Lecture by Professor Tigran Tchrakian

# Solid State Theory

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# Contents

# 1 Introduction

Books:

- Kittel: Introduction, Theory (too difficult)
- Ziman (out of print) . . . electrons in material
- Hook & Hall (not quite theoretical)
- Peierls

Content

1. Free electron gas → Pauli Paramagnetism (exclusively QM)
   - dependence of $E_0 = E_0(T)$
   - Specific heat
   - magnetisation (each electron being a permanent magnet); Paramagnetism: magnetisation $\vec{M} \parallel \vec{H}$ (both CM and QM)
2. Langevin (CM) and Brillouin (QM) (ionic) paramagnetism → Weiss' model of ferromagnetism
   only QM; for ferromagnetism for $\vec{H} \to 0$, $\vec{M} \to \vec{M}_0 \neq 0$
3. Diamagnetism (Landau) (exclusively QM)
   $\vec{M} \uparrow\downarrow \vec{H}$; due to motion of electrically charged particles in $\vec{H}$
4. "not quite free" electrons → band structure

# 2 Free electron gas

i.e. Fermi gas

$$n = \int N(E) f_{FD}(E) dE$$
$$U = \int E N(E) f_{FD}(E) dE$$

$N(E)$: density of states /unit energy range

## 2.1 Model for $N(E)$

Free electrons in large box $(L_x, L_y, L_z)$, choose periodic boundary conditions. The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\Delta\psi = E\psi$$

i.e.

$$\Delta\psi = -\frac{2mE}{\hbar^2}\psi = -|\vec{k}|^2\psi$$

Separability trial: $\psi(x, y, z) = X(x)Y(y)Z(z)$

$$YZ\frac{d^2X}{dx^2} + XZ\frac{d^2Y}{dy^2} + XY\frac{d^2Z}{dz^2} = -|\vec{k}|^2 XYZ$$
$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = -(k_x^2 + k_y^2 + k_z^2)$$

i.e. as $x, y, z$ are independent

$$\frac{d^2X}{dx^2} + k_x^2 X = 0 \qquad \Rightarrow X = e^{\pm ik_x x}$$
$$\frac{d^2Y}{dy^2} + k_y^2 Y = 0 \qquad \Rightarrow Y = e^{\pm ik_y y}$$
$$\frac{d^2Z}{dz^2} + k_z^2 Z = 0 \qquad \Rightarrow Z = e^{\pm ik_z z}$$

Impose the B.C $X(x) = X(x + L_x)$ i.e. $k_x L_x = 2l\pi$

$$k_x = \frac{2l\pi}{L_x} \qquad k_y = \frac{2m\pi}{L_y} \qquad k_z = \frac{2n\pi}{L_z}$$

i.e.

$$E = \frac{\hbar^2}{2m}|\vec{k}|^2 = \frac{\hbar^2}{2m}4\pi^2\left(\frac{l^2}{L_x^2} + \frac{m^2}{L_y^2} + \frac{n^2}{L_z^2}\right)$$

with $L_x = L_y = L_z = L$

$$E = \frac{2\hbar^2\pi^2}{mL^2}(l^2 + m^2 + n^2)$$

Sommerfeld model
The No. of states up to energy $E_{l,m,n} = M(E) =$ No. of points up to $(l, m, n)$. For large $(l, m, n)$ we regard $(l, m, n)$ as continuous. $M(E)$ =volume of sphere of radius $\rho = \sqrt{l^2 + m^2 + n^2} = \sqrt{\frac{L^2 mE}{2\pi^2\hbar^2}}$

$$M(E) = \frac{4\pi}{3}\rho^3 = \frac{4\pi}{3}\left(\frac{L^2 mE}{2\pi^2\hbar^2}\right)^{3/2} \propto E^{3/2}$$

The density, i.e. number of states/unit energy range at energy $E$ is

$$N(E) = \frac{dM}{dE} \propto E^{1/2}$$

So in the Sommerfeld model $N(E) \propto E^{1/2}$, especially is $N(E)$ monotonic and $N(0) = 0$

## 2.2 Calculate $E_0(T)$

Our electron gas follows the Fermi-Dirac distribution $f(E) = \frac{1}{e^{\beta(E-E_0(T))}+1}$. With the chemical potential $E_0(T) > 0$.
Find the $T$ dependence of $E_0(T)$ for $0 < T \ll 1$.

Assume we know $N(E)$ (e.g. from Sommerfeld model), then the total number of particles is $n = \int_0^\infty N(E)f(E)dE$.

For $T = 0$ we have $f(E) = \begin{cases} 1 & E \le E_0(0) = E_F \\ 0 & E > E_F \end{cases}$, i.e.

$$n = \int_0^\infty N(E)f(E)dE = \\ = \int_0^{E_F} N(E)dE$$

For $0 < T \ll 1$

$$n = \int N(E)f(E)dE = \int f\frac{dM}{dE}dE = \\ = [f(E)M(E)]_0^\infty - \int_0^\infty Mf'dE = \\ = -\int Mf'dE$$

As $M(0) = 0$ and $f(E)$ decreases exponentially whereas $M(E)$ is only a power. $f'(E) \approx -\delta_D(E - E_0(T))$.
Expand $M(E)$ around $E_0(T)$ (wirte $E_0(T) = E_0$)

$$M(E) = M(E_0) + M'(E_0)(E - E_0) + \frac{1}{2!}M''(E_0)(E - E_0)^2 + \dots$$

So we get

$$\begin{aligned} n = &- M(E_0)\int f'(E)dE - M'(E_0)\int (E - E_0)f'(E)dE - \\ &- \frac{M''(E_0)}{2}\int (E - E_0)^2 f'(E)dE \end{aligned}$$

We know $f$ so we can calculate $f'$: $-f'(x) = \frac{\beta e^{\beta(E-E_0)}}{\left(e^{\beta(E-E_0)}+1\right)^2}$ i.e. we get

$$n = \sum_j \frac{M^{(j)}(E_0)}{j!} I_j$$

with $I_j = \int_0^\infty (E - E_0)^j \frac{\beta e^{\beta(E-E_0)}}{\left(e^{\beta(E-E_0)}+1\right)^2} dE$. We change variables $x = \beta(E - E_0)$ to get

$$I_j = \int_{-\beta E_0}^\infty \frac{x^j}{\beta^j} \frac{e^x}{(e^x + 1)^2} dx$$

We may savely extend the lower limit to $-\infty$ as the factor $e^x$ in the integrand is already small at $x = -\beta E_0$ for small $T$. So we get

$$\begin{aligned} I_j &= \int_{-\infty}^\infty \frac{x^j}{\beta^j} \frac{e^x}{(e^x + 1)^2} dx = \\ &= \frac{1}{\beta^j} \int_{-\infty}^\infty x^j \frac{1}{\left(e^{\frac{1}{2}x} + e^{-\frac{1}{2}x}\right)^2} \end{aligned}$$

For odd $j$ this integral vanishes, as we have an asymmetric integrand and symmetric limits. For odd values of $j$ we get the definite integral from tables. $I_0 = 1, I_2 = \frac{\pi^2}{3\beta^2}, \dots$. So we get

$$n = M(E_0(T)) + \frac{\pi^2}{6\beta^2} M''(E_0(T)) + \dots$$

As $M(E_0(T)) = \int_0^{E_0(T)} N(E)dE$ and the number of particles is independent of $T$ we get

$$\begin{aligned} \int_0^{E_F} N(E)dE &= \int_0^{E_0(T)} N(E)dE + \frac{\pi^2}{6\beta^2} N'(E_0(T)) \\ \int_0^{E_F} N(E)dE - \int_0^{E_0(T)} N(E)dE &= \frac{\pi^2}{6\beta^2} N'(E_0(T)) \\ \int_{E_0(T)}^{E_F} N(E)dE &= \frac{\pi^2}{6\beta^2} N'(E_0(T)) \end{aligned}$$

recall in Sommerfeld model $N \propto N^{1/2}$ i.e. monotonic increasing and $|E_0(T) - E_F| \leq 1$ i.e. $\int_{E_0(T)}^{E_F} N(E)dE \approx N(E_0(T))[E_F - E_0(T)]$ i.e.

$$N(E_0(T)[E_F - E_0(T)] = \frac{\pi^2}{6\beta^2}N'(E_0(T))$$
$$E_0(T) = E_F - \frac{\pi^2}{6\beta^2}\frac{N'(E_0(T))}{N(E_0(T))}$$
$$E_0(T) = E_F - \frac{\pi^2}{6\beta^2}\frac{d\ln N(E)}{dE}|_{E_0(T)}$$

As $E_0(T) \approx E_F$ we get

$$E_0(T) \approx E_F - \frac{\pi^2}{6\beta^2}\frac{d\ln N(E)}{dE}|_{E_F}$$

e.g. for Sommerfeld model $N = cE^{1/2}$

$$E_0(T) \approx E_F - \frac{\pi^2}{12\beta^2}\frac{1}{E_F} = E_F\left[1 - \frac{\pi^2 k^2}{12E_F^2}T^2\right]$$

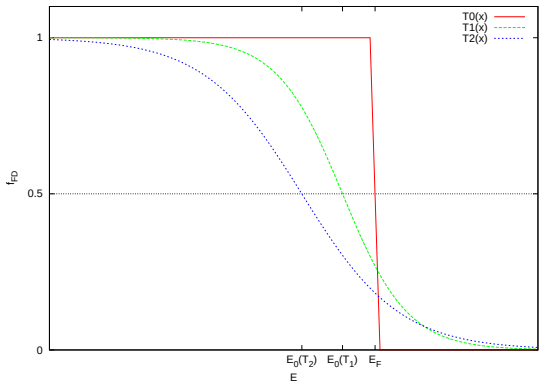



Figure 2.1: Fermi-Dirac distribution for $0 < T_1 < T_2$

## 2.3 Calculate $C_V$

$C_V = \frac{\partial U}{\partial T}$ i.e. calculate $U$.
Define $\mathcal{N} = \int_0^E E'N(E')dE'$

$$U = \int EN(E)f(E)dE = \frac{d\mathcal{N}}{dE}f(E) =$$
$$= \int_0^\infty \mathcal{N}(E)(-f'(E))dE$$

Expand $\mathcal{N}(E)$ around $E_0(T)$.

$$\mathcal{N}(E) = \mathcal{N}(E_0) + \mathcal{N}'(E_0)(E - E_0) + \frac{1}{2}\mathcal{N}''(E_0)(E - E_0)^2 + \dots$$

$$\begin{aligned} U =& \mathcal{N}(E_0)\int_0^\infty (-f')dE + \mathcal{N}(E_0)\int (E - E_0)(-f')dE + \\ &+ \frac{\mathcal{N}''(E_0)}{2}\int (E - E_0)^2(-f')dE + \dots = \\ &\approx \mathcal{N}(E_0) + \frac{\pi^2}{6\beta^2}\mathcal{N}''(E_0) \end{aligned}$$

We assume we know $N(E)$ and $E_0(T)$.

$$\begin{aligned} \mathcal{N}(E_0(T)) &= \int_0^{E_0(T)} EN(E)dE = \int_0^{E_F} EN(E)dE + \int_{E_F}^{E_0(T)} EN(E)dE = \\ &= U(0) + \int_{E_f}^{E_0(T)} EN(E)dE \end{aligned}$$

Approximation $T \ll 1$ and monotonicity of $N(E)$

$$\mathcal{N}(E_0(T)) \approx U(0) + E_0(T)N(E_0(T))[E_0(T) - E_F]$$

But previously $E_0(T) - E_F = -\frac{\pi^2}{6\beta^2}(\ln N)'|_{E_0(T)}$ so

$$\mathcal{N}(E_0(T) \approx U(0) - E_0(T)N(E_0(T))\frac{\pi^2}{6\beta^2}(\ln N)'|_{E_0(T)}$$

So the total energy is

$$\begin{aligned} U(T) &\approx U(0) - \frac{\pi^2}{6\beta^2}E_0N(E_0)(\ln N)'|_{E_0} + \frac{\pi^2}{6\beta^2}\frac{d}{dE}[EN]|_{E_0} = \\ &= U(0) - \frac{\pi^2}{6\beta^2}E_0N'(E_0) + \frac{\pi^2}{6\beta^2}[N(E_0) + E_0N'(E_0)] = \\ &= U(0) + \frac{\pi^2}{6\beta^2}N(E_0(T) = \approx U(0) + \frac{\pi^2k^2}{12}T^2N(E_F) \end{aligned}$$

So we $C_V$

$$C_V = \frac{\pi^2k^2}{3}N(E_F)T$$

And $C_V \xrightarrow{T\to 0} 0$ as predicted otherwise by 3rd law

## 2.4 Pauli spin-paramagnetism

Magnetisation of elementary permanent magnets (magnetic moment of electron spin, dipol moment $\pm\vec{\mu}$) by external field $\vec{B}$. Assume $\vec{B}$ is pointing up.
The energy of $\uparrow$ electron in external field $= -\vec{\mu}\vec{B} = \mu B$
The energy of $\downarrow$ electron in external field $= -\vec{\mu}\vec{B} = +\mu B$
For $T = 0$ all states up to $E_F$ are filled completly, each with one $\uparrow$ and one $\downarrow$ electron. However large $B$ $M = 0$ always. So magnetisation only possible for $T > 0$. Without a magnetic field the number of up-electron = number of down-electrons, since $E(\uparrow) = E(\downarrow)$. Now switch on the magnetic field.

$$E(\uparrow) = E - \mu B$$
$$E(\downarrow) = E + \mu B$$

Now the number of states for a given energy $E_{new}$ changes. For the up-electrons, the energy is decreased, i.e. if an electron has energy $E$ now, it had $E + \mu B$ before, i.e. the number of states for energy $E$ is $N_\uparrow(E) = N(E + \mu B)$. The total magnetisation is the resulting magnetic moment.

$$M = \mu \int [N(E + \mu B) - N(E - \mu B)] f(E) dE$$

Approximate for $T \ll 1$ and $\vec{B}$ weak, i.e. $\mu B \ll E$

$$N(E + \mu B) - N(E - \mu B) \approx 2\frac{dN}{dE}\mu B$$

i.e.

$$M = 2\mu^2 B \int \frac{dN}{dE} f(E) dE = 2\mu^2 B \int_0^\infty \frac{d}{dE}(Nf) dE - 2\mu^2 B \int_0^\infty N f'(E) dE =$$
$$= 2\mu^2 B \int_0^\infty N(E)(-f') dE$$

At $T = 0$ we have $M = 2\mu^2 B N(E_F)$. For $0 < T \ll 1$ expand $N$ and proceed as usual

$$M = 2\mu^2 B \left\{ N(E_0(T) + \frac{N''(E_0(T))}{2} \frac{\pi^2}{6\beta^2} \right\}$$

The susceptibility is $\chi = \frac{M}{B}$ i.e.

$$\chi = 2\mu^2 \left\{ N(E_0(T) + \frac{N''(E_0(T))}{2} \frac{\pi^2}{6\beta^2} \right\}$$

e.g. for the Sommerfeld model: $N \propto cE^{1/2}, N'' = -c\frac{1}{4}E^{-3/2}$

$$M = 2\mu^2 Bc \left\{ E_0(T)^{1/2} - \frac{\pi^2}{48\beta^2} E^{-3/2} \right\} =$$
$$= 2\mu^2 Bc E_0(T)^{1/2} \left\{ 1 - \frac{\pi^2}{48} \left( \frac{kT}{E} \right)^2 \right\}$$

and $E_0(T) = E_F \left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_F}\right)^2\right]$ so for $T \ll 1$ we have $\chi$ is independent of $T$.

# 3 Classical and quantum-mechanical ionic paramagnetism

## 3.1 Classical ionic Langevin paramagnetism

No translational or vibrational degrees of freedom.

The energy of a magnetic dipole $\vec{\mu}$ in a magnetic field $\vec{H} = (0, 0, H)$ is

$$E = -\vec{\mu}\vec{H} = -\mu H \cos\theta$$

The partition function is $Z_1 = \int e^{-\beta E} d\tau = \int e^{\beta\mu H \cos\theta} d\tau$. The phase space in this case is only $\Omega(\theta, \phi)$.

$$\begin{aligned} Z_1 &= \int e^{\beta\mu H\cos\theta} d\Omega = \int e^{\beta\mu H\cos\theta} \sin\theta d\theta d\phi = \\ &= 2\pi \int e^{\beta\mu H\cos\theta} d(-\cos\theta) = 2\pi \left[\frac{e^{\beta\mu H\cos\theta}}{\beta\mu B}\right]_0^\pi = \\ &= -\frac{4\pi}{\beta\mu H}\frac{e^{-\beta\mu H} - e^{\beta\mu H}}{2} = \\ &= \frac{4\pi}{\beta\mu H}\sinh(\beta\mu H) \end{aligned}$$

The average magnetic moment in $z$-direction is

$$\begin{aligned} M_1^z = \langle\mu_z\rangle &= \int \mu\cos\theta f_B(\theta) = \frac{\mu}{Z_1}\int \cos\theta e^{\beta\mu H\cos\theta} d\Omega = \\ &= \frac{\mu}{Z_1}\int \frac{1}{\beta\mu}\frac{d}{dH} e^{\beta\mu B\cos\theta} d\Omega = \\ &= \frac{1}{Z_1\beta}\frac{d}{dH}\int e^{\beta\mu H\cos\theta} d\Omega = \frac{1}{Z_1\beta}\frac{dZ_1}{dH} = \\ &= \frac{1}{\beta}\frac{d\ln Z_1}{dH} \end{aligned}$$

The total magnetisation is $M^z = NM_1^z$

$$\begin{aligned} M^z = NM_1^z &= \frac{N}{\beta}\frac{d}{dH}\ln Z_1 = \frac{N}{\beta}\frac{d}{dH}\sinh\left(\frac{4\pi}{\beta\mu H}\beta\mu H\right) = \\ &= \frac{N}{\beta}\frac{d}{dH}\left[\ln\sinh(\beta\mu H) - \ln H\right] = \\ &= \frac{N}{\beta}\left[\mu\beta\frac{\cosh(\beta\mu H)}{\sinh(\beta\mu H)} - \frac{1}{H}\right] = \\ &= N\mu\left[\coth(\beta\mu H) - \frac{1}{\beta\mu H}\right] = N\mu\left[\coth(x) - \frac{1}{x}\right] \end{aligned}$$

In the limits

- $T \ll 1$ and/or $H \gg 1$ i.e. $x \gg 1$

  $$\frac{M_1^z}{\mu} \approx 1 - \frac{1}{x} \approx 1$$

  i.e. no agitation or the magnetic field forces all dipoles in one direction, so we get saturation.

- $T \gg 1$ and/or $H \ll 1$ i.e. $x \ll 1$

  $$\frac{M_1^z}{\mu} \approx \frac{1 + x + \frac{x^2}{2} + 1 - x + \frac{x^2}{2}}{1 + x + \frac{x^2}{2} - (1 - x + \frac{x^2}{2})} - \frac{1}{x} = \frac{2 + x^2}{2x} - \frac{1}{x} = \frac{x}{2}$$

  i.e. very agitated system or no influence by $H$ so no magnetisation. As $H \to 0$, $M^z \to 0$

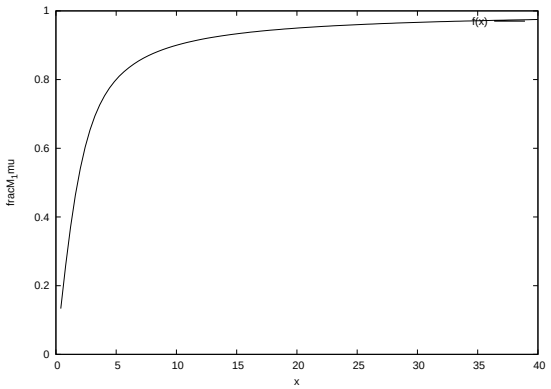



Figure 3.1: Ratio of classical magnetisation in dependence on $x = \beta\mu H$

### 3.1.1 Curie Law

For $T \gg 1$ the susceptibility goes like

$$\chi = \frac{C}{T}$$

It can be easily seen that it holds for this model as

$$\chi = \frac{M^z}{H} = \frac{1}{2}\mu^2\beta = \frac{\mu^2}{2k}\frac{1}{T}$$

### 3.1.2 Calculate $C_V$

as $C_V = \frac{\partial E}{\partial T}$ and $\langle E \rangle = -HM_1^z$ we get

$$\begin{aligned} C_V &= \frac{\partial}{\partial T}\left[-N\mu H\left(\coth(\mu\beta H) - \frac{1}{\mu\beta H}\right)\right] = \\ &= -NH\mu\frac{\partial\beta}{\partial T}\left[-\frac{\mu H}{\sinh^2(\mu\beta H)} + \frac{1}{\mu H\beta^2}\right] = \\ &= \mu NHk\beta^2\left[-\frac{\mu H}{\sinh^2(\mu\beta H)} + \frac{1}{\mu H\beta^2}\right] = \\ &= Nk\left[1 - \frac{\mu^2H^2\beta^2}{\sinh^2(\beta\mu H)}\right] \end{aligned}$$

This violates the 3rd law as $C_V \not\to 0$ as $T \to 0$. It is sensible, as this model is classical.

## 3.2 Quantum mechanical Brillouin ionic paramagnetism

Choose $H = (0, 0, H)$. Now $\langle E \rangle = -\mu H \langle J_z \rangle$, $\langle J_z \rangle = m\hbar$.

### 3.2.1 Model for $j = \frac{1}{2}$

$$Z_1 = \sum_m e^{\mu\beta Hm\hbar} = e^{\frac{1}{2}\hbar\mu H\beta} + e^{-\frac{1}{2}\hbar\mu H\beta}$$

So we get for the magnetisation

$$\begin{aligned} M_1^z &= \frac{1}{\beta}\frac{\partial}{\partial H}\ln Z_1 = \frac{1}{\beta}\frac{\partial}{\partial H}\ln\left(e^{\frac{1}{2}\hbar\mu H\beta} + e^{-\frac{1}{2}\hbar\mu H\beta}\right) = \\ &= \frac{1}{\beta}\frac{\mu\beta\hbar}{2}\frac{e^{\frac{1}{2}\hbar\mu H\beta} - e^{-\frac{1}{2}\hbar\mu H\beta}}{e^{\frac{1}{2}\hbar\mu H\beta} + e^{-\frac{1}{2}\hbar\mu H\beta}} = \\ &= \frac{\mu\hbar}{2}\tanh\left(\frac{1}{2}\hbar\mu\beta H\right) \\ \frac{M_1^z}{\frac{\mu\hbar}{2}} &= \tanh\left(\frac{1}{2}\hbar\mu\beta H\right) = \tanh x \qquad x = \frac{1}{2}\hbar\mu\beta H \end{aligned}$$

In the limits we get

- $T \ll 1$ and/or $H \gg 1$ i.e. $x \gg 1$

$$\frac{M_1^z}{\frac{\hbar\mu}{2}} \approx 1$$

Saturation

- $T \gg 1$ and/or $H \ll 1$ i.e. $x \ll 1$

$$\frac{M_1^z}{\frac{\hbar\mu}{2}} \approx \frac{1+x-(1-x)}{1+x+1-x} = x$$

The only difference to the classical calulation is the slope for $T \gg 1$

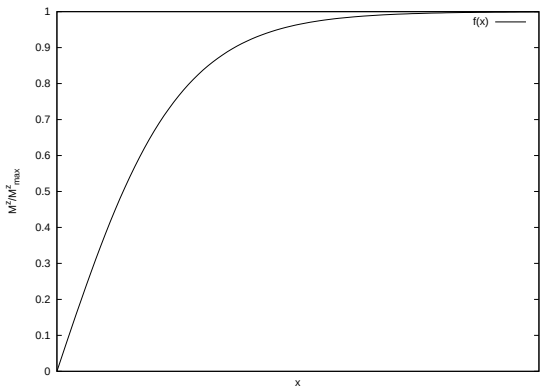



Figure 3.2: Ratio of quantum magnetisation in dependence of $x = \frac{1}{2}\hbar\mu\beta H$

### Curie Law

Again the Curie law holds for $T \gg 1$:

$$\chi = \frac{1}{2}\mu\hbar\frac{1}{2}\hbar\mu\beta = \frac{1}{4}\hbar^2\mu^2\beta =$$
$$= \frac{\hbar^2\mu^2}{4k}\frac{1}{T} = \frac{C_{\frac{1}{2}}}{T}$$

### Calculate $C_V$

$\langle E\rangle = -BM_1^z = -\frac{\hbar\mu H}{2}\tanh\left(\frac{\hbar\mu H\beta}{2}\right)$ i.e.

$$C_V = N\frac{\partial\langle E\rangle}{\partial T} = -N\frac{\hbar\mu H}{2}(-k\beta^2)\frac{1}{\cosh^2\left(\frac{\hbar\mu\beta B}{2}\right)} \xrightarrow{\beta\to\infty} 0$$

### 3.2.2 Model for $j = 1$

$$Z_1 = e^{\hbar\mu H\beta} + e^{-\hbar\mu H\beta} + 1$$

$$\begin{aligned} M_1^z &= \frac{1}{\beta}\frac{\partial}{\partial H}\ln\left(e^{\hbar\mu H\beta} + e^{-\hbar\mu H\beta} + 1\right) = \\ &= 2\hbar\mu\frac{\sinh(\hbar\mu\beta H)}{e^{\hbar\mu H\beta} + e^{-\hbar\mu H\beta} + 1} \\ \frac{M_1^z}{\hbar\mu} &= \frac{\sinh x}{e^x + e^{-x} + 1} \qquad x = \hbar\mu B\beta \end{aligned}$$

in the limits

- $T \ll 1$ and/or $H \gg 1$ i.e. $x \gg 1$

$$\frac{M_1^z}{\hbar\mu} \approx \frac{e^{\hbar\mu\beta H}}{e^{\hbar\mu\beta H} + 1} \approx 1$$

  i.e. Saturation

- $T \gg 1$ and/or $H \ll 1$ i.e. $x \gg 1$

$$\frac{M_1^z}{\hbar\mu} \approx \frac{1 + x - (1 - x)}{1 + x + 1 - x + 1} = \frac{2x}{3}$$

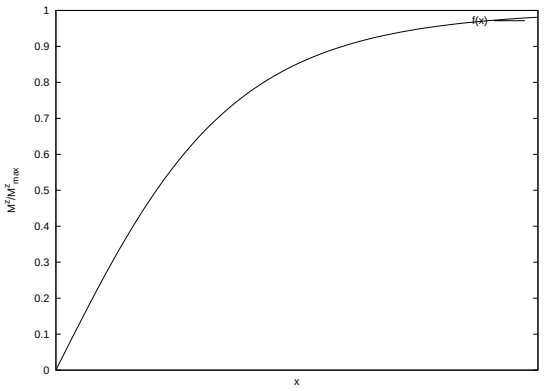



Figure 3.3: Ratio of quantum magnetisation in dependence of $x = \hbar\mu\beta H$

**Calculate $C_V$**

$\langle E\rangle = -BM_1^z = -\hbar\mu H\frac{2\sinh x)}{e^x+e^{-x}+1}$ with $x = \hbar\mu\beta H$, so

$$C_V = N\frac{\partial\langle E\rangle}{\partial T} = 2kx^2\frac{(e^x+e^{-x}+1)\cosh x - \sinh x(e^x-e^{-x})}{(e^x+e^{-x}+1)^2} =$$
$$= 2kx^2\frac{2\cosh^2 x - 2\sinh^2 x + \cosh x}{(2\cosh x+1)^2} = 2kx^2\frac{2+\cosh x}{(2\cosh x+1)^2} =$$
$$\underset{T\ll 1}{\approx} T \ll 12kx^2\frac{2+e^x}{(2e^x+1)^2} = 2kx^2e^{-x}\frac{2e^{-x}+1}{(2+e^-x)^2} \to 0$$

as in 3rd law

### 3.2.3 Brillouin functions $B_j(x)$

For arbitrary $j$ we have $-j \le m \le j$, i.e. $(2j+1)$ values for $m$. So we get for the partition function with $y = \hbar\mu\beta H$

$$Z_1 = \sum_{m=-j}^{j} e^{my} = e^{jy} + e^{(j-1)y} + \ldots e^{-jy} =$$
$$= e^{jy}\sum_{n=0}^{2j} e^{-ny} = e^{jy}\frac{1-e^{-y(2j+1)}}{1-e^{-y}} = e^{jy}\frac{e^{-y\frac{(2j+1)}{2}}\left(e^{y\frac{(2j+1)}{2}} - e^{-y\frac{(2j+1)}{2}}\right)}{e^{-\frac{y}{2}}\left(e^{\frac{y}{2}} - e^{-\frac{y}{2}}\right)} =$$
$$= e^{y\left(j-\frac{2j+1}{2}+\frac{1}{2}\right)}\frac{\sinh\left(y\frac{2j+1}{2}\right)}{\sinh\frac{y}{2}} = \frac{\sinh\left((j+\frac{1}{2})\hbar\mu\beta H\right)}{\sinh\frac{\hbar\mu\beta H}{2}}$$

Define $x = jy$, so

$$Z_1 = \frac{\sinh\left(x(1+\frac{1}{2j})\right)}{\sinh\frac{x}{2j}}$$

So for the magnetisation we get

$$\begin{aligned}
M_1^z =& \frac{1}{\beta}\frac{\partial}{\partial H}\ln Z_1 = \frac{1}{\beta}\frac{\partial x}{\partial H}\frac{\partial}{\partial x}\ln\left(\frac{\sinh\left(x(1+\frac{1}{2j})\right)}{\sinh\frac{x}{2j}}\right) = \\
=& \frac{j\hbar\mu\beta}{\beta}\frac{\sinh\frac{x}{2j}}{\sinh\left(x(1+\frac{1}{2j})\right)} \\
& \frac{\left(1+\frac{1}{2j}\right)\sinh\frac{x}{2j}\cosh\left(x(1+\frac{1}{2j})\right) - \frac{1}{2j}\cosh\frac{x}{2j}\sinh\left(x(1+\frac{1}{2j})\right)}{\sinh^2\frac{x}{2j}} = \\
=& j\hbar\mu\coth\left(x(1+\frac{1}{2j})\right) + \frac{\hbar\mu}{2}\frac{\sinh\frac{x}{2j}\cosh\left(x(1+\frac{1}{2j})\right) - \cosh\frac{x}{2j}\sinh\left(x(1+\frac{1}{2})\right)}{\sinh\frac{x}{2j}\sinh\left(x(1+\frac{1}{2j})\right)} = \\
=& j\hbar\mu\coth\left(x(1+\frac{1}{2j})\right) + \frac{\hbar\mu}{2}\left[\coth\left(\frac{x}{2j}\right) - \coth\left(x(1+\frac{1}{2j})\right)\right]
\end{aligned}$$

In the limits

- $T \ll 1$ and/or $H \gg 1$ i.e. $x \gg 1$

$$\frac{M_1^z}{j\hbar\mu} \approx 1 - \frac{1}{2j}\frac{e^x}{e^{x\left(\frac{1}{2j}+\frac{2j+1}{2j}\right)}} = 1 - \frac{1}{2je^{\frac{x}{j}}} \approx 1$$

- $T \gg 1$ and/or $H \ll 1$ i.e. $x \ll 1$

$$M_1^z \approx M_1^z(0) + M_1^z(0)'x + \ldots =$$

$M_1^z(0) = 0$, $M_1^z(0)' = \frac{\hbar\mu j(j+1)}{3j}$ (Maple). So we get

$$\frac{M_1^z}{j\hbar\mu} = \frac{j+1}{3j}x$$

Plot

Figure 3.4:

## 3.3 Ferromagnetism

Empirically we find the hysterisis loop, i.e. a residual magnetic moment. Both Para- and Ferromagnetism are due to alignmennt of elementary dipols. Both are QM effects i.e. relevant paramagnetism is Brillouin paramagnetism.

Heisenberg model: with $\vec{S}$ the spin operator. The hamiltonian is

$$H = -\sum_{i \neq j} f_{ij} \vec{s}_i . \vec{s}_j$$

$i, j$ label all permanent elementary dipols. $\left\langle \vec{S} \right\rangle$ =expectation value of $\vec{S}$. We have $\vec{S}_i \propto \vec{\mu}_i$ and $\vec{S}_i \propto \vec{M}$ total magnetisation.

We write $\vec{S}_i$ as $\vec{S}_i = \left\langle \vec{S} \right\rangle + (\vec{S}_i - \left\langle \vec{S} \right\rangle)$ In the mean field approximation we claim $|\vec{S}_i - \left\langle \vec{S} \right\rangle|$ is small vs. $\left\langle \vec{S} \right\rangle$. Then

$$\begin{aligned}
H &= -\sum_{i \neq j} f_{ij} \left[ \left\langle \vec{S} \right\rangle + (\vec{S}_i - \left\langle \vec{S} \right\rangle) \right] . \left[ \left\langle \vec{S} \right\rangle + (\vec{S}_i - \left\langle \vec{S} \right\rangle) \right] = \\
&\approx -\sum_{i \neq j} f_{ij} \left[ \left\langle \vec{S} \right\rangle^2 - 2 \left\langle \vec{S} \right\rangle^2 + \left\langle \vec{S} \right\rangle (\vec{S}_i + \vec{S}_j) \right] = \\
&= -\sum_{i \neq j} f_{ij} \left[ - \left\langle \vec{S} \right\rangle^2 + \left\langle \vec{S} \right\rangle (\vec{S}_i + \vec{S}_j) \right] = \\
&= c_1 |\vec{M}|^2 - \underbrace{c_2}_{=:\lambda N} \vec{\mu} . \vec{M}
\end{aligned}$$

The energy of a dipole moment $\vec{\mu}$ in field $\vec{B}$, $E = -\vec{\mu}.\vec{B}$, is replaced by $E = -\vec{\mu}(\vec{B} + \lambda \vec{M})$. In the Weiss model (mean field approximation) we replace the magnetic field in the Brillouin model by an effective field $B_{eff} = \vec{B} + \lambda \vec{M}$. Restrict to $j = \frac{1}{2}$ Brillouin expression.

$$M_1^z = \frac{\hbar \mu}{2} N \tanh \left( \frac{\hbar \mu}{2} \beta B_{eff} \right)$$

Define $x = \frac{\hbar \mu}{2}$. So the total magnetisation is

$$M = Nx \tanh(x \beta B + x \beta \lambda M)$$

Is there a Curie Law for $T \gg 1$ ?

$$M \approx Nxx\beta(B + \lambda M) = Nx^2 \beta B + Nx^2 \beta \lambda M$$

i.e.

$$M = \frac{Nx^2 \beta B}{1 - Nx^2 \beta \lambda} = \frac{x^2 NB}{\frac{1}{\beta} - x^2 \lambda N}$$

So we get for $\chi = \frac{M}{B}$

$$\chi = \frac{\left( \frac{\hbar \mu}{2} \right)^2 \frac{N}{k}}{T - \left( \frac{\hbar \mu}{2} \right)^2 \frac{\lambda N}{k}}$$

The Curie-Weiss Law for $T \gg 1$ is

$$\chi = \frac{C}{T - T_c}$$

With $C = \left(\frac{\hbar\mu}{2}\right)^2 \frac{N}{k}$ and $T_c = \left(\frac{\hbar\mu}{2}\right)^2 \frac{\lambda N}{k} = x^2 \frac{\lambda N}{k}$ the critical temperature. We can rewrite the magnetisation.

$$x\beta\lambda M = x^2 \beta\lambda \frac{M}{xN} N = \frac{T_c}{T} \frac{M_1^z}{x}$$

i.e. the ratio of magnetisation in z-direction becomes

$$m = \frac{M_1^z}{\frac{\hbar\mu}{2}} = \tanh\left(\frac{\hbar\mu}{2}\beta B + m\frac{T_c}{T}\right)$$

Solve graphically: $y_1(m) = m, y_2(m) = \tanh\left(\frac{\hbar\mu}{2}\beta B + m\frac{T_c}{T}\right)$ The spontaneous magnetisation for $T > T_c$ has only the trivial solution $m_W = 0$ (cf. Figure 3.5) For $T < T_C$ we

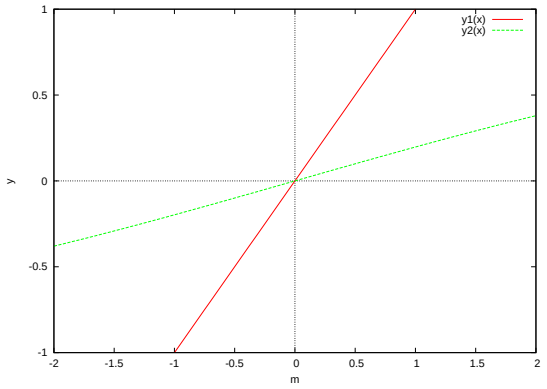



Figure 3.5:

get a nontrivial solution $m_W > 0$ (cf. Figure 3.6) Whether we have a non-trivial solution depends on the slope of $y_2$

$$\frac{dy_2}{dm}|_0 = \frac{T_c}{T} \frac{1}{\cosh^2 \frac{T_c m}{T}} = \frac{T_c}{T} = \begin{cases} > 1 & T < T_c \\ < 1 & T > T_c \end{cases}$$

i.e. we get the non-trivial solution only for $T < T_c$

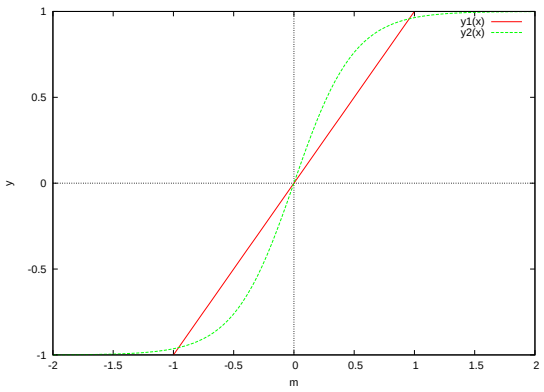



Figure 3.6:

# 4 Diamagnetism

Diamagnetic moment is result of electrons moving in "cyclotron" orbits in external uniform magnetic field $\vec{H}$. The magnetic field is characterised by $\vec{H} = \nabla\vec{A}$ and $\vec{H} \to \vec{H}$ if $\vec{A} \to \vec{A} + \nabla\Lambda$ i.e. gauge invariance of $\vec{H}$. The interaction of charged matter with $\vec{A}$ is described by

$$\vec{p} \to \vec{p} - \frac{e}{c}\vec{A}$$

## 4.1 Classically

Now calculate classically with the Boltzmann distribution

$$F = -\frac{1}{\beta}\ln Z_N \qquad\qquad \vec{M} = -\left(\frac{\partial F}{\partial H}\right)_{T,N}$$

as $P = -\frac{\partial F}{\partial V}$, when $dW = PdV$. Now $dW = \vec{M}d\vec{H}$.

$$\begin{aligned} Z_1 &= \int d\vec{p}d\vec{x}e^{-\beta E} = \\ &= \int d\vec{p}d\vec{x}\exp\left(-\frac{\beta}{2m}(\vec{p} - \frac{e}{c}\vec{A}).(\vec{p} - \frac{e}{c}\vec{A})\right) \end{aligned}$$

As $\vec{A}$ is constant we change variables to $\vec{p'} = \vec{p} + \frac{e}{c}\vec{A}$

$$Z_1 = \int d\vec{p'}d\vec{x}e^{-\frac{\beta}{2m}\vec{p'}.\vec{p'}}$$

i.e. $Z_1$ independent of $\vec{A}$ i.e. independent of $\vec{H}$, $\Rightarrow F$ is independent of $\vec{H}$

$$\Rightarrow \vec{M} = \frac{\partial F}{\partial H} = 0$$

classically no magnetisation

## 4.2 Quantum mechanically

Now calculate with Fermi-Dirac statistics[1]. Recall:

$$F = NE_0(T) - kT\sum_i \ln\left(1 + e^{\beta(E_0 - E_i)}\right)$$

[1] cf. Peierls "Quantum theory of Solids" §7.2.

### 4.2.1 Find Energy spectrum

We have to find $E_i$ i.e. solve the Stationary state Schrödinger equation. The Sch. eq. of electron of mass $m$ and charge $-e$ is

$$\begin{aligned}
\hat{H}\psi &= E\psi \\
\frac{1}{2m}\hat{p}^2\psi &= E\psi \\
\frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}\right)^2\psi &= E\psi \\
\left(\frac{\partial}{\partial x_i}-\frac{ie}{c\hbar}A_i\right)^2\psi &= -\underbrace{\frac{2mE}{\hbar^2}}_{=:k_0^2}\psi
\end{aligned}$$

Where $\vec{A}$ is the magnetic vector potential of the uniform magnetic field $\vec{H}$. Choose $\vec{H}=(0,0,H)$. As we $\vec{A}$ is not uniquely defined, we can choose $\vec{A}=(0,Hx,0)$.

$$\left(\frac{\partial}{\partial x_i}-\frac{ie}{c\hbar}A_i\right)^2=\frac{\partial^2}{\partial x^2}+\left(\frac{\partial^2}{\partial y^2}-\frac{ie}{c\hbar}Hx\right).\left(\frac{\partial^2}{\partial y^2}-\frac{ie}{c\hbar}Hx\right)+\frac{\partial^2}{\partial z^2}$$

The differential operator only involves $x$. Try the following $\psi$:

$$\psi(x,y,z)=u(x)e^{i(yk_y+zk_z)}$$

$$\begin{aligned}
\frac{\partial^2}{\partial x^2}\psi &= \frac{\partial^2 u}{\partial x^2}e^{i(yk_y+zk_z)} \\
\frac{\partial^2}{\partial z^2}\psi &= -k_z^2\psi \\
\left(\frac{\partial^2}{\partial y^2}-\frac{ie}{c\hbar}Hx\right).\left(\frac{\partial^2}{\partial y^2}-\frac{ie}{c\hbar}Hx\right)\psi &= \left(ik_y-\frac{ieH}{\hbar c}x\right)^2\psi=-\left(k_y-\frac{eH}{\hbar c}x\right)^2\psi
\end{aligned}$$

So the Schrödinger equation becomes

$$\left[\frac{\partial^2 u}{\partial x^2}-\left(k_y-\frac{eH}{\hbar c}x\right)^2u-k_z^2u\right]e^{i(yk_y+zk_z)}=-\frac{2mE}{\hbar^2}ue^{i(yk_y+zk_z)}$$

This is a 1 dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial x^2}+\frac{\hbar^2}{2m}\frac{e^2H^2}{\hbar^2c^2}\left(x-\frac{\hbar c}{eH}k_y\right)^2u=\left(E-\frac{\hbar^2}{2m}k_z^2\right)u$$

We transform it to a SHO. Let $\xi=x-\frac{\hbar c}{eH}k_y$ i.e.

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial \xi^2}+\frac{1}{2}m\frac{e^2H^2}{m^2c^2}\xi^2u=\left(E-\frac{\hbar^2}{2m}k_z^2\right)u$$

With the cyclotron frequency $\omega_H = \frac{eH}{mc}$ and $E' = E - \frac{\hbar^2}{2m}k_z^2$ this is the "normal" SHO Sch. eq. centered on $x = \frac{\hbar c}{eH}k_y$

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial \xi^2} + \frac{1}{2}m\omega_H^2\xi^2 u = E'u$$

The energy spectrum is

$$E'_n = \left(n + \frac{1}{2}\right)\hbar\omega_H$$

i.e. the real energy spectrum is

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_H + \frac{\hbar^2}{2m}k_z^2$$

Impose Boundary conditions in $y$ and $z$. We have a free particle in a large box of sides $(L_x, L_y, L_z)$ i.e.

$$k_y = \frac{2\pi}{L_y}l \qquad\qquad k_z = \frac{2\pi}{L_z}m$$

$n$ and $m$ are related via $E_n$; $m = \frac{L_z}{2\pi}k_z = \pm\frac{L_z}{2\pi}\frac{\sqrt{2m}}{\hbar}\sqrt{E_n - \left(n+\frac{1}{2}\right)\hbar\omega_H}$
The centre of motion is $x_0 = \frac{\hbar c}{eH}k_y$ but $x$ is restricted to $0 \le x \le L_x$ i.e. $0 \le k_y \le \frac{eH}{c\hbar}L_x$.

### 4.2.2 Calculate $g(E)$

Estimate $g(E)$ to do statmech, i.e. find $h(E)$ such that $g(E) = \frac{dh}{dE}$. The number of states up to energy $E_n = \left(n+\frac{1}{2}\right)\hbar\omega_H$ is $h(E_n) = \sum_{n'=0}^{n} lm(n')$ as for each energy we have a degeneracy of $l$ in $y$-direction; and for given $n'$ we have $m(n')$ possible values for $m$ so the total energy does not exceed $E_n$.

$$\begin{aligned}
h(E_n) &= \sum_{n'=0}^{n} lm = \\
&= \sum_{n'} \frac{L_y L_z}{(2\pi)^2}k_y k_z = \\
&= \frac{L_y L_z}{(2\pi)^2}\sum_{n'}{}' \frac{eH}{c\hbar}L_x\frac{\sqrt{2m}}{\hbar}\sqrt{E_n - \left(n'+\frac{1}{2}\right)\hbar\omega_H} = \\
&= \frac{L_x L_y L_z}{(2\pi)^2}\frac{eH\sqrt{2m}}{\hbar^2 c}\sum_{n'}{}' \sqrt{E_n - \left(n'+\frac{1}{2}\right)\hbar\omega_H}
\end{aligned}$$

$\sum'$ subject to sqrt being real. Now treat energy continuous and calculate $F$.

### 4.2.3 Calculate $\chi$

$$
\begin{aligned}
F &= NE_0 - kT \int \ln\left[1 + e^{\beta(E_0 - E)}\right] (g(E)dE) = \\
&= NE_0 - kT \int \ln\left[1 + e^{\beta(E_0 - E)}\right] \frac{dh}{dE} dE = \\
&= NE_0 - kT \left\{ \left[ h \ln\left[1 + e^{\beta(E_0 - E)}\right] \right]_0^\infty - \int h \frac{d}{dE} \ln\left[1 + e^{\beta(E_0 - E)}\right] dE \right\} = \\
&= NE_0 - kT\beta \int \frac{h(E)}{e^{\beta(E - E_0)} + 1} dE = \\
&= NE_0 - \int h(E) f_{FD}(E) dE
\end{aligned}
$$

This being a low $T$ phenomenon: $f_{FD}(E) = \theta(E - E_0)$;

$$
\begin{aligned}
h &= \ldots \sum_{n'} \left[ E - \left( n + \frac{1}{2} \right) \omega_H \hbar \right]^{1/2} = \\
&= \ldots \sum_{n'} \frac{2}{3} \frac{d}{dE} \left[ E - \left( n + \frac{1}{2} \right) \omega_H \hbar \right]^{3/2}
\end{aligned}
$$

i.e. we get

$$
\begin{aligned}
F &= NE_0 - \frac{2}{3} \frac{L_x L_y L_z}{(2\pi)^2} \frac{e\sqrt{2m}}{\hbar^2 c} H \int f_{FD}(E) \frac{d}{dE} \sum_{n'} \left[ E - \left( n + \frac{1}{2} \right) \omega_H \hbar \right]^{3/2} dE = \\
&= NE_0 - \frac{2}{3} \frac{L_x L_y L_z}{(2\pi)^2} \frac{e\sqrt{2m}}{\hbar^2 c} H \int_0^{E_0} \frac{d}{dE} \sum_{n'} \left[ E - \left( n + \frac{1}{2} \right) \omega_H \hbar \right]^{3/2} dE = \\
&= NE_0 - \frac{2}{3} \frac{L_x L_y L_z}{(2\pi)^2} \frac{e\sqrt{2m}}{\hbar^2 c} H \sum_{n'} \left[ E_0 - \left( n + \frac{1}{2} \right) \omega_H \hbar \right]^{3/2} = \\
&=
\end{aligned}
$$

Now evaluate $\sum$ (not us!) (Poisson summation formula[2])

$$
\sum \left[ \epsilon_0 - \frac{1}{2} - n \right]^{3/2} = \frac{2}{5} \epsilon_0^{5/2} - \frac{1}{16} \epsilon_0^{1/2}
$$

[2] cf. Titchmarsh "Theory of Fourier integral" §2.8.

i.e. with $\epsilon_0 = \frac{E_0}{\omega_H \hbar}$

$$
\begin{aligned}
F &= NE_0 - \frac{2}{3}\frac{L_x L_y L_z}{(2\pi)^2}\frac{e\sqrt{2m}}{\hbar^2 c} H(\hbar\omega_H)^{3/2}\left[\frac{2}{5}\epsilon_0^{5/2} - \frac{1}{16}\epsilon_0^{1/2}\right] = \\
&= NE_0 - \frac{2}{3}\frac{L_x L_y L_z}{(2\pi)^2}\frac{e\sqrt{2m}}{\hbar^2 c} H(\hbar\omega_H)^{3/2}\left(\frac{1}{\hbar\omega_H}\right)^{5/2}\left[\frac{2}{5}E_0^{5/2} - \frac{1}{16}E_0^{1/2}(\hbar\omega_H)^2\right] = \\
&= NE_0 - \frac{2}{3}\frac{L_x L_y L_z}{(2\pi)^2}\frac{e\sqrt{2m}}{\hbar^3 c}\left[\frac{2}{5}E_0^{5/2} - \frac{1}{16}E_0^{1/2}\left(\frac{eH}{c}\right)^2\right] = \\
&= NE_0 - \frac{2}{3}\frac{L_x L_y L_z}{(2\pi)^2}\frac{e\sqrt{2m}}{\hbar^3 c}E_0^{1/2}\left[\frac{2}{5}E_0^2 - \frac{1}{16}\left(\frac{eH}{c}\right)^2\right]
\end{aligned}
$$

i.e. the magnetisation is

$$
\begin{aligned}
M = -\frac{\partial F}{\partial H} &= -\frac{2}{16}\frac{2}{3}\frac{L_x L_y L_z}{(2\pi)^2}\frac{e\sqrt{2m}}{\hbar^3 c}E_0^{1/2}H = \\
&= -\frac{1}{12}\frac{L_x L_y L_z}{(2\pi)^2}\frac{e\sqrt{2m}}{\hbar^3 c}E_0^{1/2}H
\end{aligned}
$$

The susceptibility is

$$
\chi = \frac{\partial M}{\partial H} = -\frac{1}{12}\frac{L_x L_y L_z}{(2\pi)^2}\frac{e\sqrt{2m}}{\hbar^3 c}E_0^{1/2} < 0
$$

i.e. against the external field.

# 5 Electrons in periodic potential

The electrons move in a periodic potential, e.g. a crystal lattice.

## 5.1 Periodic Functions

We need to describe periodic functions $f(x) = f(x+L)$. We do this, using Fourier Series:

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{k_n i x}$$

with the wave-"vector" $k_n = \frac{2\pi n}{L}$ and $c_n = \frac{1}{L}\int_0^L f(x)e^{-ik_n x}dx$. In 3 dimensions we get

$$f(\vec{x}) = \sum_{\{n\}} e^{i\vec{k}_{\{n\}}\vec{x}}$$

with $\vec{k}_{\{n\}} = \frac{2\pi}{L}\left(n_1\vec{k}_1 + n_2\vec{k}_2 + n_3\vec{k}_3\right)$ and $c_{\vec{k}} = \frac{1}{L^3}\int d^3x f(x)e^{-i\vec{k}\vec{x}}$. $\vec{k}$ is the reciprocal vector to $\vec{x}$. So if $f$ is periodic along the standard axis $\vec{e}_1, \vec{e}_2, \vec{e}_3$ we get reciprocal wave-vectors $\vec{k}_{\{n\}}$ so that for any periodic translation $\vec{X}_{\{m\}} = m_1 L\vec{e}_1 + m_2 L\vec{e}_2 + m_3 L\vec{e}_3$ the inner product $\vec{k}_{\{n\}}.\vec{X}_{\{m\}} = l2\pi$ i.e. this means periodicity.

## 5.2 Bravais Lattice

A periodic 3 dimensional structur (crystal) can be described using the Bravais Lattice, using three vectors $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ to form a parallelepiped. After every translation by a vector $\vec{X}_{\{n\}} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ with $n_1, n_2, n_3 \in \mathbb{N}$ the structure looks the same. The volume of this parallelopiped is

$$V_a = |\vec{a}_1.(\vec{a}_2 \times \vec{a}_3)| \qquad \text{cyclic in } 1,2,3$$

or using the Levi-Civita symbol

$$V_a = |\epsilon_{ijk}(a_1)_i(a_2)_j(a_3)_k|$$

Now we have to expand a function periodic on the Bravais Lattice

$$f(\vec{x}) = f(\vec{x} + \vec{X}_{\{n\}})$$

with $\vec{X}_{\{n\}} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ i.e. we need an analogue of Fourier Series, i.e. we need to find a "reciprocal lattice" space with wave-vectors $\vec{K}_{\{m\}}$ such that $\vec{K}_{\{m\}}.\vec{X}_{\{n\}} = l2\pi$

## 5.3 Reciprocal Lattice

We have the Bravais Lattice $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ and define the reciprocal lattice $(\vec{b}_1, \vec{b}_2, \vec{b}_3)$ by

$$\vec{b}_1 = \frac{c}{V_a}(\vec{a}_2 \times \vec{a}_3)$$

with a dimensionless constant $c$. Using the Levi-Civita symbol

$$\vec{b}_i = \frac{c}{2V_a}\epsilon_{ijk}(\vec{a}_j \times \vec{a}_k)$$

(The 2 in the denominater results from summation and antisymmetry of Levi-Civita-symbol)

The reciprocal of $(\vec{b}_1, \vec{b}_2, \vec{b}_3)$ should be $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$. So calculate the reciprocal of $\vec{b}_1$

$$\begin{aligned}
\vec{c}_1 &= \frac{c}{V_b}(\vec{b}_2 \times \vec{b}_3) \\
(c_1)_i &= \frac{c}{V_b}\epsilon_{ijk}(b_2)_j(b_3)_k = \\
&= \frac{c}{V_b}\epsilon_{ijk}\left[\frac{c}{V_a}\epsilon_{jmn}(a_3)_m(a_2)_n\right]\left[\frac{c}{V_a}\epsilon_{kpq}(a_1)_p(a_2)_q\right] = \\
&= \frac{c^3}{V_a^2 V_b}\epsilon_{ijk}\epsilon_{kpq}\epsilon_{jmn}(a_3)_m(a_1)_n(a_1)_p(a_2)_q = \\
&= \frac{c^3}{V_a^2 V_b}\epsilon_{ijk}\epsilon_{pqk}\epsilon_{jmn}(a_3)_m(a_1)_n(a_1)_p(a_2)_q =
\end{aligned}$$

Using the identity $\epsilon_{ijk}\epsilon_{pqk} = \delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp}$ we get

$$(c_1)_i = \frac{c^3}{V_a^2 V_b}\epsilon_{jmn}(a_3)_m(a_1)_n\left[(a_1)_i(a_2)_j - (a_1)_j(a_2)_i\right] =$$

The first term is $\epsilon_{jmn}(a_2)_j(a_3)_m(a_1)_n = V_a$, the second term is $\epsilon_{jmn}(a_1)_n(a_1)_j = 0$ because of antisymmetry of $\epsilon$. SO we have

$$\begin{aligned}
(c_1)_i &= \frac{c^3}{V_a^2 V_b}(a_1)_i V_a = \\
&= \frac{c^3}{V_a V_b}(a_1)_i = (a_1)_i
\end{aligned}$$

provided $c^3 = V_a V_b$

*Note.* Works in 4 dimension too.

$$\begin{aligned} V_a &= \epsilon_{ijkl}(a_1)_i(a_2)_j(a_3)_k(a_4)_l \\ (b_1)_i &= \frac{c}{V_a}\epsilon_{ijkl}(a_2)_j(a_3)_k(a_4)_l \\ (b_2)_i &= -\frac{c}{V_a}\epsilon_{ijkl}(a_3)_j(a_4)_k(a_1)_l \\ (b_3)_i &= \frac{c}{V_a}\epsilon_{ijkl}(a_4)_j(a_1)_k(a_2)_l \\ (b_4)_i &= -\frac{c}{V_a}\epsilon_{ijkl}(a_1)_j(a_2)_k(a_3)_l \end{aligned}$$

And $\vec{c}_1 = \vec{a}_1$ provided $c^4 = V_a V_b$.
For 2 dimensions

$$V_a = \epsilon_{ij}(a_1)_i(a_2)_j$$

and the reciprocals are defined as

$$\begin{aligned} (b_1)_i &= \frac{c}{V_a}\epsilon_{ij}(a_2)_j \\ (b_2)_i &= -\frac{c}{V_a}\epsilon_{ij}(a_1)_j \end{aligned}$$

Again $\vec{c}_1 = \vec{a}_1$ provided $c^2 = V_a V_b$

Now back to 3d again. We had

$$(b_l)_i = \frac{c}{2V_a}\epsilon_{lmn}\epsilon_{ijk}(a_m)_j(a_n)_k$$

Now calculate the inner product of a lattice vector and a reciprocal lattice vector. e.g. for $\vec{a}_l.\vec{b}_1$. As $\vec{b}_1 = \frac{c}{V_a}\vec{a}_2 \times \vec{a}_3$ we get

$$\vec{a}_i\vec{b}_1 = \begin{cases} \frac{c}{V_a}\vec{a}_1(\vec{a}_2 \times \vec{a}_3) & i = 1 \\ \frac{c}{V_a}\vec{a}_i(\vec{a}_2 \times \vec{a}_3) & i = 2,3 \end{cases} = \begin{cases} c & i = 1 \\ 0 & i = 2,3 \end{cases}$$

So for general vectors it is easy to see

$$\vec{a}_i\vec{b}_j = c\delta_{ij}$$

Now define a $\vec{K}_{\{m\}} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$. Then for a translation $\vec{X}_{\{n\}} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ in x-space we get

$$\vec{K}.\vec{X} = \sum_{i,j} n_i m_j \vec{a}_i\vec{b}_j = \sum_{i,j} n_i m_j c\delta_{i,j} = c\sum_i n_i m_i$$

i.e. to get a multiple of $2\pi$ for arbitrary $n, m$ we must have

$$c = 2\pi$$

Then the reciprocal lattice is defined by

$$\vec{b_l} = \frac{2\pi}{2V_a}\epsilon_{lmn}\left(\vec{a}_m \times \vec{a}_n\right) \tag{5.1}$$

And the Fourier decomposition of $f$ is

$$f(\vec{x}) = \sum_{\{m\}} c_{\{m\}} e^{i\vec{K}_{\{m\}}.\vec{x}}$$

## 5.4 Bloch's theorem

We have the stationary state Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\Delta + V(\vec{x})\right]\psi = E\psi$$

Our solution should satisfy

$$|\psi(\vec{x}+\vec{X})|^2 = |\psi(\vec{x})|^2$$

i.e.

$$\psi(\vec{x}+\vec{X}) = e^{i\alpha}\psi(\vec{x})$$

For some real phase $\alpha$. Now Bloch's theorem is that

$$\psi(\vec{x}+\vec{X}) = e^{i\vec{k}.\vec{X}}\psi(\vec{x}) \tag{5.2}$$

For some wave-vector $\vec{k}$ in reciprocal space. (5.2) expresses the action of a generator of translations on the lattice. (For generator of translations in continuum see Note below)

*Note.* In continuum theory we can define the generator of translations via:

$$\begin{aligned}
\psi(\vec{x}+\vec{a}) &= \psi(\vec{x}) + a_i\frac{\partial\psi}{\partial x_i}|_{\vec{x}} + \frac{1}{2!}a_i a_j \frac{\partial}{\partial x_i}\frac{\partial\psi}{\partial x_j}|_{\vec{x}} + \ldots = \\
&= \psi(\vec{x}) + ia_i\left(-i\frac{\partial}{\partial x_i}\right)\psi + \frac{1}{2!}ia_i ia_j\left(-i\frac{\partial}{\partial x_i}\right)\left(-i\frac{\partial}{\partial x_j}\right)\psi + \ldots = \\
&= \psi(\vec{x}) + ia_i k_i\psi + \frac{1}{2!}ia_i ia_j k_i k_j\psi + \ldots = \\
&= e^{i\vec{k}\vec{a}}\psi
\end{aligned}$$

with $\vec{k} = \frac{\vec{p}}{\hbar}$.

### 5.4.1 Brillouin Zone

As $\vec{k}$ is unique up to addition of a reciprocal lattice vector, we can restrict $\vec{k}$ to the basic cell of the reciprocal lattice, also called Brillouin Zone. The Brillouin zone is defined as Wigner-Seitz primitive cell in the reciprocal lattice. To construct the Brillouin zone, choose a lattice point as origin and connect it to every lattice point nearby. On each connecting line draw at a perpendicular plane at the midpoint. The enclosed space is a primitiv cell. No two points in the interior are equal (with respect to addition of lattice vectors) and the whole space can be filled with these cells. For example in one dimension our Bravais lattice is defined by $a$, then the reciprocal lattice vector is $\frac{2\pi}{a}$ and the reciprocal lattice is given by $n\frac{2\pi}{a}$. So our Brilloun zone is just $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$.
For two dimensions, let us take a reciprocal lattice defined by the primitive vectors $\vec{b}_1 = (3, 0)$ and $\vec{b}_2 = (1, 2)$ Then the Brillouin zone has the form shown in Figure 5.1

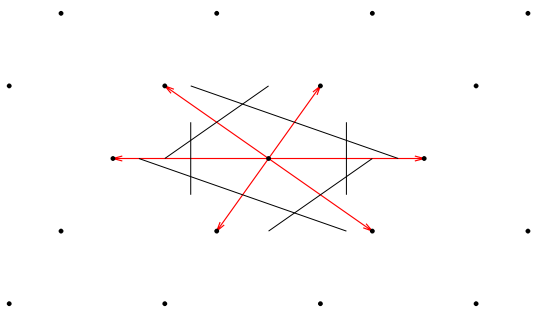


Figure 5.1: Brillouin zone for $\vec{b}_1$ and $\vec{b}_2$

## 5.5 Schrödinger equation

Now exploit Bloch's theorem. Factor out $e^{i\vec{k}\vec{x}}$ from $\psi(\vec{x})$

$$\begin{aligned}\psi(\vec{x}) =& e^{i\vec{k}\vec{x}} u_{\vec{k}}(\vec{x}) \\ \psi(\vec{x}+\vec{X}) =& e^{i\vec{k}\vec{x}} e^{i\vec{k}\vec{X}} u_{\vec{k}}(\vec{x}+\vec{X})\end{aligned}$$

By Bloch's theorem we have we get

$$\begin{aligned}e^{i\vec{k}\vec{X}}\psi(\vec{x}) &= e^{i\vec{k}\vec{x}} e^{i\vec{k}\vec{X}} u_{\vec{k}}(\vec{x}+\vec{X}) \\ e^{i\vec{k}\vec{X}} e^{i\vec{k}\vec{x}} u_{\vec{k}}(\vec{x}) &= e^{i\vec{k}\vec{x}} e^{i\vec{k}\vec{X}} u_{\vec{k}}(\vec{x}+\vec{X})\end{aligned}$$

i.e.

$$u_{\vec{k}}(\vec{x}+\vec{X}) = u_{\vec{k}}(\vec{x}) \tag{5.3}$$

Now tackle the Schrödinger equation:

$$\begin{aligned}
\Delta\psi &= \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_i}\psi = \\
&= \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_i}\left(e^{ik_jx_j}u_{\vec{k}}(\vec{x})\right) = \\
&= \frac{\partial}{\partial x_i}\left(e^{ik_jx_j}\frac{\partial u_{\vec{k}}}{\partial x_i} + ik_ie^{ik_jx_j}u_{\vec{k}}(\vec{x})\right) = \\
&= e^{i\vec{k}\vec{x}}\left(\Delta u_{\vec{k}}(\vec{x}) + 2ik_i\frac{\partial u_{\vec{k}}}{\partial x_i} + (ik_i)^2\right) = \\
&= e^{i\vec{k}\vec{x}}\left(\frac{\partial}{\partial x_i} + ik_i\right)^2 u_{\vec{k}}(\vec{x}) = \\
&= e^{i\vec{k}\vec{x}}\left(\nabla + i\vec{k}\right)^2 u_{\vec{k}}(\vec{x})
\end{aligned}$$

So we get a new Schödinger equation

$$\left(\nabla + i\vec{k}\right)^2 u_{\vec{k}} + \frac{2m}{\hbar^2}\left(E - V(x)\right)u_{\vec{k}} = 0 \tag{5.4}$$

Now if $u_{\vec{k}}$ is solution with $E(\vec{k})$ so is $u^*_{\vec{k}}$. Conjugate equation (5.4) to get

$$\left(\nabla - i\vec{k}\right)^2 u^*_{\vec{k}} + \frac{2m}{\hbar^2}\left(E - V(x)\right)u^*_{\vec{k}} = 0$$

But this is the equation for $-\vec{k}$, so $u^*_{\vec{k}} = u_{-\vec{k}}$ and $E(-\vec{k}) = E(\vec{k})$ But for some points on the Boundary of the Brillouin zone $\vec{k} = -\vec{k}$ (with respect to r.l. vector addition) and so

$$\begin{aligned}
E(\vec{k}) &= E(-\vec{k}) \\
\nabla E(\vec{k})|_{\vec{k}} &= \nabla E(-\vec{k})|_{-\vec{k}} \\
\nabla E(\vec{k})|_{\vec{k}} &= -\nabla E(\vec{k})|_{-\vec{k}} \\
\nabla E(\vec{k})|_{\vec{k}} &= -\nabla E(\vec{k})|_{\vec{k}} \\
\nabla E(\vec{k})|_{\vec{k}} &= 0
\end{aligned}$$

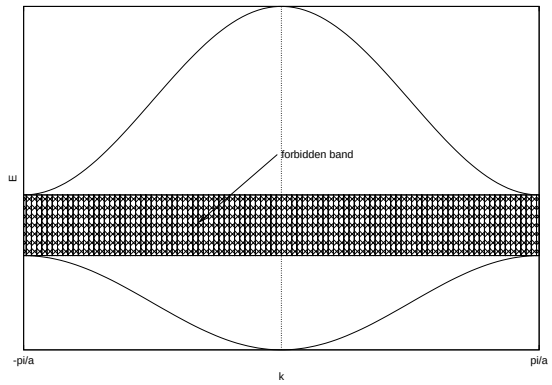
i.e. at some points of the Boundary the derivative of $E$ vanishes. Furthermore, if the lattice has sufficient symmetry, the symmetry also carries on to the reciprocal lattice. e.g. symmetry at the plane $x = 0$, i.e. $(k_x, k_y, k_z) = (-k_x, k_y, k_z)$ for some points on the boundary and therefore

$$\begin{aligned}
E(k_x, k_y, k_z) &= E(-k_x, k_y, k_z) \\
\frac{\partial}{\partial k_x}E(k_x, k_y, k_z)|_{\vec{k}} &= \frac{\partial}{\partial k_x}E(-k_x, k_y, k_z)|_{-k_x,k_y,k_z} \\
\frac{\partial}{\partial k_x}E(\vec{k})|_{\partial BZ} &= 0
\end{aligned}$$

In general, it can be shown, that for sufficient symmetry the derivative of $E$ in direction normal to the boundary vanishes.
e.g. in one dimension our lattice is obviously symmetric in the $x$-direction and we get $\frac{\partial E}{\partial k_x}|_{\pm\frac{\pi}{a}} = 0$

## 5.6 Band structure

Restrict to one dimensional case. From our previous results (and experiments) we expect to see band structures in the energy, as in Figure 5.6.




### 5.6.1 Effective Mass

The velocity of an electron is the group velocity of its wave-packet and is given by

$$v = \frac{1}{\hbar}\frac{\partial E}{\partial k} \tag{5.5}$$

Now an external force $F$ acting on the electron results in an acceleration:

$$\frac{dv}{dt} = \frac{1}{m}F \tag{5.6}$$

But we also have

$$\frac{dv}{dt} = \frac{1}{\hbar}\frac{\partial^2 E}{\partial k^2}\frac{dk}{dt}$$

But $k = \frac{p}{\hbar}$ and $F = \frac{dp}{dt}$, so we get

$$\frac{1}{m}F = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}\frac{dp}{dt} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}F$$

So we define the effective mass as

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2} \tag{5.7}$$

The particle would react to an external force, as if it had a mass $m^*$4.

- At the bottom of the higher band, the curvature of the energy is positiv, so our particle has positive effective mass, and $\frac{m^*}{m} < 1$
- At the top of the lower band, the curvature of the energy is negative, so our particle would have negative mass. It is an effective antiparticle or "hole"

### 5.6.2 Strong binding

$$V(x) = \sum_k U_k(x)$$

with $U_k(x)$ being the potential of the individual atomic cites, $U_k(x) = U(x-ka)$. Assume our potential is (spherically) symmetric, i.e. the Hamiltonian is symmetric, i.e. our eigenfunctions are symmetric or antisymmetric. Only small overlap, i.e. restrict to nearest neighbours, i.e. for an electron trapped primarly at atomic cite $m$, $\phi_m \approx 0$ outside the potentials $m-1, m, m+1$. The Schrödinger equation we have to solve is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + \sum_k U_k(x)\psi = E\psi \tag{5.8}$$

Now we have solutions $\phi_m(x)$ for each individual potential, i.e.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi_m + \sum_m U_k(x)\phi_m = E_0\phi_m$$

and we can write the solutions as

$$\phi_m(x) = \phi(x - ma)$$

with $\phi(x)$ being the solution for the potential at the origin.

Use perturbation theory to calculate $\psi(x)$. Take $\psi$ as a linear superpositions of the unperturbed solutions

$$\psi(x) = \sum_m A_m\phi_m(x) \tag{5.9}$$

and use variational method to minimize the energy

$$\delta_{A_m} E = 0$$

Now the energy is

$$\begin{aligned}
E = \langle H\rangle &= \frac{\langle\psi, H\psi\rangle}{\langle\psi,\psi\rangle} = \\
&= \frac{\int \left(\sum_m A_m^*\phi_m^*\right) H \left(\sum_n A_n\phi_n\right) dx}{\int \left(\sum_m A_m^*\phi_m^*\right)\left(\sum_n A_n\phi_n\right) dx} = \\
&= \frac{A_m^*\int \phi_m^* H\phi_n dx A_n}{A_m^*\int \phi_m^*\phi_n dx A_n} = \\
&= \frac{A_m^* H_{mn} A_n}{A_m^* J_{mn} A_n} = \\
&= \frac{(A, HA)}{(A, JA)}
\end{aligned}$$

We notice, that trivially $J_{mn} = J^*_{nm}, H_{mn} = H^*_{nm}$ as the identity and the Hamiltonian are hermitian. Because of periodicity the Hamiltonian can write

$$\begin{aligned} H_{mn} &= \int \phi^*_m H \phi_n dx = \int \phi^*(x - ma) H \phi(x - na) dx = \\ &= \int \phi^*(x) H \phi(x + (m-n)a) dx \end{aligned}$$

Then because of (anti-)symmetry of our eigen-functions and of the Hamiltonian we can reflect at the origin and get

$$\begin{aligned} H_{mn} &= \int \phi^*(-x) H \phi(-x + (m-n)a) dx = \\ &= \int \phi^*(-x) H \phi(x) H \phi(-(x - (m-n)a)) dx = \\ &= \int \phi^*(x) H \phi(x + (n-m)a) dx = H_{nm} \\ &= H(|m-n|) \end{aligned}$$

Additionally, as $H$ is hermitian and symmetric, it must be real. Now variate

$$\begin{aligned} 0 = \delta_{A^*_k} E &= \sum \frac{\partial E}{\partial A^*_k} \delta A^*_k = \\ &= \frac{1}{(A, JA)} \sum_k \left[ \frac{\partial}{\partial A^*_k} (A, HA) - \frac{(A, HA)}{(A, JA)} \frac{\partial}{\partial A^*_k} (A, JA) \right] \delta A^*_k = \\ &= \frac{1}{(A, JA)} \sum_k \sum_n \left[ H_{kn} A_n - E J_{kn} A_n \right] \delta A^*_k = \end{aligned}$$

For arbitrary $\delta_{A^*_k}$

$$\sum_n \left( H_{kn} - E J_{kn} \right) A_n = 0$$

Now calculate the matrix element $H_{mn}$:

$$\begin{aligned} H_{mn} &= \int \phi^*_m(x) \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \sum_k U_k(x) \right] \phi_n(x) dx = \\ &= \int \phi^*_m \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U_n \right] \phi_n dx + \int \phi^*_m \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V - U_n \right] \phi_n dx = \\ &= \int \phi^*_m E_0 \phi_n dx + \int \phi^*_m \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V - U_n \right] \phi_n dx = \\ &= E_0 J_{mn} + h_{mn} \end{aligned}$$

Again $h_{mn} = h(|m-n|)$ as $H$ and $J$ are. Our variational equation becomes

$$\sum_n (H_{mn} - EJ_{mn})\, A_n = 0$$
$$\sum_n (E_0 J_{mn} + h_{mn} - EJ_{mn})\, A_n = 0$$
$$\sum_n (E - E_0) J_{mn} A_n = h_{mn} A_n$$

Now the overlap restricts the function only to the nearest neighbours

$$J_{mn} A_n \approx A_m$$

and

$$\begin{aligned} h_{mn} \approx & h_{m,m-1} A_{m-1} + h_{m,m} A_m + h_{m,m+1} A_{m+1} = \\ & = (A_{m-1} + A_{m+1}) \int \phi_m^* (V - U_{m-1}) \phi_{m-1} dx + \\ & \quad + A_m \int \phi_m^* (V - U_m) \phi_m dx = \\ & = A_m \int \phi_m^* \left(U_{m-1} + U_{m+1}\right) \phi_m dx + \\ & \quad + (A_{m-1} + A_{m+1}) \int \phi_m^* U_{m+1} \phi_{m-1} dx \end{aligned}$$

Now use the differences notation:

$$\int \phi_m^* \left(U_{m-1} + U_{m+1}\right) \phi_m dx = h(0) = \int \phi^*(x) \left(U(x+a) + U(x-a)\right) \phi(x) dx$$
$$\int \phi_m^* U_{m+1} \phi_{m-1} dx = h(1) = \int \phi^*(x) U(x-a) \phi(x-a) dx$$

So we get

$$\begin{aligned} h_{mn} A_n &= h(0) A_m + h(1)(A_{m-1} + A_{m+1}) \\ &= (E - E_0) J_m n A_n \end{aligned}$$

or

$$E - E_0 = \frac{h_{mn} A_n}{J_{mn} A_n} = h(0) + h(1) \frac{A_{m-1} + A_{m+1}}{A_m} \tag{5.10}$$

We can express the complex numbers $A_m$ as $A_m = e^{im\kappa}$ for a complex number $\kappa$. So we get with our lattice constant $a$

$$\psi(x) = \sum_m A_m \phi_m(x) = \sum_m e^{im\kappa} \phi_m(x) = \sum_m e^{im\kappa} \phi(x - ma)$$

Bloch's theorem stated

$$\psi(x+a) = e^{ika}\psi(x)$$

and so

$$\sum_m e^{im\kappa}\phi(x-(m-1)a) = e^{ika}\sum_n e^{in\kappa}\phi(x-na)$$

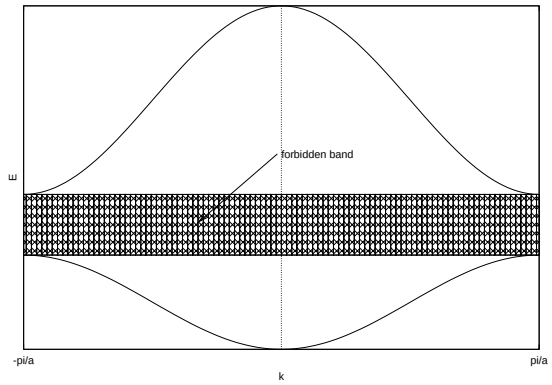
equation equal functions gives $n = m-1$ and so

$$\begin{aligned} e^{im\kappa} &= e^{i(k+n\kappa)a} \\ e^{im\kappa} &= e^{i(k+(m-1)\kappa)a} \\ e^{i\kappa a} &= e^{ika} \end{aligned}$$

with $k$ and $a$ real, so we can re-express our energy change

$$E - E_0 = h(0) + h(1)\frac{A_{m-1} + A_{m+1}}{A_m} = h(0) + h(1)2\cos ka \tag{5.11}$$

Note that our "constants" $h(0)$ and $h(1)$ were dependent on our eigen-functions i.e. on our energy level $E_0$. Our energy level becomes stretched into a band of width $4h(1)$. If the original energy levels are further apart than $4h(1)$ we get forbidden band between them.




### 5.6.3 Weak binding, Nearly free electrons (NFE)

Use stationary state perturbation theory. The unperturbed eigenstate of the electron is the plane wave

$$\psi(x) = \frac{1}{\sqrt{L}}e\frac{i}{\hbar}px$$

The energy is

$$E_p \propto p^2$$

So we have degenerate energy levels. We therefore need to calculate perturbation for degenerate levels

### Degenerate energy level perturbation

Start we the exactly solvable problem

$$H_0\psi^{(0)} = E^{(0)}\psi^{(0)}$$

And assume there exist two distinc solutions with the same (degenerate ) $E^{(0)}$

$$H_0\psi_1^{(0)} = E^{(0)}\psi_1^{(0)}$$
$$H_0\psi_2^{(0)} = E^{(0)}\psi_2^{(0)}$$

As they are distinct we can assume $\left\langle \psi_1^{(0)}, \psi_2^{(0)} \right\rangle = 0$. Now introduce a small perturbing potential $V$

$$H = H_0 + gV$$

And we have to solve the Schrödinger equations

$$H\psi_1 = E_1\psi_1 \tag{5.12}$$
$$H\psi_2 = E_2\psi_2 \tag{5.13}$$

where $E_1 \neq E_2$ (degeneracy removed) and

$$E_1 = E^{(0)} + gE_1^{(1)} + \dots$$
$$E_2 = E^{(0)} + gE_2^{(2)} + \dots$$

and

$$\psi_1 = c_{11}\psi_1^{(0)} + c_{12}\psi_2^{(0)} + g\psi_1^{(1)} + \dots$$
$$\psi_2 = c_{21}\psi_1^{(0)} + c_{22}\psi_2^{(0)} + g\psi_2^{(1)} + \dots$$

Substituting these into (5.12) and (5.13) and comparing coefficients up to $g^1$ we get

$$c_{11}\left(E^{(0)} - H_0\right)\psi_1^{(0)} + c_{12}\left(E^{(0)} - H_0\right)\psi_2^{(0)} = 0 \tag{5.14}$$
$$\left(E^{(0)} - H_0\right)\psi_1^{(1)} + \left(E_1^{(1)} - V\right)\left(c_{11}\psi_1^{(0)} + c_{12}\psi_2^{(0)}\right) = 0 \tag{5.15}$$
$$c_{21}\left(E^{(0)} - H_0\right)\psi_1^{(0)} + c_{22}\left(E^{(0)} - H_0\right)\psi_2^{(0)} = 0 \tag{5.16}$$
$$\left(E^{(0)} - H_0\right)\psi_2^{(1)} + \left(E_2^{(1)} - V\right)\left(c_{21}\psi_1^{(0)} + c_{22}\psi_2^{(0)}\right) = 0 \tag{5.17}$$

Now taking inner product of (5.15) with $\psi_1^{(0)}$ we get

$$E^{(0)}\left\langle \psi_1^{(0)}, \psi_1^{(1)} \right\rangle - \left\langle \psi_1^{(0)}, H_0\psi_1^{(1)} \right\rangle + c_{11}E_1^{(1)} - c_{11}\left\langle \psi_1^{(0)}, V\psi_1^{(0)} \right\rangle - c_{12}\left\langle \psi_1^{(0)}, V\psi_2^{(0)} \right\rangle = 0$$

So in our matrix notation we get

$$V_{11}c_{11} + V_{12}c_{12} = E_1^{(1)}c_{11}$$

And take inner product of (5.15) with $\psi_2^{(0)}$

$$E^{(0)}\left\langle \psi_2^{(0)}, \psi_1^{(1)} \right\rangle - \left\langle \psi_2^{(0)}, H_0\psi_1^{(1)} \right\rangle + c_{12}E_1^{(1)} - c_{11}V_{21} - c_{12}V_{22} = 0$$

$$V_{21}c_{11} + V_{22}c_{12} = E_1^{(1)}c_{12}$$

Doing the same with (5.17) yields

$$V_{11}c_{21} + V_{12}c_{22} = E_2^{(1)}c_{21}$$
$$V_{21}c_{21} + V_{22}c_{22} = E_2^{(1)}c_{22}$$

So both first order corrections can be calculated from solving the eigenvalue equation

$$\begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E^{(1)} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

So we get the two corrections by solving

$$\det \begin{bmatrix} V_{11} - E^{(1)} & V_{12} \\ V_{21} & V_{22} - E^{(1)} \end{bmatrix} = 0$$

### Nearly free electrons

Our unperturbed eigen-functions were

$$\psi_k(x) = \frac{1}{\sqrt{L}} e^{ikx}$$

with $L = Na$ and the energy-eigenvalues were degenerate, as

$$E_p = ck^2 = E_{-k}$$

Now calculate the first order energy corrections on introducing our perturbing potential. Our potential is periodic, so we can express it as a Fourier Series

$$V(x) = \sum_{n=-\infty}^{\infty} c_n e^{i\frac{2\pi n}{a}x}$$

To calculate the energy corrections we need to calculate the matrix elements between two degenerate eigen-functions $\psi_k$ and $\psi_{-k}$.

$$V_{kk'} = \frac{1}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} V(x)e^{i(k'-k)x}dx$$

Now for $k' = k$ we get

$$V_{kk} = \frac{1}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} V(x)dx$$

By choosing our energy zero level, we can always make this integral zero. The off-diagonal matrix elements are

$$V_{k,-k} = \frac{1}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} V(x)e^{i2kx}dx =$$
$$= \frac{1}{L}\sum_n c_n \int_{-\frac{L}{2}}^{\frac{L}{2}} e^{i\left(\frac{2\pi n}{a}+2k\right)x}dx$$

And $V_{-k,k} = V^*_{k,-k}$

At the Borders of our Brillouin Zones $k = m\frac{\pi}{a}$, so we get

$$V_{m\frac{\pi}{a},-m\frac{\pi}{a}} = \frac{1}{L}\sum_n c_n \int_{-\frac{L}{2}}^{\frac{L}{2}} e^{i\left(\frac{2\pi n}{a}+2m\frac{\pi}{a}\right)x}dx =$$
$$= \frac{1}{L}\sum_n c_n \int_{-\frac{L}{2}}^{\frac{L}{2}} e^{i\frac{2\pi}{a}(n+m)x}dx =$$

Unless $n + m = 0$ this integral is zero because of periodicity. So we obtain

$$V_{m\frac{\pi}{a},-m\frac{\pi}{a}} = c_{-m}$$

So by solving the for the roots of

$$\det\begin{bmatrix} -E_m^{(1)} & V_{m,-m} \\ V_{-m,m} & -E_m^{(1)} \end{bmatrix} = 0$$

We get the energy correction at the zone Boundary as

$$E_m^{(1)} = \pm|c_m| \tag{5.18}$$