into a little relevant mathematical background.

Bravais Lattice

An array of points in space parametrised by $n_i \in \mathbb{Z}$, $\vec{R} = \sum_{i=1}^{3} n_i \vec{a}_i$, but there is a further criterion:

The orientation and arrangement of the surrounding points must appear the same from any point in the lattice.

This is not a consequence of periodicity, though it may seem so initially. For example, in a hexagonal lattice, some points have a point directly above them, and the rest have no point directly above them, but instead one directly below.

There is a workaround - if we club together every vertical pair of points in a hexagonal lattice, then we can make a bravais lattice out of these composite points. This is known as having a basis.

Lecture 6 - 436

≔ Course	PH 436 - CMP
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Next:

A doubt about the hall effect was asked, **_understand_** what the doubt and the solution was.

Lattice vectors

There can be many choices for the lattice vectors for a lattice. A bcc lattice can also be written using purely lattice vectors:

$$\mathbf{a_1} = a\hat{x}, \quad \mathbf{a_2} = a\hat{y}, \quad \mathbf{a_3} = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z}).$$

As can fcc, simply using tetrahedrons as building blocks:

$$\mathbf{a_1} = \frac{a}{2}(\hat{y} + \hat{z}), \quad \mathbf{a_2} = \frac{a}{2}(\hat{z} + \hat{x}), \quad \mathbf{a_3} = \frac{a}{2}(\hat{x} + \hat{y}).$$

Coordination number - number of nearest neighbours.

Unit cell - a structure which we translate using the lattice vectors and completely fills space with no overlaps or gaps. We're allowed to use some multiples of the lattice vectors, though.

Primitive unit cell - One lattice point per unit cell.

Sometimes these are harder to visualise, so we stick to conventional unit cells instead, which are more symmetric.

Wigner-Seitz unit cell - Take a lattice point, draw lines to all nearest neighbours, bisect these lines, and the shape formed (hexagonal for square lattices) is the unit cell, always a primitive.

A region of space that is closer to a lattice point than any other lattice point.

Basis

Attach more structure to each lattice point - for example, in CMP a basis is generally a set of atoms with displacements from the lattice point they're attached to, such that populating each lattice point with a basis creates the complete atomic structure of the material.

Reciprocal Lattice

A set of all the wave vectors $\vec{k}$ which yield plane waves with the periodicity of a given braivais lattice. $\vec{R} = \sum_i n_i \vec{a}_i$, $e^{i\vec{k}\cdot\vec{R}} = 1$.

For $\vec{a}_i, i = 1, 2, 3$, the **reciprocal vectors** which form the **primitive** reciprocal lattice vectors (which you can use to write a general $\vec{k}$) are :

$$\vec{b}_i = 2\pi \frac{\vec{a}_{i+1} \times \vec{a}_{i+2}}{\begin{bmatrix} \vec{a}_1 & \vec{a}_2 & \vec{a}_3 \end{bmatrix}}$$

These ensure $\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$, and we can write any $\vec{k}$ as $\sum_i k_i \vec{b}_i, k_i \in \mathbb{N}$. We can prove this by showing that

1. $\vec{a}_i$ are not coplanar $\implies$ $\vec{b}_j$ are not coplanar either.

2. Hence $\vec{k}$ can be written in terms of $\vec{b}_j$ for any $\vec{k}$. Then impose $\vec{k} \cdot \vec{R} = 2\pi N$, this will force $k_i \in \mathbb{N}$.

Note that the reciprocal lattice of the reciprocal lattice is the original lattice, as one would expect.

For 2D lattices, assume a useless $\hat{k}$ vector for calculations.

Brillouin zone

Now we have a lattice in k-space. Create a Wigner-Seitz unit cell in k-space - this is the first Brillouin zone.

Further Brillouin zones can be defined, but are rarely used and so were not introduced in the lecture.

Family of Lattice Planes

A set of constant-separation parallel planes such that they contain all the points in a lattice.

The reciprocal lattice provides a way to categorise all possible lattice planes.

Theorem. For a family of lattice planes with separation d, there exists a unique family of reciprocal lattice vectors perpendicular to the planes with the shortest one having length $2\pi/d$.

This relation is a bijection, so the converse is also true - given a reciprocal lattice vector K, the shortest vector parallel to it having length $2\pi/d$, there exists a family of lattice planes with separation d perpendicular to K.

Miller Indices

These are a way to characterise families of lattice planes, specify their orientation. We do that by taking the shortest reciprocal lattice vector perpendicular to the family of lattice planes, and write it in terms of a specific primitive reciprocal basis as $\vec{K} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ - then the miller indices for that family of planes are (h, k, l).

Note a convention that when a miller index is negative, instead of a minus sign it is denoted with a bar, like so - $(\bar{1}, 0, 1)$.

Lecture 7 - 436

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Next:

Bragg Diffraction

To test for the crystalline nature and lattice size of materials, the father-son duo theorised parallel lattice planes and only specular radiation reflecting off these planes (following the laws of optics, $i = r$), and derived a condition for constructive interference for light striking planes of separation d at an angle θ (with the plane) :

$$\text{Bragg condition} : 2d \sin \theta = n\lambda$$

Laue Condition

Light strikes any two lattice points separated by $\vec{d}$, and we maintain the assumption of elastic scattering and hence the wavelength stays the same. Incident and reflected wave vectors are $\vec{k} = \frac{2\pi}{\lambda}\hat{n}, \vec{k}' = \frac{2\pi}{\lambda}\hat{n}'$. Angles of these with $\vec{d}$ are θ, θ'. Constructive interference:

$$\vec{d} \cdot (\hat{n} - \hat{n}') = \underbrace{d \cos \theta + d \cos \theta'}_{\text{path difference}} = m\lambda$$

And then we can replace $\vec{d}$ by the general lattice vector $\vec{R} = \sum_i n_i \vec{a}_i$ for the general condition:

$$\vec{R} \cdot (\hat{n} - \hat{n}') = m\lambda$$
$$\implies \vec{R} \cdot (\vec{k} - \vec{k}') = 2\pi m$$
$$\implies e^{i(\vec{k}-\vec{k}')\cdot\vec{R}} = 1$$

So $\vec{k} - \vec{k}'$ must be a reciprocal lattice vector!

A geometric representation of this condition is that the tips of both the incident and reflected wave vectors must lie on a plane bisecting the reciprocal lattice vector. We're not talking about a lattice plane here - yet.

Now we've looked at two conditions - does one subsume the other? Nope, turns out they are exactly equivalent!

Recall that every reciprocal lattice vector $\vec{k} - \vec{k}' = \vec{K} = l\vec{k}_0$ is normal to some family of lattice planes with $\vec{k}_0$ being the shortest such vector and $l \in \mathbb{Z}$. The difference between the planes being d, $k_0 = \frac{2\pi}{d}$, and $2k\sin\theta = K$ because $k = k'$. Thus

$$2\left(\frac{2\pi}{\lambda}\right)\sin\theta = l\left(\frac{2\pi}{d}\right)$$
$$\implies 2d\sin\theta = l\lambda, l \in \mathbb{Z}$$

Which is exactly the Bragg condition.

Fermi's Golden Rule for Scattering

$$\Gamma(\vec{k}', \vec{k}) = \frac{2\pi}{\hbar}|\langle\vec{k}'|U|\vec{k}\rangle|^2 \delta(E_{\vec{k}} - E_{\vec{k}'})$$

Giving the scattering (transition from one momentum state to another) probability for a black box scattering with potential operator U. The delta function imposes elasticity.

$$\langle\vec{k}'|U|\vec{k}\rangle = \int \frac{1}{\sqrt{V}}e^{-i\vec{k}'\cdot\vec{r}}U(\vec{r})\frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}dr$$
$$= \frac{1}{V}\int U(\vec{r})e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}dr$$

Which is simply a Fourier transform!

Now we apply the assumption that $U(\vec{r})$ is periodic with a lattice, so we write $\vec{r} = \vec{R} + \vec{\rho}$, $\vec{\rho}$ being inside a unit cell.

$$= \frac{1}{V} \underbrace{\sum_{\vec{R}} e^{i(\vec{k}-\vec{k}')\cdot\vec{R}}}_{N\delta_{\vec{k},\vec{k}'+\vec{K}}} \int_{\text{unit cell}} e^{i(\vec{k}-\vec{k}')\cdot\vec{\rho}} U(\vec{\rho}) \, d\vec{\rho}$$

Because $\vec{R}$ are a discrete infinite (technically N, but that is large) set, so we get a summation which goes to 0 if the terms are oscillatory. The summation is non-zero only when $\vec{k} - \vec{k}' = \vec{K}$, a reciprocal lattice vector.

Furthermore, consider a basis attached to a lattice. The previous two conditions do not take that possibility into account, but here they can be accounted for using $U(\vec{\rho})$.

Lecture 8 - 436

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Next:

Two tutorial classes happened between this and lecture 7, the slides of which have been uploaded here. I have not made notes of those classes.

Scattering using Fermi's Golden Rule, continued

$$\Gamma(\vec{k}', \vec{k}) = \frac{2\pi}{\hbar} |\langle \vec{k}'|V|\vec{k}\rangle|^2 \delta(E_{\vec{k}} - E_{\vec{k}'})$$

$$\langle \vec{k}'|V|\vec{k}\rangle = n\delta_{\vec{k}, \vec{k}' + \vec{K}} \int_{\text{unit cell}} e^{i(\vec{k} - \vec{k}')\cdot\vec{r}} V(\vec{r}) \, d\vec{r}$$

$$\propto n\delta_{\vec{k}, \vec{k}' + \vec{K}} \int_{\text{all space}} e^{i(\vec{k} - \vec{k}')\cdot\vec{r}} V(\vec{r}) \, d\vec{r}$$

doubt - How is it valid to integrate over all space instead?

We can use $V(\vec{r}) = \sum_j V_j(\vec{r} - \vec{d}_j)$ to account for a basis. Substitute $\vec{r}'_j = \vec{r} - \vec{d}_j$,

$$\langle \vec{k}'|V|\vec{k}\rangle = n\sum_{\vec{K}} S(\vec{K})$$

$$S(\vec{K}) = \underbrace{\sum_j e^{i\vec{K}\cdot\vec{d}_j} \underbrace{\int d\vec{r}'_j e^{i\vec{K}\cdot\vec{r}'_j} V_j(\vec{r}'_j)}_{\text{Form factor}}}_{\text{Structure factor}}$$

The form factor is a fourier transform of V_j. When the V_js are identical, this is simply a function of $\vec{K}$ scaling the structure factor, and is not called the form factor - it is only called the form factor when it appears as $\sum_j f_j(\vec{K})e^{i\vec{K}\cdot\vec{d}_j}$.

▼ Example

Let's treat a BCC as having vectors $a\hat{x}_i$ with a basis $\{\vec{0}, \frac{a}{2}\sum_i \hat{x}_i\}$.

The reciprocal lattice vectors are then $\frac{2\pi}{a}\hat{x}_i$ (not FCC because the lattice here is not BCC, lattice plus basis is BCC. If you take the reciprocal of BCC as a lattice you do get an FCC in k-space.)

$$S(\vec{K}) = f(\vec{K})\sum_j e^{i\vec{K}\cdot\vec{d}_j}$$

$$= f(\vec{K})\left[1 + \exp\left(i\frac{2\pi}{a}(n_1\hat{x} + n_2\hat{y} + n_3\hat{z})\cdot\frac{a}{2}(\hat{x} + \hat{y} + \hat{z})\right)\right]$$

$$= f(\vec{K})(1 + (-1)^{\sum_i n_i})$$

$$= \begin{cases} 2f(\vec{K}) & \sum_i n_i \text{ is even} \\ 0 & \sum_i n_i \text{ is odd} \end{cases}$$

This makes perfect sense, because when we look at the actual reciprocal space of a BCC, when we start from the actual lattice vectors of the BCC, the reciprocal lattice has half the points this reciprocal lattice has. The figure below illustrates this : The circles are all the reciprocal lattice points obtained here as $\frac{2\pi}{a}\hat{x}_i$, the black ones are the ones which remain when you calculate the reciprocal lattice of a BCC using the actual primitive lattice vectors.
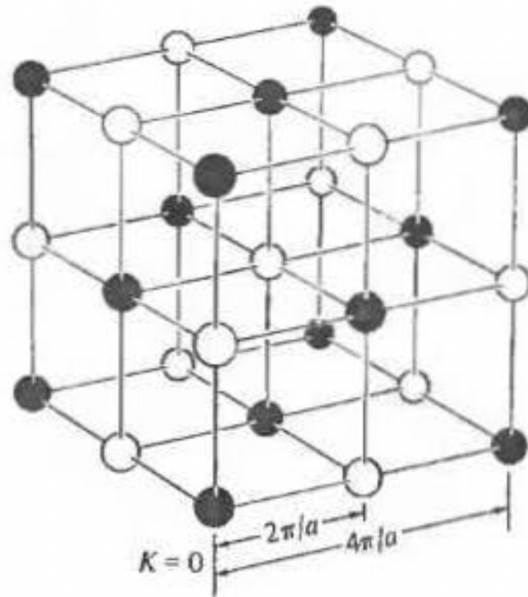
The white ones disappear when we calculate the reciprocal from BCC's primitives. The black ones clearly form an FCC as expected.

And now we get down to business

Apparently CMP finally starts now.

Bloch Theorem

Given a lattice with vectors $\vec{R} = \sum_i n_i \vec{a}_i$, or more generally a periodic potential $U(\vec{r}) = U(\vec{r} + \vec{R})$, the eigenvectors of the hamiltonian always have the form

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r}), \text{ Where } u_{n\vec{k}}(\vec{r} + \vec{R}) = u_{n\vec{k}}(\vec{r})$$
$$\text{Alt}: \psi_{n\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r})$$

▼ Aside

What followed was a discussion on how, fundamentally, the Schrodinger equation and quantum mechanics motivates fourier transforms and plane wave solutions and decompositions. That is why scattering arises so often - it refers to the very general class of problems where an incoming free wave scatters and we try to determine the outgoing waves - so the fourier transform of the wavefunction.

▼ Proof

We will prove the alternate form of the theorem.

$$\text{Define } T_{\vec{R}} : T_{\vec{R}} \psi_{n\vec{k}}(\vec{r}) = \psi_{n\vec{k}}(\vec{r} + \vec{R})$$
$$T_{\vec{R}}(H\psi) = H(\vec{r} + \vec{R})\psi(\vec{r} + \vec{R}) = H(\vec{r})T_{\vec{R}}\psi(\vec{r})$$
$$\implies [H, T_{\vec{R}}] = 0$$
$$\implies \text{They share eigenvectors} \implies$$
$$\text{For } H\psi = \varepsilon\psi, \ T_{\vec{R}}\psi = C(\vec{R})\psi$$
$$T_{\vec{R}}T_{\vec{R}'} = T_{\vec{R}'}T_{\vec{R}} = T_{\vec{R}+\vec{R}'}$$
$$\implies C(\vec{R})C(\vec{R}') = C(\vec{R}')C(\vec{R}) = C(\vec{R} + \vec{R}')$$
$$\vec{R} = \sum_i n_i \vec{a}_i \implies C(\vec{R}) = \prod_i C(\vec{a}_i)^{n_i}$$
$$\exists x_i \in \mathbb{C} \text{ s.t. } C(\vec{a}_i) = e^{i 2\pi x_i}$$
$$\text{Define reciprocal basis vectors } \vec{b}_i, \vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$
$$\text{And } \vec{k} := \sum_i x_i \vec{b}_i, \text{ so } C(\vec{R}) = e^{i\vec{k}\cdot\vec{R}}$$

We will complete the proof in the next lecture.

Lecture 9 - 436

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Next: <ins>Lecture 10 - 436</ins>

Continued proof of Bloch's theorem

Note, we are proving the second form of Bloch's theorem, as homework prove that they are equivalent statements.

▼ A recap of last time

$$T_{\vec{R}} : T_{\vec{R}}\psi_{n\vec{k}}(\vec{r}) = \psi_{n\vec{k}}(\vec{r} + \vec{R})$$
$$[H, T_{\vec{R}}] = 0, H\psi = \varepsilon\psi, \ T_{\vec{R}}\psi = C(\vec{R})\psi$$
$$C(\vec{R})C(\vec{R}') = C(\vec{R}')C(\vec{R}) = C(\vec{R} + \vec{R}')$$
$$\vec{R} = \sum_i n_i \vec{a}_i \implies C(\vec{R}) = \prod_i C(\vec{a}_i)^{n_i}$$
$$\exists x_i \in \mathbb{C} \text{ s.t. } C(\vec{a}_i) = e^{i2\pi x_i}$$
$$\text{And } \vec{k} := \sum_i x_i \vec{b}_i, \text{ so } C(\vec{R}) = e^{i\vec{k}\cdot\vec{R}}$$

Continuing the proof, now we use the Born-Von Karman boundary condition, assuming the material consists of N_i cells along $\vec{a}_i$. Then

$$\psi(\vec{r} + N_i\vec{a}_i) = \psi(\vec{r})$$
$$\implies \exp(i2\pi N_i X_i) = 1$$
$$\implies X_i = \frac{m_i}{N_i}, m_i \in \mathbb{Z}$$

Now there can be boundary conditions which do not impose reality on $X_i, \vec{k}$ - some conditions cause decay, which will be accounted for by the complex $\vec{k}$.

Density of k-states: (k-points per unit volume)

$$\Delta\vec{k} = \left[\frac{\vec{b_1}}{N_1} \quad \frac{\vec{b_2}}{N_2} \quad \frac{\vec{b_3}}{N_3} \right]$$

$$= \frac{1}{N} \underbrace{\left[\vec{b_1} \quad \vec{b_2} \quad \vec{b_3} \right]}_{\text{k-space unit cell volume}}$$

$$= \frac{1}{N} \frac{(2\pi)^3}{V/N} = \frac{(2\pi)^3}{V}$$

▼ The volume of a reciprocal lattice primitive cell

is $\frac{(2\pi)^3}{v}$, where $v = V/N$ is the volume of a direct lattice primitive cell. This is easy to prove, calculate the box-product for a general set of reciprocal primitives.

This is exactly what we got in Sommerfeld!

Some ideas about $\vec{k}$:

- It is only worthwhile to talk about $\vec{k}$ within the first Brillouin zone. Any other $\vec{k}'$ is simply some $\vec{k} + \vec{K}$, and the reciprocal lattice vector gives $e^{i\vec{k}'\cdot\vec{R}} = e^{i\vec{k}\cdot\vec{R}} \underbrace{e^{i\vec{K}\cdot\vec{R}}}_{1}$, hence they are redundant.

- Is $\vec{k}$ the momentum? Let's check.

$$-i\hbar\nabla\psi = \hbar\vec{k}\psi + e^{i\vec{k}\cdot\vec{r}}(-i\hbar)\nabla u(\vec{r})$$

So ψ is not an eigenstate of $\hat{p}$, so $\vec{k}$ can't be the momentum for the state - but also, under electric and magnetic fields, $\vec{k}$ behaves exactly like momentum! It mimics momentum at many levels, and it is useful to think of it as some related quantity.

Why have we been using $\psi_{n\vec{k}}$ and $u_{n\vec{k}}$? What are these ns?

These are labelling energy levels. The DE for u becomes

$$\hat{H}\psi = \varepsilon\psi$$

$$\left[\frac{\hbar^2}{2m}\left(\frac{\nabla}{i} + \vec{k}\right)^2 + U(\vec{r})\right] u_{\vec{k}}(\vec{r}) = \varepsilon u_{\vec{k}}(\vec{r})$$

Hence u follows a modified Schrodinger equation (different potential), and the periodic boundary condition is in a way saying u is bound to the finite region $\prod_i [0, \vec{a}_i]$. So like (but not exactly like) a particle in a box, it will have quantised energy levels, which n labels. This is a common theme in QM - restriction to finite regions, or some sort of boundary condition, is what leads to quantisation.

Velocity

Velocity of electrons is an idea which came up again and again in our classical models, so it may be helpful to have an expression associated with it here too. We define

$$\vec{v}_n = \frac{1}{\hbar}\nabla_k \varepsilon_n(\vec{k})$$

And motivate it with the following perturbative calculation: (Using H' as u's hamiltonian)

$$\varepsilon_n(\vec{k} + \vec{q}) = \varepsilon_n(\vec{k}) + \vec{q}\cdot\nabla_k\varepsilon_n(\vec{k}) + \dots \text{ for small } \vec{q}$$

$$H'_{\vec{k}+\vec{q}} = H'_{\vec{k}} + \vec{q}\cdot\frac{\hbar^2}{m}\left(\frac{\nabla}{i} + \vec{k}\right) + \dots$$

$$= H'_0 + V$$

$$E = E_0 + \langle u_0|V|u_0\rangle + \dots (1^{\text{st}} \text{ order perturbation})$$

$$\therefore \vec{q}\cdot\nabla_k\varepsilon_n(\vec{k}) = \langle u_0|V|u_0\rangle$$

$$= \int d^3\vec{r}\, u_{n\vec{k}}^* \vec{q}\cdot\frac{\hbar^2}{m}\left(\frac{\nabla}{i} + \vec{k}\right) u_{n\vec{k}}$$

$$\nabla_k\varepsilon_n(\vec{k}) = \hbar\int d\vec{r}\, \psi_{n\vec{k}}^*(\vec{r})\underbrace{\left(-i\frac{\hbar}{m}\nabla\right)}_{\hat{v}}\psi_{n\vec{k}}(\vec{r})$$

$$\therefore \langle\hat{v}\rangle = \frac{1}{\hbar}\nabla_k\varepsilon_n(\vec{k})$$

There's also another interesting result to be derived using perturbation theory. Let us work with ψ and its hamiltonian, and assume the potential is much smaller than the kinetic energy. How does that impact our eigenenergies?

$$\varepsilon(\vec{k}) = \varepsilon_0(\vec{k}) + \langle \vec{k}|U|\vec{k}\rangle$$

Recall that we evaluated $\langle \vec{k}'|U|\vec{k}\rangle$ for the Fermi rule calculation. At $\vec{k}' = \vec{k}$, the fourier transform gives the average of $U(\vec{r})$, which is merely a constant shift in the energy and not interesting. So we look at second-order perturbations in the next class.

$$\varepsilon(\vec{k}) = \varepsilon_0(\vec{k}) + \sum_{\vec{k}' - \vec{k} = \vec{K} \neq 0} \frac{|\langle \vec{k}'|U|\vec{k}\rangle|^2}{\varepsilon_0(\vec{k}) - \varepsilon_0(\vec{k}')}$$

Lecture 10 - 436

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Next:

Note to self: Revise perturbation theory and degenerate perturbation theory for CMP.

Periodic Potential and Energy levels using Perturbation Theory

Recall from last lecture,

$$\varepsilon(\vec{k}) = \varepsilon_0(\vec{k}) + \sum_{\vec{k'}-\vec{k}=\vec{K}\neq 0} \frac{|\langle \vec{k'}|U|\vec{k}\rangle|^2}{\varepsilon_0(\vec{k}) - \varepsilon_0(\vec{k'})}$$

$\varepsilon_0(\vec{k})$ is merely the energy of a solution of the unperturbed hamiltonian, which is the free hamiltonian, so $\varepsilon_0(\vec{k}) = \frac{\hbar^2 k^2}{2m}$, which is parabolic. But this means at $k' = -k$ (in the 1D case), their energies are equal, these eigenstates are degenerate, so we need to use degenerate perturbation theory at those points.

(Also note that to evaluate the energy, we need to consider $\vec{k'} - \vec{k} = \vec{K}$, a reciprocal lattice vector.)

So the only points where degenerate perturbation theory is required are $k = K/2 = \frac{n\pi}{a}$, and then too only for the term $k' = -K/2 = -\frac{n\pi}{a}$. We're not actually interested in the rest of the points, there's a qualitative results about these points that we want to derive.

▼ Degenerate Perturbation Theory Revision

In degenerate perturbation theory, we shift to a basis which has the hamiltonian diagonalised. To keep things simple we'll do this starting from a basis of $|k\rangle, |k+K\rangle$. This is sufficient since we only have pairs of degenerate states to consider.

First, find the matrix elements:

$$\langle k|\hat{H}_0 + U|k\rangle = \varepsilon_0(\vec{k})$$
$$(+V_0, \text{ which is an overall shift we put to } 0)$$
$$\langle k'|\hat{H}_0 + U|k'\rangle = \varepsilon_0(\vec{k} + \vec{K})$$
$$\langle k|\hat{H}_0 + U|k'\rangle = U^*(\vec{K})$$
$$\langle k'|\hat{H}_0 + U|k\rangle = U(\vec{K})$$

Due to reality of $U(\vec{r})$, the fourier transform of $U(\vec{K})$ has $U(-\vec{K}) = U^*(\vec{K})$.

So in our basis, we have the eigenvalue equation

$$\begin{pmatrix} \varepsilon_0(\vec{k}) & U^*(\vec{K}) \\ U(\vec{K}) & \varepsilon_0(\vec{k} + \vec{K}) \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$
$$\implies \left(\varepsilon_0(\vec{k}) - E\right)\left(\varepsilon_0(\vec{k} + \vec{K}) - E\right) - |U(\vec{K})|^2 = 0$$

Thus we have the characteristic equation.

doubt - *Book mentions variational principle and stuff, understand it*

doubt - Intuit the degen perturbation theory bit

doubt - Why does looking for eigenvalues of this give us second-order results, and not first or third? Perhaps because second-order energies arise solely from considering the energy due to H' for the first-order perturbed eigenstates?

Using Degenerate Perturbation Theory

The perturbed hamiltonian will have eigenvalues:

$$\varepsilon(\vec{k}) = \frac{1}{2}(\varepsilon_0(\vec{k}) + \varepsilon_0(\vec{k} + \vec{K})) \pm \sqrt{\left(\frac{\varepsilon_0(\vec{k}) - \varepsilon_0(\vec{k} + \vec{K})}{2}\right)^2 + |U(\vec{K})|^2}$$

At $\vec{k} = \frac{n\pi}{a}, \vec{K} = -\frac{2n\pi}{a}$, we get

$$\varepsilon\left(\frac{n\pi}{a}\right) = \varepsilon_0\left(\frac{n\pi}{a}\right) \pm \left|U\left(\frac{2n\pi}{a}\right)\right|$$

With the corresponding eigenvectors being $\frac{1}{\sqrt{2}}\left(|k = \frac{n\pi}{a}\rangle \pm |k = -\frac{n\pi}{a}\rangle\right)$.

What does this mean? This means that at these degeneracy points, the perturbation causes linear combinations of the two eigenstates to seperate in energy and create a discontinuity, a gap - a band gap! We have quantisation, ladies and gentlemen.

(Note - there will be other correction terms to the energy from non-degenerate perturbtation theory applied to the rest of the $\vec{K}$ *complete*

Because of scattering from the Bragg planes - scattering from the potentials at reciprocal lattice vectors - we get discontinuities at the reciprocal lattice vectors in the graph of ε vs k, quantisation.

As for the rest of the points in k-space, the rest of the momenta, we've got the energy changing smoothly, because our non-degenerate formula works.

Sidenote, this was all a 1D discussion - in higher dimensions, it's not points but whole surfaces in k-space at which we have degeneracy and hence discontinuities, and these surfaces are the Brillouin zone boundaries.

What's the limiting behaviour to the degenerate points?

- A discussion on why delta is small or can be small - *complete*

-

Tight-Binding Method

Lecture 11 - 436

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Next:

Tight-binding model

Working with a 1D model for simplicity,

$$H = K + \sum_j V_j = (K + V_m) + \sum_{j \neq m} V_j$$

$$\therefore H_{nm} = \langle n|H|m \rangle = \varepsilon_{\text{at}} \delta_{nm} + \sum_{j \neq m} \langle n|V_j|m \rangle$$

Nearest-neighbour approximation, $\langle n|m \rangle = \delta_{nm}$, and we assume

$$\sum_{j \neq m} \langle n|V_j|m \rangle = \begin{cases} V_0 & n = m \\ -t & |n - m| = 1 \\ 0 & \text{otherwise} \end{cases}$$. Thus

$$H_{nm} = \underbrace{(\varepsilon_{\text{at}} + V_0)}_{\varepsilon_0}\delta_{nm} - t(\delta_{n,m-1} + \delta_{n,m+1})$$

Periodic boundary conditions: $\psi(n + N) = \psi(n)$, where $N = L/a$ is length of chain.

Solution

Ansatz: $\frac{1}{\sqrt{N}} \sum_n e^{-ikna}|n\rangle$, $|n\rangle$ being an orbital of the nth atom.

The boundary conditions require $k = 2\pi m/L$.

$$\sum_{nm} H_{nm}\phi_m = E_n\phi_n$$

$$\implies \varepsilon_0 \frac{1}{\sqrt{N}} e^{-ikna} - \frac{t}{\sqrt{N}}\left(e^{-ik(n+1)a} + e^{-ik(n-1)a}\right) = E_n \frac{1}{\sqrt{N}} e^{-ikna}$$

$$\implies E = \varepsilon_0 - 2t\cos ka$$

Lecture 12 - 436

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Next: <u>Lecture 13 - 436</u>

Extending band-gap picture to 2D

$$V(x, y) = V(\cos\left(\frac{2\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right)) + \tilde{V}(\cos\left(\frac{2\pi y}{a}\right) + \sin\left(\frac{2\pi y}{a}\right))$$

Square lattice, so square Brillouin zone. The edge-centres of this Brillouin zone have degeneracies with the opposite edge-centres, so those are two band gaps (different along k_x and k_y). The vertices of the zone are all degenerate with each other, which causes a different band gap.

Extending further to 3D and weirder symmetries, we'll get weirder and more complex degeneracies and hence band gap distributions.

Back to Tight Binding

Why does tight-binding not give band baps? It's because we construct it using a 1e orbital basis from the atoms. It's a fundamentally different starting point than imposing a potential on free electrons as we did to obtain the band gaps.

Does the TB solution satisfy Bloch's theorem?

$$\psi(n) = \frac{1}{\sqrt{N}} \sum_n e^{-ikna} |n\rangle$$

$$\implies \psi(x) = \frac{1}{\sqrt{N}} \sum_i e^{-\iota k x_i} |x_i\rangle = \frac{1}{\sqrt{N}} \sum_i e^{-\iota k x_i} \phi(x - x_i)$$

$$\psi(x + R) = \frac{1}{\sqrt{N}} \sum_i e^{-\iota k x_i} \phi(x - x_i + R)$$

$$x_i - R = \tilde{x}_i,$$

$$= e^{\iota k R} \frac{1}{\sqrt{N}} \sum_i e^{-\iota k \tilde{x}_i} |\tilde{x}_i\rangle = e^{\iota k R} \psi(x)$$

Yep.

Extending TB to real applications

- Higher dimensions

- Orbitals/bases

  We'll consider both of these by labelling states at x_i as $|i, s\rangle$, s denoting internal degrees of freedom.

▼ Notation

$$\sum_{\langle ij \rangle} \to \text{sum over nearest neighbours}$$

$$\sum_{\langle\langle ij \rangle\rangle} \to \text{sum over nearest and next-nearest neighbours}$$

First extend the 1D picture to a more general hamiltonian,

$$\langle n|H|m\rangle \equiv H_{nm} = \varepsilon_0 \delta_{nm} - t(\delta_{n+1,m} + \delta_{n-1,m})$$
$$\downarrow$$
$$H = \sum_i \varepsilon_0 |\vec{R}_i\rangle\langle\vec{R}_i| - t \sum_{\langle ij \rangle} \left(|\vec{R}_i\rangle\langle\vec{R}_j| + |\vec{R}_j\rangle\langle\vec{R}_i| \right)$$

$$H = \begin{array}{c} \\ R_1 \\ R_2 \\ R_3 \\ \vdots \\ R_N \end{array} \begin{array}{c} \begin{matrix} R_1 & R_2 & R_3 & \dots & R_N \end{matrix} \\ \begin{pmatrix} \varepsilon_0 & -t & -t/0 & \dots & -t \\ -t & \varepsilon_0 & -t & \dots & 0 \\ -t/0 & -t & \ddots & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & -t \\ -t & 0 & 0 & -t & \varepsilon_0 \end{pmatrix} \end{array}$$

Note two things:

1. The number of $-t$ terms in a row is the number of nearest neighbours a point has, which will be larger in higher D. For 1D, only the tridiagonal elements (plus the other two vertices, see next point) are non-zero.

2. The elements farthest from the diagonal, $|R_1\rangle\langle R_n|$ and it's h.c., will also exceptionally have $-t$ terms because of the periodic boundary conditions. Imagine tiling with the matrix (in the 1D case for simplicity) and requiring a continuous tridiagonal repitition, then these corner elements will become part of the global tridiagonals of sorts.

N is the total number of lattice points (combined from all dimensions). Extending to orbitals and bases, the dimensions of H will become $Ns \times Ns$, over basis $|\vec{R}_{n,s}\rangle$.

$$H = \sum_i \sum_{s,r} \varepsilon_0 |\vec{R}_{is}\rangle\langle\vec{R}_{ir}| - t \sum_{\langle is,jr\rangle} \left(|\vec{R}_{is}\rangle\langle\vec{R}_{jr}| + \text{ h.c.} \right)$$

▼ **Example: Graphene**

Use lattice vectors $\vec{a}_1 = \frac{\sqrt{3}a}{2}\hat{x} + \frac{3a}{2}\hat{y}, \vec{a}_2 = -\frac{\sqrt{3}a}{2}\hat{x} + \frac{3a}{2}\hat{y}$, and a basis $\{\vec{0}, -a\hat{y}\}$ for the hexagonal 2D lattice. Let's label atoms at the lattice points with A and those off the lattice points B, $\vec{R}_j = \sum_i m_{ij}\vec{a}_i, \vec{R}_{jA} = \vec{R}_j, \vec{R}_{jB} = \vec{R}_j - a\hat{y}$.

We assume 0 on-site energies ε_0 - valid here, may not be in other problems.

$$H = -t \sum_{\langle i,j\rangle} \left(|\vec{R}_{iA}\rangle\langle\vec{R}_{jB}| + \text{ h.c.} \right)$$

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{N}} \sum_j e^{i\vec{k}\cdot\vec{R}_j} (c_A \phi(\vec{r} - \vec{R}_{jA}) + c_B \phi(\vec{r} - \vec{R}_{jB}))$$

$$\implies \varepsilon(\vec{k})c_A = -t(e^{-i\vec{k}\cdot\vec{a}_1} + e^{-i\vec{k}\cdot\vec{a}_2} + 1)c_B$$

$$\varepsilon(\vec{k})c_B = -t(\underbrace{e^{i\vec{k}\cdot\vec{a}_1} + e^{i\vec{k}\cdot\vec{a}_2} + 1}_{f^*(\vec{k})})c_A$$

We obtained the above equations

Why is graphene interesting?

- K, K', Γ are the non-redundant points in k-space

- Using the approach above, evaluate the energy gap at the K-points, then you get a dispersion relation $\varepsilon = \pm i\hbar|\vec{q}|$. The band structure becomes linear around the K-points, with the electrons acting like massless particles - hence graphene becomes a test bed for many relativistic and QFT ideas and experiments.

Lecture 13 - 436

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Next: <u>Lecture 14 - 436</u>

Next extra: <u>Tutorial 3 - 436</u>

Conductors vs Insulators - Interpreting the gap

Metals have partially-filled bands, semi-metals have multiple partially-filled bands, and non-metals have completely filled bands.

This difference occurs because of the magnitude of the band gap. The canonical ensemble applies here, $p(E) \sim e^{-\beta E}$, hence the filling (at non-zero temperatures) is not optimised to fill up to an energy before going to higher energies, but rather higher energy regions are only partially filled and the rest of the electrons go to even higher energies (with the probability falling off exponentialy).

This means a small band gap allows this probability distribution to properly manifest, while a large band gap means the excited electrons can't go to the higher band and so clump up in a lower band. This leads to (almost) fully-filled bands.

Any insulator always has an even number of particles arising from each lattice point, because to fill up a full band with n states, $2n$ spin states need to be filled up.

We can estimate this quantitatively: band gaps much larger than $k_B T \sim 10^{-2}$ at RT tend to be insulators, whereas much smaller tend to be conductors, and the same order, then semi-conductors.

Semi-conductors have two bands very close together, can be overlapping, even (when one trough is shifted in k-space). There are zero-gap semiconductors, like graphene at 0T, as well as other weird behaviours.

Fermi Surfaces

Fermi surfaces - surfaces which separate occupied and unoccupied levels, $\varepsilon = \varepsilon_F$ - can be disconnected, have multiple branches, though every k-point must be allowed.

They are mostly closed in 2D, but in 3D it is not difficult to obtain open Fermi surfaces. In 2D, topological materials do so. Magnetic fields also break time-reversal symmetry by breaking the symmetry between $k, -k$ and hence can open Fermi surfaces. Even spin-orbital coupling, which is when a moving electron feels a magnetic field in another frame, can break the degeneracy.

HW. Finding an open Fermi Surface

A multi-layered material with edge-length a and tight-binding t in the plane, and $b, t_\perp$ with other planes, $b \gg a, t_\perp \ll t$. Write the TB model and show that the fermi-surface will be open at the top.

Even the simple case of $\varepsilon = -2t(\cos(ak_x) + \cos(bk_y))$, if you fill up the states you first have closed fermi surfaces but beyond a point (once they start intersecting the first brillouin zone) they become open.

Fermi surfaces are useful for characterising materials - under the influence of a magnetic field, when Laundau levels form, various properties of the material (like hall coefficient, resistance, etc) oscillate with a frequency proportional to the area of the fermi surface. For multiple surfaces, superimpose frequencies.

Quantum CMP

We've treated potentials quantum mechanically, but what if we try to include electric fields, can we talk about conductance? What about magnetic fields?

This is a very hard problem, in general requiring field theory Green's functions (and something called the Kubo formula), but we have a couple of workarounds.

Semi-Classical Dynamics

We treat the kinetic energy with the intrinsic potential exactly quantum mechanically, and the potential of the electric field is treated classically. This is much easier and gives correct answers, but it is very difficult to justify it or prove that this is a valid map from a general hamiltonian.

Postulates

We start with wave packets, a superposition, spread in r and in k.

1. Band index n is a constant of motion.

2. $\dot{\vec{r}} = v_n(\vec{k}) = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\vec{k})}{\partial \vec{k}}$, $\hbar\dot{\vec{k}} = e[\vec{E}(\vec{r},t) + \vec{v}_n(\vec{k}) \times \vec{B}(\vec{r},t)]$ (force)

3. All the $\vec{k}$ are defined in one Brillouin zone, and wave packets are distributed with Fermi-Dirac statistics.

Current

$$\vec{j} = -e \int \frac{d\vec{x}}{4\pi^3} \frac{1}{\hbar} \frac{\partial \varepsilon_n(\vec{k})}{\partial \vec{k}} \sim \int d\varepsilon_n$$

Thus a fully-filled band cannot give you any current - integrate over one brillouin zone, which is one period of the periodic behaviour, then $\varepsilon_f - \varepsilon_i = 0$.

If we apply an electric field, there will be another energy term in the integral, so the integral becomes $\sim \varepsilon^2$. Still no current, because insulator.

DC Electric field

$$\vec{k}(t) = \vec{k}(0) - \frac{e\vec{E}t}{\hbar}$$
$$\vec{v}(\vec{k}(t)) = \vec{v}(\vec{k}(0) - \frac{e\vec{E}t}{\hbar})$$
$$\sim \sin(k - eEt)$$

The velocity will become 0 at the brillouin zone boundaries - we can intuit this through scattering. This also means the velocity and momentum are no longer collinear.

This also suggests we see electrons reaching higher and higher momenta until they start to accelerate in the other direction! We'll learnt that these are now holes.

Lecture 14 - 436

≣ Course	PH 436 - CMP
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Next:

(The beginning of this lecture may seem a little *scattered* (pun-intended), refer to the previous lecture, this is merely a recap.)

Semi-classical Dynamics : Effect of EM fields

1. Band index n is constant

2. We use $\vec{v}_n = \frac{1}{\hbar} \nabla_k \varepsilon_n(\vec{k})$ as the velocity in the lorentz force and equate the force to $h\dot{\vec{k}}$.

3. Fermi-Dirac statistics

Consequences

1. Filled bands are inert $\rightarrow j_{\text{filled band}} = 0$

2. $\vec{k}(t) = \vec{k}(0) - \frac{e\vec{E}t}{m}$

Scattering happens at the boundaries of the Brillouin zone, so the momentum can be decreasing when the acceleration due to EM fields is positive, because the collisions with the atoms are causing loss of momentum.

$$j = -e \int_{\text{occupied}} \frac{d^3 \vec{k}}{4\pi^3} \vec{v}(\vec{x})$$

$$\int_{1 \text{ Brillouin Zone}} \cdots = 0 = \int_{\text{Unoccupied energy levels}} + \int_{\text{Occupied}}$$

$$\therefore j = -e \int_{\text{Occupied}} = +e \int_{\text{Unoccupied}} = j_{\text{holes}}$$

Thus we can interpret the current as motion of electrons or holes, either picture will do.

Now recall that we taylor-expanded the energy distribution at the minima of a band to get an electron's effective mass. We do the same at the band maxima for the hole's effective mass.

Minima

$$\varepsilon_{\min}(k) = \varepsilon_0 + A(k - k_0)^2 + \ldots, \quad A > 0$$

$$v(k) = \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k} = \frac{\hbar}{\tilde{m}}(k - k_0)$$

$$\vec{a} = \frac{d\vec{v}(\vec{k})}{dt} = \frac{\hbar}{\tilde{m}}\dot{\vec{k}}$$

$$\hbar\dot{\vec{k}} = -e\left(\vec{E} + \vec{v} \times \vec{B}\right)$$

$$\implies \tilde{m}\vec{a} = -e\left(\vec{E} + \vec{v} \times \vec{B}\right)$$

Maxima

$$\varepsilon_{\max}(k) = \varepsilon_0' + A'(k - k_0')^2 + \ldots, \quad A' > 0$$

$$v(k) = \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k} = -\frac{\hbar}{\tilde{m}'}(k - k_0')$$

$$\vec{a} = \frac{d\vec{v}(\vec{k})}{dt} = -\frac{\hbar}{\tilde{m}'}\dot{\vec{k}}$$

$$\hbar\dot{\vec{k}} = -e\left(\vec{E} + \vec{v} \times \vec{B}\right)$$

$$\implies -\tilde{m}'\vec{a} = -e\left(\vec{E} + \vec{v} \times \vec{B}\right)$$

Now we could either treat the holes as being positively charges and have the same effective mass as the electron, or we could have the charge remain negative and think of the effective mass as being negative.

The basic physics is merely that the periodic energy distribution is causing the acceleration and the momentum's time derivative to be antiparallel in the higher parts of the band.

You should stick to one picture - electrons or holes - and be consistent. There is no more correct picture in any region or part of the band, it is only convenience.

More generally, if the acceleration and momentum derivative are not parallel or anti-parallel, we get an effective mass tensor M:

$$M^{-1}(\vec{k})_{ij} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon(\vec{k})}{\partial k_i \partial k_j}$$

Note that the energy distribution we have arrived at, the wavefunctions, are all stationary states, they don't change with time, so the velocity won't change even in the absence of an electric field. Any electron with an initial velocity maintains that velocity, the momentum never dies, so there is infinite conductivity - while there is scattering at the positive centres, the wavefunction is what has been obtained after constructive interference of all possible scattering-inclusive paths - "coherent addition of scattered waves". (Very hand-wavy, ik.)

Why this discord with our practical observations? It's because we've assumed a perfect lattice. In a real lattice, the imperfections break our assumption of periodic potential.

The Drude model isn't quite wrong even then - it's just that the mean free path does not arise from the periodic lattice, as Drude thought, but is way more complicated.

That is the 0-temp picture. At non-zero temp, there are also phonon modes, the atoms vibrate, which also slightly breaks periodicity.

Another interesting phenomenon is that in the presence of an electric field, in a perfect lattice the electrons would oscillate back and forth, the actual current would be 0. These are called Bloch oscillations, and have only recently been observed.

Including the Magnetic Field

Our governing equation is

$$h\dot{\vec{k}} = -e(\vec{v} \times \vec{B})$$

We could solve this equation, but we can note certain constants of motion and gain a lot of understanding even with just those.

1. For a field $\vec{B} = B\hat{k}$, $\dot{k}_z = 0$.

2. Energy is a constant of motion $\rightarrow \frac{d\varepsilon(\vec{k})}{dt} = \frac{d\varepsilon(\vec{k})}{d\vec{k}}\frac{d\vec{k}}{dt} \sim \vec{v} \cdot (\vec{v} \times \vec{B}) = 0$

Thus the isoenergy countours in $k_x - k_y$ space are what the electrons follow.

It is interesting to note about the isoenergy countours in a brillouin zone that they can be disjoint. Consider the tight-binding square brillouin zone.

$$h\dot{\vec{k}} = -e(\vec{v} \times \vec{B})$$
$$\implies \vec{B} \times h\dot{\vec{k}} = -e\vec{B} \times (\underbrace{\vec{v}}_{\dot{\vec{r}}} \times \vec{B}) = -eB\vec{r}_\perp$$
$$\vec{r}_\perp := \vec{r}\text{'s component perp } \vec{B}$$
$$\therefore \vec{r}_\perp(t) - \vec{r}_\perp(0) = -\frac{\hbar}{eB}\hat{B} \times (\vec{k}(t) - \vec{k}(0))$$

For $\hat{B} = \hat{k}$, $\Delta\vec{k}$ is in $k_x - k_y$ and so $\Delta\vec{r}_\perp$ is perpendicular to $\Delta\vec{k}$ in the x-y plane in real space.

Recall the 2D tight-binding iso-energy countours, along which the electron will move. The higher energy countours - the disjoint ones - moving clockwise in one of those corresponds to moving counter-clockwise in the square centred at $\left(\frac{\pi}{a}, \frac{\pi}{a}\right)$, the hole's square. This explains the positive charge we sometimes saw in the hall effect. Again, somewhat hand-wavy - the rigorous argument is that looking from $\left(\frac{\pi}{a}, \frac{\pi}{a}\right)$, the energy is increasing as countours go towards $0, 0$, so dE/dk (which is the velocity in the lorentz force) has the sign reversed.

Lecture 15 - 436

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Next:

A discussion on Wave Packets

First we discuss the free wave packets:

$$\psi(\vec{r}, t) = \int A(\vec{k}) e^{i(\vec{k}\cdot\vec{r} - \omega(\vec{k})t)} d\vec{k}$$

This is a wavepacket when $A(\vec{k})$ is sharply peaked around $\vec{k} = \vec{k}_0$. Also, $\omega(\vec{k}) = \frac{\hbar k^2}{2m}$. Expand around $\vec{k}_0$,

$$\omega(\vec{k}) = \omega_0 + \Delta\vec{k} \cdot \nabla_{\vec{k}} \omega(\vec{k}) + \dots$$

Now let us consider Bloch electron wavepackets:

$$\psi_n(\vec{r}, t) = \sum_{\vec{k}} g(\vec{k}) \psi_{nk}(\vec{r}) e^{-\frac{i}{\hbar}\varepsilon_n(\vec{k})t}$$
$$\psi_{nk}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{nk}(\vec{r})$$

Where $g(\vec{k})$ is sharply peaked at $\vec{k}_0$. Now this is a Bloch wavefunction, so what happens when we shift by R?

$$\psi_n(r_0 + R, t) = \sum_k \underbrace{[g(\vec{k})\psi_{nk}(\vec{r}_0)]}_{\tilde{g}(\vec{k})} e^{i\vec{k}\cdot\vec{R}} e^{-\frac{i}{\hbar}\varepsilon_n(\vec{k})t}$$

$\tilde{g}(\vec{k})$ is also peaked around $\vec{k}_0$, clearly.

how does this tell us the following?

Thus $\Delta r \propto \frac{1}{\Delta k}$.

The constraint this gives is that whatever perturbation we add must have a variation many times Δr, or our semiclassical Bloch dynamics break down, we can't treat the system using one-electron wave packets anymore when one wavepacket doesn't even feel a single value of the electric field.

Now when we add an external perturbation, to deal with that semi-classically, we try to write a Lagrangian for it with generalised coordinates the expectation values of $\vec{r}, \vec{k}$ for the wave packet - we remove terms due to the wave packet spread ($\Delta r, \Delta k$), treating them as higher-order corrections.

Then when we calculate $\dot{\vec{r}}, \dot{\vec{k}}$, we get the equations we had written earlier. The group velocity of the wavepacket is the same as the actual average quantum mechanical velocity of the bloch electron.

Now the ions move

A lot of measured properties and observed phenomena can't be explained by the models we've had so far - $C_V \sim \alpha T + \beta T^3$ (the cubic dependence), solids melting, etc.

The answer lies in the degrees of freedom we have ignored throughout our studies - ions can move. A little bit, but they do like to move it.

Classical treatment of a harmonic crystal

We treat the ion movement classically, and assume it remains small because they are heavy.

$$\vec{r}(\vec{R}) = \vec{R} + \vec{u}(\vec{R})$$

A perturbation to the atomic positions. But wait, why do we have a lattice in the first place? It brings equilibirium with respect to the inter-atomic forces, of course. So there is a potential keeping the atoms in place, due to interactions between every pair of atoms.

$$U = \frac{1}{2} \sum_{\vec{R},\vec{R}'} \phi(\vec{R} - \vec{R}')$$

$$H = \sum_{\vec{R}} \frac{p(\vec{R})^2}{2m} + U$$

Well, that's how the potential was - but now, with moving ions,

$$U = \frac{1}{2} \sum_{\vec{R},\vec{R}'} \phi(\vec{r}(\vec{R}) - \vec{r}(\vec{R}'))$$

$$= \frac{1}{2} \sum_{\vec{R},\vec{R}'} \phi(\vec{R} - \vec{R}' + \vec{u}(\vec{R}) - \vec{u}(\vec{R}'))$$

$$= \frac{1}{2} \sum_{\vec{R},\vec{R}'} \phi(\vec{R} - \vec{R}') + \frac{1}{2} \sum_{\vec{R},\vec{R}'} \left(\vec{u}(\vec{R}) - \vec{u}(\vec{R}') \right) \cdot \nabla \phi(\vec{R} - \vec{R}') + \frac{1}{4} \sum_{\vec{R},\vec{R}'} \left(\vec{u}(\vec{R}) - \vec{u}(\vec{R}') \cdot \nabla \right)^2 \phi(\vec{R} - \vec{R}') + \dots$$

Now we do the usual shenanigans:

- Remove constant terms $\frac{1}{2} \sum_{\vec{R},\vec{R}'} \phi(\vec{R} - \vec{R}')$
- Net force at any $\vec{R}$ is zero, hence $u(\vec{R}) \cdot \sum_{\vec{R}'} \nabla \phi(\vec{R} - \vec{R}') = 0$, and this can be extended to the whole second term being zero in the above expression ($\nabla_{\vec{R}} \phi(\vec{R} - \vec{R}') = -\nabla_{\vec{R}'} \phi(\vec{R} - \vec{R}')$).
- Good afternoon, ma amie. How do you do?

So then U becomes, for $\partial_\mu \partial_\nu \phi(\vec{R} - \vec{R}') \equiv \phi_{\mu\nu}$,

$$U = \frac{1}{4} \sum_{\vec{R},\vec{R}'} \left(\vec{u}(\vec{R}) - \vec{u}(\vec{R}') \cdot \nabla \right)^2 \phi(\vec{R} - \vec{R}')$$

$$= \frac{1}{4} \sum_{\vec{R},\vec{R}'} (u_\mu(\vec{R}) - u_\mu(\vec{R}')) \phi_{\mu\nu} (u_\mu(\vec{R}) - u_\mu(\vec{R}'))$$

$$= COMPLET$$

Complete from Ashcroft

how did we argue that CV+= 3NkbT?

Normal Modes

Recall PH 202,

$$U_{\text{harm}} = K \sum_n$$

Boundary Conditions

$$u(ma) = u((N+m)a)$$

Which tells us that $u(na) \sim e^{ikna}$, hence $k = \frac{2\pi n}{Na}, n \in \mathbb{N}$

Lecture 16 - 436

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Recall

$$U_{\mathrm{harm}} = \frac{1}{2} \sum_{R,R'} u_\mu(R) D_{\mu\nu}(R - R') u_\nu(R')$$

In today's lecture, R, R' are always vectors, though the arrow is omitted for conciseness.

We'll try to exploit the:

Symmetries of $D_{\mu\nu}$

1. Mixed partials: $D_{\mu\nu}(R - R') = \frac{\partial^2 U_{\mathrm{harm}}}{\partial u_\mu(R) \partial_\nu(R')}$, so $D_{\mu\nu}(R - R') = D_{\nu\mu}(R' - R)$.

2. If the displacements were $u'(R) = u(-R)$, we would have the same energy of the system - **doubt**i- what exactly is the constraint here?

   Thus, $D_{\mu\nu}(R - R') = D_{\mu\nu}(R' - R)$.

3. Combining the above two symmetries, we get $D_{\mu\nu}(R - R') = D_{\nu\mu}(R - R')$.

4. $\sum_R D_{\mu\nu}(R) = 0$ - **why?**

5. Make a uniform displacement at all points in the lattice, no change in energy:

   .bcomplete

Solving the DE

$$M\ddot{u}_\mu(R) = -\frac{\partial U_{\text{harm}}}{\partial u_\mu(R)} = -\sum_{R'} D_{\mu\nu}(R - R')u_\nu(R')$$

This form of the equation suggests a sinusoidal solution, $u_\mu(R,t) \sim \epsilon_\mu e^{i(\vec{k}\cdot\vec{R} - \omega t)}$
So substitute that as an ansatz, then fourier with respect to R (well, not exactly, the fourier weight factor is already present here from the ansatz, so we're doing only an integral over R, but it is effectively a fourier transform of part of the expression) - which here will be a sum, not an integral, because discrete lattice space.

Thus the RHS is already a convolution, and hence should simply give a product in fourier space. But Prof has also instructed that we do it the old-fashioned way, the convolution argument perhaps does not hold generally for the DFT.

$$M\omega^2 \epsilon_\mu = \tilde{D}_{\mu\nu}(k)\epsilon_\nu$$

Now we can use the symmetries of $D_{\mu\nu}$:

$$\tilde{D}(k) = \sum_R D(R)e^{-i\vec{k}\cdot R}$$
$$= \frac{1}{2}\sum_R D(R)(e^{-i\vec{k}\cdot R} + e^{i\vec{k}\cdot R})$$
$$= \sum_R D(R)\cos(\vec{k}\cdot R)$$
$$\overset{\text{Subtract } \sum_R D(R)=0}{=\!=\!=} -2\sum_R D(R)\sin^2\left(\frac{\vec{k}\cdot R}{2}\right)$$
$$\overset{\text{small } |\vec{k}|}{\approx} \frac{-k^2}{2}\sum_R (\hat{k}\cdot R)^2 D(R)$$

When we try to find the eigenvalues of $\tilde{D}$, $\tilde{D}(k)\vec{\epsilon}_s(\vec{k}) = \lambda_s(\vec{k})\epsilon_s(\vec{k})$, it is quite obvious that $\lambda_s \sim k^2$ at small k. Then from our DE, our frequency will be:

$$\omega_s(\vec{k}) = \sqrt{\frac{\lambda_s(\vec{k})}{M}}$$
$$\therefore \omega_s(\vec{k}) \sim k \text{ for small } k$$

We will have a maximum of 3 unique eigenvalues, so 3 unique branches in the energy-momentum(k) diagram, all of them starting linearly around $k = 0$. N lattice

points means N reciprocal lattice points ($\vec{k}$ modes), and 3 frequencies at each, so we get a total of $3N$ lattice modes available - makes sense, we had $3N$ degrees of freedom for the lattice.

Quantum Treatment

Make it an operator:

$$\hat{H}_{\text{harm}} = \sum_R \frac{1}{2m}\hat{\vec{p}}(R)^2 + \frac{1}{2}\sum_{R,R'} \hat{u}_\mu(R)D_{\mu\nu}(R-R')\hat{u}_\nu(R')$$

Now what? Well, these are coupled harmonic oscillators - and we've already calculated the normal modes! Thus the total energy is

$$\sum_{\vec{k},s} \hbar\omega_s(\vec{k})(n_{\vec{k},s} + \frac{1}{2})$$

These quantised-energy mechanical waves are phonons.

Now let's use some stat mech. Working in the canonical ensemble, $Z = \sum_{\{\mu\}} e^{-\beta E(\mu)}$, the energy density becomes $u = \frac{\langle E\rangle_T}{V} = -\frac{1}{V}\frac{\partial \ln Z}{\partial \beta}$.

$$Z = \sum_{n_{ks}} e^{-\beta \sum_{ks}(n_{ks}+1/2)\hbar\omega_s(\vec{k})}$$

$$= \prod_{ks}\sum_{n_{ks}\in\mathbb{N}} e^{-\beta(n_{ks}+1/2)\hbar\omega_s(\vec{k})}$$

$$= \prod_{ks} \frac{e^{-\beta\hbar\omega_s(\vec{k})/2}}{1 - e^{-\beta\hbar\omega_s(\vec{k})}}$$

Now we can calculate the average energy density in terms of the temperature:

$$u = \frac{1}{V}\sum_{ks}\frac{1}{2}\hbar\omega_s(k) + \frac{1}{V}\sum_{ks}\frac{\hbar\omega_s(k)}{e^{\beta\hbar\omega_s(k)} - 1}$$

And hence phonon number:

Specific heat

$$c_v = \frac{\partial u}{\partial T} = \frac{1}{V} \sum_{ks} \frac{\partial}{\partial T} \frac{\hbar \omega_s(k)}{e^{\beta \hbar \omega_s(k)} - 1}$$

High temperature limit

$$k_B T \gg \hbar \omega_s(k):$$
$$\frac{\hbar \omega_s(k)}{e^{\beta \hbar \omega_s(k)} - 1} \approx \frac{\hbar \omega_s(k)}{\beta \hbar \omega_s(k)} = k_B T$$
$$\implies c_v = \frac{1}{V} 3 N k_B$$

Which is the Dulong-Petite law. Do we actually observe this? Well, no, because at high temperatures anharmonic terms become more significant. When using QFT, we understand these as phonon-phonon interaction terms.

Low temperature limit

$$k_B T \ll \hbar \omega_s(k)$$

Or is it? ω_s could take as low a value as we want at a k of our choice, this statement doesn't make much sense for all k.

So we'll understand this limit in another way - only very small energies will contribute because $\hbar \omega_s(k)/k_B T$ will become large and hence the denominator of u will become small at higher energies. In our region of interest, $\omega_s(k) \approx c_s(\hat{k})k$, and we'll variable sub to $x = \beta \hbar c_s(\hat{k})k$:

$$c_v = \partial_T \sum_s \int \frac{d^3 \vec{k}}{(2\pi)^3} \frac{\hbar \omega_s(\vec{k})}{e^{\beta \hbar \omega_s(\vec{k})} - 1}$$
$$\approx \partial_T \frac{(k_B T)^4}{(\hbar \tilde{c})^3} \frac{3}{2\pi^2} \int_0^\infty \frac{x^3}{e^x - 1} dx$$

Where

1. We have changed the x upper limit to infinity because at higher x, the integrand does not contribute.

2. $c_v \sim T^3$

3. We have define $\tilde{c}$ as

$$\frac{1}{\tilde{c}} = \left(\frac{1}{3} \sum_s \int \frac{d\Omega}{4\pi} \frac{1}{c_s(\hat{k})^3} \right)^{1/3}$$

Lecture 17 - 436

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Next:

> If you want to understand something, hit it with something.
>
> - Hridis Pal, 2023

> Violence is always the answer.
>
> - Harshda Saxena, 2023

The Debye Interpolation Scheme

Read from Ashcroft, pg 458.

Topology in CMP

What is Topology? It studies the invariants under smooth, continuous deformations of geometrical objects. Let us look at an example.

Gauss-Bonnet Theorem

The gaussian curvature K can be defined for a surface. This theorem states that for a closed surface M, the following holds:

$$\frac{1}{2\pi} \oint_M K dA = 2 - 2g_M$$

Where g_M is the genus of the object - *number of holes* at a basic level. For a sphere, $g_M = 0, K = 1/r_1r_2 = 1/R^2$ (r_1, r_2 being two principal radii), and hence we can verify this.

Recall

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r}), H\psi = \varepsilon\psi$$
$$h(\vec{k}) = \frac{\hbar^2}{2m}\left(\frac{\nabla}{i} + \vec{k}\right)^2 + U(\vec{r}),$$
$$h(\vec{k})u_{n\vec{k}}(\vec{r}) = \epsilon_n(\vec{k})u_{n\vec{k}}(\vec{r})$$

So everything we're doing is in momentum space, let's try to understand objects and surfaces (like the Fermi surface) in k-space using topology.

Berry Curvature

Berry Connection : $\vec{A}_n(\vec{k}) = i\langle u_{n\vec{k}}|\nabla_{\vec{k}} u_{n\vec{k}}\rangle$ - Physically, considers the overlap between a point

Berry Curvature : $\Omega_n^{\mu\nu}(\vec{k}) = i\langle\partial_{\vec{k}} u_{n\vec{k}}| \times |\partial_{\vec{k}} u_{n\vec{k}}\rangle$ (k-space cross product of k-space vectors)

When we're limited to 2/3D, we can write $\Omega^{\mu\nu} = \nabla_{\vec{k}} \times \vec{A}$.

(Note that we are working in only one band for all of this.)

We can then calculate the **Berry Phase** :

$$\gamma_n = \int \vec{\Omega}_n \cdot d\vec{s}$$

In general, this theory is applicable to any hamiltonian with a parameter λ - topology is applied to the parameter space, and time evolution of the wavefunction accrues the berry phase as a phase factor.

Applied to the first Brillouin zone

The FBZ is a 3-torus in 3D because of periodic boundary conditions in all 3 directions - 2-torus in 2D, ofc. Then the berry phase becomes the Chern number, $\frac{1}{2\pi}\int \Omega_n dk_x dk_y$.

Recall that for simple cases, we argued and believed that the following hold:

$$\dot{\vec{r}} = \frac{1}{\hbar} \nabla_k \varepsilon_k$$
$$\hbar \dot{\vec{k}} = -\nabla_{\vec{r}} v(\vec{r}) - e(\dot{\vec{r}} \times \vec{B})$$

When we account for more complicated situations where Ω is non-zero,

$$\dot{\vec{r}} = \frac{1}{\hbar} \nabla_k \varepsilon_k - \dot{\vec{k}} \times \vec{\Omega}_n(\vec{k})$$

Hence there is an effective k-space magnetic field which influences real space evolution the same way the real magnetic field influences k-space evolution.

Quantum Hall Effect and Landau levels

Missed this. Was a short discussion.

Surface states and complex k

For the bloch wavefunction, surface states get complex k and hence decaying solutions. If we can define non-zero topological invariants like the Chern number in the bulk of a material, the surface states have fixed energy - we can't remove these surface states, and they are also very robust in that slightly off preparation of a sample still gives the same surface states.

When time reversal symmetry has not been broken, the chern number is 0, and hence does not give any non-trivial results. There are other invariants non-zero in various symmetries.

Furthermore, what the Chern number is also tells us a lot about these interesting results - the magnitude is the number of such states.