Preview:

- Pauli Exclusion rule
- $N_f = E_f$

\[
\psi(r) = \frac{e^{-iK\cdot r}}{2\pi}
\]

\[
-H\psi = \frac{\hbar^2}{2m} \nabla^2 \psi + \frac{\hbar^2 k^2}{2m} e^{iK\cdot r} = E e^{iK\cdot r}
\]

\[
E = \frac{\hbar^2 k^2}{2m}
\]

\[
\langle k \rangle = \frac{e}{\hbar}, \quad \langle 0 \rangle = \frac{i0}{\hbar}
\]

\[
E_f = \frac{\hbar^2 k_f^2}{2m}
\]

We find $k_f$ by summing all occupied states:

\[
\frac{2\pi}{L} = \frac{2\pi}{L} = \left( \frac{2\pi}{L} \right)^3
\]

\[
= \left( \frac{2\pi}{L} \right)^3 K^3 = \text{space volume per electron}
\]

\[
DOS_k = 2 \cdot \left( \frac{L}{2\pi} \right)^3 = \frac{2V}{(2\pi)^3}
\]

\[
N = DOS_k \cdot \text{volume of } k_f
\]

\[
= \frac{2V}{(2\pi)^3} \cdot \frac{4\pi^2}{3} a_f^3
\]

\[
= \frac{V}{3\pi^2} a_f^3 \rightarrow k_f = \left( \frac{3\pi^2 N/V}{a_f^3} \right)^{1/3}
\]

\[
k_f = \frac{\hbar}{m}
\]

\[
E_f = \frac{\hbar^2 k_f^2}{2m}
\]

\[
T_f = E_f/k_p
\]

$10^8 \text{cm/s}$

$1-10 \text{eV}$

$10^4 \text{K}$
We now want to calculate thermal properties of the electron gas. Our calculations are much simplified if we work w/ \( D(E) \), the density of states per unit energy:

\[
N_{\leq E} = 2 \cdot \left( \frac{1}{2\pi} \right)^{3/2} \frac{V}{\frac{3}{2}} \, K^3
\]

\[
= \frac{\sqrt{V}}{3\pi^{1/2}} \, K^3
\]

\[
= \frac{\sqrt{V}}{3\pi^{1/2}} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{3/2} = N_{\leq E}
\]

We want the states per unit energy between \( E \) & \( E + dE \), so

\[
\frac{N_{\leq E + dE} - N_{\leq E}}{dE} \bigg|_{dE \to 0} = \frac{dN_{\leq E}}{dE}
\]

\[
D(E) = \frac{dN_{\leq E}}{dE} = \frac{\sqrt{V}}{3\pi^{1/2}} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}
\]

Using \( N_{\leq E} \),

\[
D(E) = \frac{3N_{\leq E}}{dE}
\]
Ground state! $e^{-T=0}$

The total energy of the ground state is:

$$E_{tot} = \int_{0}^{E_f} E D(E) dE$$

$$= \int_{0}^{E_f} E \frac{3N_{EE}}{2E} \left( \frac{\sqrt{2mE}}{\hbar} \right) dE$$

$$= \frac{3N_{EE}}{2} \left( \frac{\sqrt{2m}}{\hbar} \right)^{3/2} \int_{0}^{E_f} \sqrt{E} dE$$

$$= \frac{3}{2} \left( \frac{\sqrt{2m}}{\hbar} \right)^{3/2} E_f^{5/2}$$

[ $T=0$ ]

What is $E(T)$?

(electrons)

Only particles near $E_f$ can move as we increase $T$ from 0.
We need to know the thermal occupation of single electron states.

At $T=0$:

At higher $T$, we use the Gibb's Factor:

$$p(n) = \frac{e^{-n(E-E_F)/k_B T}}{Z_6} \quad \text{[For fixed $E, \mu, T$]}
$$

$$Z_6 = \sum_n e^{-n(E-E_F)/k_B T}
$$

For electrons, $n = 0, 1$, then $Z_6 = 1 + e^{-(E-E_F)/k_B T}$

Then

$$\langle n \rangle = \sum_n n p(n)
$$

$$= 0 \cdot 1 + 1 \cdot \frac{e^{-(E-E_F)/k_B T}}{1 + e^{-(E-E_F)/k_B T}}
$$

$$= \frac{e^{-(E-E_F)/k_B T}}{1 + e^{-(E-E_F)/k_B T}}
$$

$$f(E, \mu, T) \quad n = \frac{1}{e^{(E-E_F)/k_B T} + 1} \quad \text{[Fermi-Dirac Distribution]}$$
Q. Does \( f(E, M, T) \) reproduce known \( T = 0 \) occupation?

\[
f(E, M, 0) = \begin{cases} \frac{1}{2} & E = M \\ 1 & E < M \\ 0 & E > M \end{cases}
\]

A PPT of \( f(E, M, T) \)

The transition from occupied to unoccupied occurs at \( E = M \), which is also the Fermi Energy, \( \mu \)

\[
\mu = E_f \quad [T = 0]
\]

The chemical potential can be viewed as the free energy per particle, so at \( T = 0 \), adding one more particle (electron) will add \( E_f \) of energy to the system since available states are at the Fermi energy.

At \( T > 0 \), only electrons near \( E_f \) can gain extra energy (thermal), how much energy?

\[
\Delta(E_f) = \frac{2N}{2E_f}
\]

\[ \text{# of electrons} \int_{E_f - k_B T}^{E_f} dE = \frac{3N}{2E_f} k_B T = \frac{3N}{2} \frac{T}{T_f} \]

Total # of electrons in system

\[
U = \frac{3}{2} N \frac{T}{T_f} k_B T
\]

Heat capacity \( T > 0 \) but not too high \( T \).

\[
C = \frac{dU}{dT} = 3N k_B \frac{T}{T_f}
\]
This is a good approximation since $T \ll T_f$ for most metals. In fact

$$T_{\text{melting}} \ll T_f$$

From the curves of $F(E, N, T)$, we also note that $M \propto E_f$ for many temperatures of interest.

If we do a better job of calculating $\Delta U$, then

$$\Delta U = \int_{U(T \neq 0)}^{E_f} (E) f(E) dE - \int_{0}^{E_f} (E) f(E) dE$$

$$= \frac{C_u}{d} = \frac{\pi^2}{2} N k_B \frac{1}{T_f}$$

Hence, for $T \ll T_f$ and $T > 7.0$, the total heat capacity includes electronic + phononic contributions:

$$C = C_{el} + C_{ph}$$

$$= \gamma T + AT^3$$

$$\gamma = \frac{1}{2} \pi^2 N k_B \frac{1}{T_f}$$

$$\langle E \rangle = \gamma + AT^2$$

$$(C_T) = A g_{\gamma} T^2$$
Electron Heat Capacity Coefficient

\[
\frac{f}{2} = \frac{\pi^2 N k_B T}{h^2} \cdot \frac{1}{3\pi^2 n^3} \Rightarrow \rho \propto M^3
\]

\(\text{density of electron}^3\)

From experimental data:

\[
\frac{\rho_{\text{eexp}}}{\rho_{\text{therm}}} = \frac{M_{\text{eexp}}}{M_{\text{eexp}}} = \frac{m_{\text{eexp}}}{m_{\text{eexp}}} = \frac{m^*}{m}
\]

\[
M^* = \frac{\rho_{\text{exper}}}{\rho_{\text{therm}}} \cdot M
\]

<table>
<thead>
<tr>
<th>Material</th>
<th>(\rho_{\text{eexp}})</th>
<th>(\rho_{\text{therm}})</th>
<th>(\frac{m^*}{m})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>7.4</td>
<td>7.4</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>Na</td>
<td>4.1</td>
<td>4.1</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>Cu</td>
<td>5.5</td>
<td>5.5</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>Mn</td>
<td>5.2</td>
<td>5.2</td>
<td>&gt; &gt; 1</td>
</tr>
</tbody>
</table>

\(m^* < m\)

- Band structure mass of \(e^-\) in periodic potential \(m^* = \frac{\hbar^2}{2} \frac{1}{\text{dE/dH}}\)
- Electron-Phonon interaction: electron drag ion core.
- Electron-Electron interaction.

There were some early signs of the limitations of the free electron gas theory.
Magnetic Spin Susceptibility (Pauli Paramagnetism):

Why?

\[ H = \frac{p^2}{2m} + g_J m_B \vec{B} \cdot \vec{S} \]

\[ m_B = \frac{eB}{2mc} \times 0.67 \text{ K}_B \quad (\text{Kilojoule/Mole}) \]

\[ E(\uparrow) = \frac{\hbar^2 k^2}{2m} + m_B B \]

\[ E(\downarrow) = \frac{\hbar^2 k^2}{2m} - m_B B \]

The spin magnetization of the system (moments per unit volume):

\[ M = -\frac{1}{V} \frac{\partial E}{\partial B} \]

\[ = - \left( \frac{\# \uparrow - \# \downarrow}{V} \right) m_B \]

\[ B \to 0 \]

\[ D_\uparrow(E) \quad \text{and} \quad D_\downarrow(E) \]

\[ p_0 \quad \text{and} \quad E_F \]
The \# of spins that your nuclei form \( \uparrow \rightarrow \downarrow \): ?

\[ D(E_F) \cdot \mu_B \cdot B \]

\[ M = \frac{D(E_F) \mu_B B}{v} \]

Electron Spin Magnetization
Review:

\[ D(E) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} \]

\[ f(F, M, T) = \frac{1}{e^{(F/E_F)/k_B T} + 1} \quad \text{[From Dirac Distribution]} \]

\[ C = \frac{\pi^2}{2} \frac{N k_B T}{F_F} \]

\[ C = \gamma T + A T^3 \]

\[ m_{\text{bulk}}^* = \frac{\gamma_{\text{ext}}}{\gamma_{\text{thr}}}, \quad m > m^* \]

\[ h = \frac{p^2}{2M} + \frac{e}{M} \bar{b} \cdot \bar{\sigma} \]

\[ \mathcal{E}(\mathbf{K}, \pm \mathbf{K}) = \frac{\hbar^2 k^2}{2} \pm \bar{M} \cdot \mathbf{b} \]

\[ M = \frac{(N_d - N_F) M_B}{\sqrt{V}} \]

\[ = \frac{D(E_F) M_B}{\sqrt{V}} \cdot \bar{b} \]

\[ = \frac{3 N_M M_B^2}{V E_F} - \bar{b} \]
Electrons in Fields (Drude Model):

\[ \vec{e} \rightarrow n \quad \vec{E}, \vec{B} \]

\[ N, 2 \Rightarrow \quad \vec{F} = \frac{d\vec{p}}{dt} = \frac{\hbar \dot{\vec{\pi}}}{\hbar} = -e \left( \vec{E} + \vec{v} \times \vec{B} \right) - \frac{\vec{p}}{\tau} \quad \Rightarrow \text{scattering time} \]

\[ \vec{B} = 0; \text{ In steady state, } \frac{d\vec{p}}{dt} = 0 \quad \Rightarrow \]

\[ \vec{p} = -e\vec{E} \quad \Rightarrow \quad \vec{\pi} = \frac{\hbar \vec{v}}{\hbar} \]

\[ \begin{align*}
\vec{E} & \quad \vec{E} \\
\vec{K} & \quad \frac{\vec{E}}{e}
\end{align*} \]

\[ \begin{align*}
\vec{p}_{\text{tot}} & \neq 0!!
\end{align*} \]

\[ \vec{v}_x = -\frac{e\vec{E}x}{m} \quad \Rightarrow \quad \vec{J} = -ne\vec{v}_x \]

\[ \begin{align*}
\vec{J} & = ne^2 \frac{\vec{E}}{m} \\
\rho & = \frac{m}{ne^2} \]

\[ \sigma = \frac{ne^2}{m} \]

Determined by phonons, impurities, & electrons.

At high, \[ \gamma \frac{1}{\tau} \ll \sigma \frac{1}{\tau} \]}
In a magnetic field, $\mathbf{B} = Bz$

\[
\mathbf{E} = \frac{d\mathbf{p}}{dt} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \frac{\mathbf{p}}{m}
\]

\[
\mathbf{v} = -\frac{e}{m} (\mathbf{E} + \mathbf{v} \times \mathbf{B})
\]

\[
\mathbf{v}^2 = M^2 \mathbf{E}^2 \\ \Rightarrow \quad \mathbf{E} = -e\mathbf{v} = -e\mathbf{v} \mathbf{B} = \mathbf{E} \mathbf{B}
\]

\[
\begin{pmatrix}
  v_x \\
  v_y \\
  v_z 
\end{pmatrix} = \begin{pmatrix}
  -e\frac{\mathbf{E}_x}{m} - e^2 \mathbf{v} \cdot \mathbf{v}_y \\
  -e\frac{\mathbf{E}_y}{m} + e^2 \mathbf{v} \cdot \mathbf{v}_x \\
  -e\frac{\mathbf{E}_z}{m}
\end{pmatrix}
\]

\[
\mathbf{E} = \frac{eB}{m} \mathbf{v}_y \\
\omega_c \equiv \frac{eB}{m} \quad \text{[Cyclotron Frequency]}
\]

Transverse electric field required for $v_y = 0$.

\[E_y = -e\frac{\mathbf{E}_x}{m} \mathbf{E}_x\]

\[
\mathbf{E} = \mathbf{v} \times \mathbf{B} \\
\text{where} \quad \mathbf{v} = \begin{pmatrix}
  0 \\
  -\frac{e}{m} \\
  \frac{e}{m}
\end{pmatrix} \quad \rho = \frac{ne^2 \gamma}{m}
\]

\[
\mathbf{v} = \frac{eB}{m} \mathbf{v}_y \\
\mathbf{J} = \mathbf{v} \mathbf{B} \\
\mathbf{J} \times \mathbf{B} \\
\mathbf{E} = \frac{eB}{m} \mathbf{v}_y
\]

\[
\mathbf{B}_H = \frac{\mathbf{J} \times \mathbf{B}}{|J|} = -\frac{E_y}{J_x B} = -\frac{1}{ne}
\]

\[
\text{[Hall Coefficient]}
\]
The Hall measurement allows me to measure the electron density $n$.

It also lets me calculate the valence:

$$ n = \frac{1}{-eB_H} $$

$$ \frac{c}{n_{\text{atomic}}} = \frac{1}{-eB_H \cdot n_{\text{atomic}}} $$

<table>
<thead>
<tr>
<th>Material</th>
<th>$n_{\text{atomic}}$</th>
<th>Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>Na</td>
<td>1.2</td>
<td>1</td>
</tr>
<tr>
<td>K</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>Cu</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>Be</td>
<td>-0.2</td>
<td>2</td>
</tr>
<tr>
<td>Mg</td>
<td>-0.4</td>
<td>2</td>
</tr>
</tbody>
</table>

Works quite well for some simple metals.

For Be, Mg & others, it gets the sign wrong. Later we'll see that $B_H > 0 \Rightarrow$ charge carriers are positive.

The Drude model cannot account for this positive $B_H$.

Since $B_H = \frac{E_y}{j_x B} = -\frac{1}{n e}$

If we know $n$, $j_x$, then $B_H$, thus we can measure $B$

$$ B = \frac{E_y}{j_x B_H} = -\frac{n e E_y}{j_x} \quad \text{(Hall sensor)} $$
In Hall effect, one chooses materials with smaller $\gamma$ so bigger $B_H$
\[ E_y = B_{J_x} B_H \]
which makes them easier to measure.

**Thermal Transport**

The electronic thermal conductivity is:

\[ K_{el} = \frac{1}{3} \frac{C_v V^2}{T} \]

for an electron? What does use
\[ = \frac{1}{3} \frac{\pi^2}{2} N_h b \frac{T}{T_f} \frac{1}{V} \cdot V_f \cdot (V_f \cdot \gamma) \]

electron move, mean free path, that can move of electrons near $V_f$

\[ = \frac{\pi^2}{3} N_h b \frac{T}{T_f} \left( \frac{1}{2} m V_f^2 \cdot \frac{1}{m} \right) \gamma \]

\[ = \frac{\pi^2}{3} N_h b \frac{T}{T_f} \frac{1}{m} \text{En} \gamma \]

\[ = \frac{\pi^2 n k_B^2 T \gamma}{3 m} \]

- Drude obtained same result by using Boltzmann's Kinetic Theory:
  \[ C_v = \frac{3}{2} n k_B \]
  \[ \overline{v} = \sqrt{\frac{8 k_B T}{m}} \]
Even though he used the incorrect $C_0$ and $\gamma$, the effects cancel if he arrived at the corrected $\kappa\ell$.

A triumph of the Drude theory & the free electron theory was the Wiedemann-Franz Law, which had been known experimentally for a long time:

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

Here:

$$\frac{\kappa\ell}{\sigma\ell} = \frac{T \tau^2 k_B n \frac{T \pi e^2}{m}}{n e^2 \gamma / m}$$

$$= \frac{T \tau^2}{\gamma} \left( \frac{k_B}{e^2} \right)^2 \cdot T$$

$$= L \cdot T$$

$$L = \frac{T \tau^2}{\gamma} \left( \frac{k_B}{e^2} \right)^2 \quad \text{(from \#)}$$

$$\approx 2.45 \times 10^{-5} \text{ W} \cdot \text{m} / \text{K}^2$$

<table>
<thead>
<tr>
<th>Material</th>
<th>$L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
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</tr>
<tr>
<td>Na</td>
<td>2.12</td>
</tr>
<tr>
<td>Cu</td>
<td>2.20</td>
</tr>
<tr>
<td>Fe</td>
<td>2.61</td>
</tr>
<tr>
<td>Br</td>
<td>3.53</td>
</tr>
<tr>
<td>Mg</td>
<td>2.14</td>
</tr>
</tbody>
</table>
The Peltier Effect

Electrical current is also heat current

Peltier current

\[ \overrightarrow{J}_p = \nabla T \overrightarrow{V} \]

heat current density
electrical current density

we have

\[ \overrightarrow{J}_p = \frac{1}{3} C V T \overrightarrow{V} \]

\[ = \frac{\hbar}{6} T T \frac{\alpha}{\nu} \frac{\nu \overrightarrow{V}}{\nu} \]

\[ \overrightarrow{J}_p = \frac{\hbar}{6} \frac{T T \alpha}{T} \overrightarrow{V} \]

\[ \overrightarrow{J} = -ne \overrightarrow{V} \]

\[ \nabla \overrightarrow{\Pi} = -\frac{\eta \hbar}{T} T \overrightarrow{e} \]

\[ \nabla \overrightarrow{\Pi} = -\frac{\eta \hbar}{T} T^2 \overrightarrow{e} \]
The Seebeck coefficient gives the thermo power:

\[ S = \frac{\pi}{T} \]

\[ = -\frac{17^2 \mu B}{6 \mu \ell} \]

\[ \approx -4.3 \times 10^{-6} \text{ V/K} \]

\[ \Delta T = 1 \text{ K} \Rightarrow -4.3 \times 10^{-6} \text{ V} \]
Review:

The free electron model predicts an electronic participation:

\[ \sigma = \sigma(E) \]

\[ \Rightarrow \quad \sigma = \sigma_0 \]

Result of treating electron as a wave.
Result of Pauli exclusion principle.

Electrons in fields:

\[ \frac{d\mathbf{\dot{r}}}{dt} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \frac{m\mathbf{\ddot{r}}}{\epsilon} \]

\[ \mathbf{\dot{v}} = \mathbf{E} \quad \text{and} \quad \mathbf{\ddot{v}} = \mathbf{E} \]

\[ \mathbf{\dot{v}} = \nabla \times (\mathbf{E} \times \mathbf{B}) \]

Hall Field

\[ E_y = \frac{-e\mathbf{v}_y}{m} \mathbf{E}_x \]

This model predicts that the following ratio involving measured or experimentally controllable quantities is related to the \( \mathbf{H} \) density of charge carriers:

\[ \mathbf{R}_H = \frac{E_y}{\mathbf{J}_x B} = -\frac{1}{\mathbf{n} e} \]

Hall coefficient

So \( \mathbf{R}_H \rightarrow \mathbf{n} = \mathbf{e} \mathbf{J} \) (with knowledge of \( m \))
We can also predict the volume, \( n/\text{m}^3 \), from \( n \).

This model also predicts positive Hall Coefficient, which implies a positive charge carrier.

\[
B(E_y) = \frac{E_y}{J_x \cdot A_H}
\]

Thermoelectric:

\[
K_{el} = \frac{1}{3} C_{el} \left( \frac{\mu}{e} \right)^2
\]

\[
= \frac{\pi^2 n k_B^2 e^2}{3m} \cdot T
\]

\[\text{[Thermal conductivity of Electron Gas]}
\]

Wiedeman-Franz Law:

\[
\frac{K_{el}}{\sigma_{el}} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 \cdot T
\]

So measuring \( K_{el} \) and \( \sigma_{el} \) gives a determination of \( k_B \).

The Peltier Effect:

\[
\frac{\Delta T}{\Delta V} = \frac{n k_B T^2}{6 e T^*}
\]

\[\text{[Peltier Coefficient]}
\]

Thermoelectric Effect

\[
S = -4.3 \times 10^{-6} \text{ V/}^\circ
\]

\[\text{[Seebeck Coefficient]}
\]
Where are we?

Bonding:

Reciprocal Space & Direct Space:

\[ f(x) = \sum A_n e^{iG \cdot x} \]

\[ \mathbf{G}_n = \frac{2\pi}{a} \mathbf{n} \]

Crystals:

Scattering of Waves:

\[ \mathbf{K} = \mathbf{K}' + \mathbf{G} \]

\[ \mathbf{K} \cdot (\frac{1}{2} \mathbf{L}) = (\frac{1}{2} \mathbf{L}') \]

\[ e^{i\mathbf{K} \cdot \mathbf{r} - \omega t} \]

Vibrational Waves in Crystals:

Thermal Properties of Phonons:

Each mode

\[ \omega(k) = \sum \omega_n (n_b + 1/2) \]

\[ C = \frac{1}{3} K \]

\[ K = \frac{1}{3} g \]

\[ \mathbf{T}^3 \]
Electronic energy states in a 1D chain (Tight Binding Chain):

\[ |\Psi\rangle = \sum \phi_n |n\rangle \quad \text{[LCAO]} \]

\[ E(k) = -\frac{\hbar^2}{2m} k^2 \]

\[ |g\rangle \text{ not free } e^- \]

Free Electron Model:

Quantum:

\[ H\Psi = E\Psi \quad (Pam\') \]

Classical:

\[ e^- \rightarrow \text{probe} \]

\[ \frac{\hbar^2}{2m} \]

\[ \frac{\nabla}{\nabla} = \sigma E \]

\[ \sigma, \beta_H, E_x \]

\[ f(E_{\text{int}}, T) = \frac{1}{e^{(E_{\text{int}} - E)/k_B T} + 1} \]

\[ C_{\text{el}}(T), K_{\text{el}}(T), M(T) \]

Foilworg (chemical inadequacy):

\[ \beta_H = \frac{1}{ne} > 0 \]

Positive charge carried?

Valence (i.e., number of electrons):

\[ m^* = \frac{m}{k_B T} \]

Electrons are heavier in crystals.

Polar or Insulators?

Bond gaps?

Mean free path can be \(10^8\) a.u.

We have ignored the periodic potential.
Electrons in a periodic potential:

In tight-binding, the electrons are bound tightly to the atomic core and interact weakly with nearest neighbors but not at all with next nearest neighbors:

![Diagram showing overlap and no overlap between orbitals.]

Now we approach the problem from a completely different angle: we assume the electrons are free but interact weakly with all the cores.

**Nearly Free Electron Model:**

\[ H\psi = E\psi \quad \text{where} \quad H = \frac{\hbar^2}{2m} \nabla^2 + V(r) = H_0 + V(r) \]

where \( V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r}) \) (i.e., \( V(\mathbf{r}) \) is periodic in \( \mathbf{R} \)) \( \mathbf{R} \in \text{[Lattice vectors]} \)

We'll take the energy eigenstates of \( H_0 \) as plane waves:

\[ |\mathbf{k}\rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{R}} \]

\[ \langle \mathbf{k}' | \mathbf{k} \rangle = 1 \]

So

\[ H|\mathbf{k}\rangle = \frac{\hbar^2 k^2}{2m} |\mathbf{k}\rangle \]

we now treat \( V(\mathbf{r}) \) as a perturbation and use perturbation theory. In pert. theory, we'll use \( |\mathbf{k}\rangle \) to build up approximate \( |\psi\rangle \) with \( H = H_0 + V(r) \) and also \( E \). In particular,

\[ E = E_0 + E_1 + E_2 + \ldots \]

\[ \frac{\hbar^2 k^2}{2m} \quad \text{1st order} \quad \frac{V(\mathbf{r})}{2m} \quad \text{2nd order} \quad \text{correction} \]
The matrix elements \( \langle \hat{r}', \hat{V}\hat{r} \rangle \) are used in calculating \( E_x \)'s. These elements are:

\[
V_{\hat{r}', \hat{r}} = \langle \hat{r}', \hat{V}\hat{r} \rangle = \frac{1}{L^3} \int_{\text{cubical}} \hat{z} \cdot \hat{r}' \cdot \hat{r} V(\hat{r}) e^{i \hat{r}' \cdot \hat{r}} d\hat{r}
\]

\[
= \frac{1}{L^3} \int \hat{z} \cdot (\hat{r}' - \hat{r}) \cdot \hat{r} V(\hat{r}) d\hat{r}
\]

\[
= \frac{1}{L^3} \sum_{\hat{R}} \int \hat{z} \cdot (\hat{R}' - \hat{R}) \cdot (\hat{X} + \hat{R}) V(\hat{X} + \hat{R}) d\hat{X}
\]

\[
= \frac{1}{L^3} \sum_{\hat{R}} \hat{z} \cdot (\hat{R}' - \hat{R}) \cdot \hat{R} \int_{\text{with \ cau}} V(\hat{X}) e^{i \hat{R}' \cdot \hat{X}} d\hat{X}
\]

\[
= 0 \quad \text{unless} \quad \hat{r}' - \hat{r} = \hat{0} \quad \text{Also} \quad V_{\hat{r}' = \hat{r}}
\]

To first order (nondegenerate)

\[
E(\hat{r}) = E_0(\hat{r}) + \frac{\langle \hat{r}', \hat{V}\hat{r} \rangle}{2}
\]

\[
V_0 = \frac{1}{L^3} \int V(\hat{r}) d\hat{r} \quad \text{[constant for all } \hat{r}] \]

This just shifts all energies by \( V_0 \), we can ignore this, and set it to zero.

To second order (nondegenerate)

\[
E(\hat{r}) = E_0(\hat{r}) + \sum_{\hat{r}' \neq \hat{r}} \frac{|\langle \hat{r}', \hat{V}\hat{r} \rangle|^2}{E_0(\hat{r}) - E_0(\hat{r}')}
\]