

Chapter 7. Electrons in a solid

I. One electron approximation

1. Total (non-relativistic) Hamiltonian of a lattice:

$$H_{\text{Tot}} = \underbrace{\sum_i \frac{\bar{p}_i^2}{2m}}_{\text{electrons' KE}} + \underbrace{\sum_I \frac{\bar{p}_I^2}{2M_I}}_{\text{Nuclei KE}} + \underbrace{\sum_i V_{\text{nucl}}(\bar{r}_i)}_{\text{electron-nucleus interaction}} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\bar{r}_i - \bar{r}_j|}}_{\text{electron-electron interaction}} + \underbrace{\frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\bar{R}_I - \bar{R}_J|}}_{\text{nucleus-nucleus interaction}}$$

$$V_{\text{nucl}}(\bar{r}) = - \sum_I \frac{Z_I e^2}{|\bar{r} - \bar{R}_I|}$$

2. Large difference between electron and nuclear masses \Rightarrow Nuclei kinetic energy can be neglected.

3. If the nuclei have a fixed configuration, the nucleus-nucleus is a constant term and it can be disregarded if we are considering just the electronic states.

4. Hence the *many-body* Hamiltonian for a system of N *interacting* electrons in the presence of nuclei can be written in the form

$$H_e = \underbrace{\sum_i \frac{\bar{p}_i^2}{2m}}_{\text{electrons' KE}} + \underbrace{\sum_i V_{\text{nucl}}(\bar{r}_i)}_{\text{electron-nucleus interaction}} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\bar{r}_i - \bar{r}_j|}}_{\text{electron-electron interaction}}$$

$$= \sum_i \frac{\bar{p}_i^2}{2m} + V_{\text{nucl}}(\bar{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{\bar{r}_{ij}}$$

The goal is to find the solution of the Eigenvalue problem

$$H_e \Psi(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, \dots, \mathbf{r}_N \sigma_N) = E \Psi(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, \dots, \mathbf{r}_N \sigma_N)$$

5. Hartree approximation 1:

The total wave function Ψ is a product of orthonormalized one-electron wave functions ψ :

$$\Psi(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, \dots, \mathbf{r}_N \sigma_N) = \psi_1(\mathbf{r}_1 \sigma_1) \psi_2(\mathbf{r}_2 \sigma_2) \dots \psi_N(\mathbf{r}_N \sigma_N)$$

The subscript i in $\mathbf{r}_i \sigma_i$ indexes the electrons. The subscript i in ψ_i indexes the wave function. ψ is the product of two parts – spatial $\phi(\mathbf{r})$ and spin $\chi(\sigma)$ so that $\psi(\mathbf{r}\sigma) = \phi(\mathbf{r})\chi(\sigma)$. The problem is now to determine $\psi(\mathbf{r}\sigma)$.

6. The electron charge density is given by

$$\rho(\bar{r}) = (-e) \sum_i \phi_i^*(\bar{r}) \phi_i(\bar{r})$$

The summation is over all electrons.

7. Hartree approximation 2:

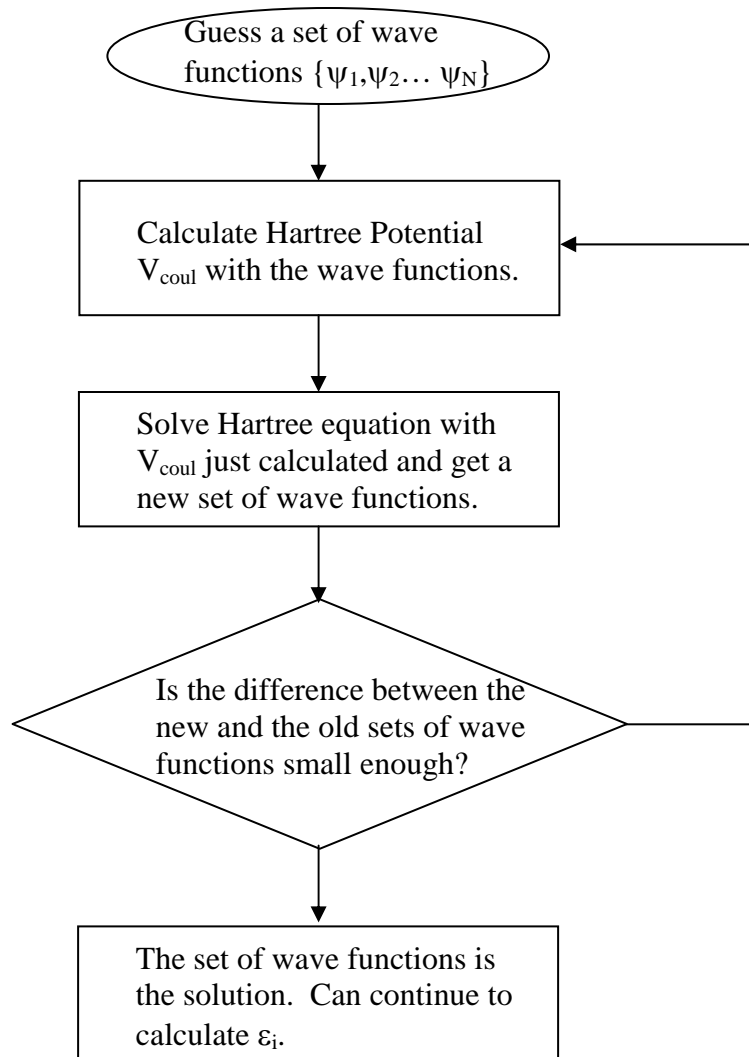
The Coulomb potential experienced by an electron due to other electrons is approximated by the Hartree potential V_{coul} , which is actually the potential due to *all* electrons. It is further assumed that all electrons experience the *same* potential. In this way, the multi-electrons problem is reduced to one electron problem.

$$V_{\text{Coul}}(\vec{r}) = \sum_j \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' = \sum_j \int \varphi_{j,i}^*(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \varphi_{j,i}(\vec{r}') d^3\vec{r}'$$

From these we have the Hartree equation:

$$\left[\frac{\bar{p}^2}{2m} + V_{\text{nucl}}(\vec{r}_i) + V_{\text{Coul}}(\vec{r}) \right] \psi_i = \epsilon_i \psi_i$$

8. The solution is a set of wave function $\{\psi_1, \psi_2, \dots, \psi_N\}$ determined by *self-consistency*:



9. Problem of the Hartree approximation: the wave functions do not take into the fact that electrons are Fermion and hence the wave function $\psi(\mathbf{r}\sigma)$ should be anti-symmetric (i.e. Pauli exclusion principle).

II. Hartree-Fock equation

1. If $\psi_1(\mathbf{r}_1\sigma_1)\psi_2(\mathbf{r}_2\sigma_2)\dots\psi_N(\mathbf{r}_N\sigma_N)$ is a solution of $H_e\Psi = E\Psi$, then so is any permutation like $\psi_1(\mathbf{r}_N\sigma_N)\psi_2(\mathbf{r}_2\sigma_2)\dots\psi_N(\mathbf{r}_1\sigma_1)$ and any linear combination of these permutations.

2. Electron is a Fermion, exchanging any two electrons will change sign of the wave function, i.e. $\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_N\sigma_N) = -\Psi(\mathbf{r}_N\sigma_N, \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_1\sigma_1)$ and so on.

3. Furthermore, no two electrons can occupy the same state. For example, $\psi_1(\mathbf{r}_1\sigma_1)\psi_2(\mathbf{r}_2\sigma_2)\dots\psi_1(\mathbf{r}_N\sigma_N) = 0$

4. The Slater determinant constructed from $\psi_1(\mathbf{r}_N\sigma_N), \psi_2(\mathbf{r}_2\sigma_2), \dots, \psi_N(\mathbf{r}_1\sigma_1)$ processes all of the above properties:

$$\begin{aligned} \Psi(\bar{\mathbf{r}}_1\sigma_1, \bar{\mathbf{r}}_2\sigma_2, \dots, \bar{\mathbf{r}}_N\sigma_N) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\bar{\mathbf{r}}_1\sigma_1) & \psi_1(\bar{\mathbf{r}}_2\sigma_2) & \dots & \psi_1(\bar{\mathbf{r}}_N\sigma_N) \\ \psi_2(\bar{\mathbf{r}}_1\sigma_1) & \psi_2(\bar{\mathbf{r}}_2\sigma_2) & \dots & \psi_2(\bar{\mathbf{r}}_N\sigma_N) \\ \dots & \dots & \dots & \dots \\ \psi_N(\bar{\mathbf{r}}_1\sigma_1) & \psi_N(\bar{\mathbf{r}}_2\sigma_2) & \dots & \psi_N(\bar{\mathbf{r}}_N\sigma_N) \end{vmatrix} \\ &= \frac{1}{\sqrt{N!}} \det\{\psi_1\psi_2 \dots \psi_N\} \quad (\text{in short hand.}) \end{aligned}$$

5. The Hamiltonian matrix element for the total wave function can be calculated for the Slater determinant:

$$\begin{aligned} &\left\langle \Psi(\bar{\mathbf{r}}_1\sigma_1, \bar{\mathbf{r}}_2\sigma_2, \dots, \bar{\mathbf{r}}_N\sigma_N) \left| \sum_i \frac{\bar{\mathbf{p}}_i^2}{2m} + V_{\text{nucl}}(\bar{\mathbf{r}}_i) \right| \Psi(\bar{\mathbf{r}}_1\sigma_1, \bar{\mathbf{r}}_2\sigma_2, \dots, \bar{\mathbf{r}}_N\sigma_N) \right\rangle \\ &= \sum_i \left\langle \frac{1}{\sqrt{N!}} \det\{\underbrace{\psi_1\psi_2 \dots \psi_N}_{N! \text{ permutations}}\} \left| \frac{\bar{\mathbf{p}}_i^2}{2m} + V_{\text{nucl}}(\bar{\mathbf{r}}_i) \right| \frac{1}{\sqrt{N!}} \det\{\psi_1\psi_2 \dots \psi_N\} \right\rangle \\ &= \sum_i \left\langle \frac{1}{\sqrt{N!}} \psi_i(\bar{\mathbf{r}}_i\sigma_i) \left| \frac{\bar{\mathbf{p}}_i^2}{2m} + V_{\text{nucl}}(\bar{\mathbf{r}}_i) \right| \frac{1}{\sqrt{N!}} \psi_i(\bar{\mathbf{r}}_i\sigma_i) \right\rangle \times N! \\ &= \sum_i \left\langle \psi_i(\bar{\mathbf{r}}_i\sigma_i) \left| \frac{\bar{\mathbf{p}}_i^2}{2m} + V_{\text{nucl}}(\bar{\mathbf{r}}_i) \right| \psi_i(\bar{\mathbf{r}}_i\sigma_i) \right\rangle \end{aligned}$$

$$\begin{aligned}
& \left\langle \Psi(\bar{\mathbf{r}}_1\sigma_1, \bar{\mathbf{r}}_2\sigma_2, \dots, \bar{\mathbf{r}}_N\sigma_N) \left| \frac{1}{2} \sum_{i \neq j} \frac{e^2}{\bar{r}_{ij}} \right| \Psi(\bar{\mathbf{r}}_1\sigma_1, \bar{\mathbf{r}}_2\sigma_2, \dots, \bar{\mathbf{r}}_N\sigma_N) \right\rangle \\
&= \left\langle \frac{1}{\sqrt{N!}} \det \underbrace{\{\psi_1\psi_2 \dots \psi_N\}}_{N! \text{ permutations}} \left| \frac{1}{2} \sum_{i \neq j} \frac{e^2}{\bar{r}_{ij}} \right| \frac{1}{\sqrt{N!}} \det \{\psi_1\psi_2 \dots \psi_N\} \right\rangle \\
&= \left\langle \left\langle \frac{1}{\sqrt{N!}} \psi_i(\bar{\mathbf{r}}_1\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{1}{2} \sum_{i \neq j} \frac{e^2}{\bar{r}_{ij}} \right| \frac{1}{\sqrt{N!}} \psi_i(\bar{\mathbf{r}}_1\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \right\rangle \right. \\
&\quad \left. - \left\langle \frac{1}{\sqrt{N!}} \psi_i(\bar{\mathbf{r}}_1\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{1}{2} \sum_{i \neq j} \frac{e^2}{\bar{r}_{ij}} \right| \frac{1}{\sqrt{N!}} \psi_j(\bar{\mathbf{r}}_1\sigma_i) \psi_i(\bar{\mathbf{r}}_j\sigma_j) \right\rangle \right\rangle \times N! \\
&= \frac{1}{2} \sum_{i \neq j} \left\langle \psi_i(\bar{\mathbf{r}}_1\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{e^2}{\bar{r}_{ij}} \right| \psi_i(\bar{\mathbf{r}}_1\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \right\rangle - \underbrace{\frac{1}{2} \sum_{i \neq j} \left\langle \psi_i(\bar{\mathbf{r}}_1\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{e^2}{\bar{r}_{ij}} \right| \psi_j(\bar{\mathbf{r}}_1\sigma_i) \psi_i(\bar{\mathbf{r}}_j\sigma_j) \right\rangle}_{\text{"Exchange"}}
\end{aligned}$$

The electron-electron repulsive energy on the antisymmetric wave function is always lower than the repulsive energy on the “simple” wave function used in the Hartree equation.

6. Hartree-Fock equation can be obtained by variational principle in minimizing $\langle \Psi | H_e | \Psi \rangle$ under the constraint that $\langle \psi_i | \psi_j \rangle = \delta_{ij}$. Apply Lagrange multipliers ϵ_{ij} :
Define Operators:

$$\begin{aligned}
E &= \sum_i \left\langle \psi_i(\bar{\mathbf{r}}_1\sigma_i) \left| \frac{\bar{p}_i^2}{2m} + V_{\text{nucl}}(\bar{\mathbf{r}}_i) \right| \psi_i(\bar{\mathbf{r}}_1\sigma_i) \right\rangle \\
&\quad + \frac{1}{2} \sum_{i,j} \left[\left\langle \psi_i(\bar{\mathbf{r}}_1\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{e^2}{\bar{r}_{ij}} \right| \psi_i(\bar{\mathbf{r}}_1\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \right\rangle - \left\langle \psi_i(\bar{\mathbf{r}}_1\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{e^2}{\bar{r}_{ij}} \right| \psi_j(\bar{\mathbf{r}}_1\sigma_i) \psi_i(\bar{\mathbf{r}}_j\sigma_j) \right\rangle \right] \\
&\quad - \epsilon_{ij} \langle \psi_i(\bar{\mathbf{r}}_1\sigma_i) | \psi_j(\bar{\mathbf{r}}_j\sigma_j) \rangle
\end{aligned}$$

Consider arbitrary variation $\langle \delta\psi_i |$ and variations $|\delta\psi_i \rangle \equiv 0$:

$$\delta E = 0$$

$$\begin{aligned} \Rightarrow \sum_i \left\langle \delta\psi_i(\bar{\mathbf{r}}_i\sigma_i) \left| \frac{\bar{\mathbf{p}}_i^2}{2m} + V_{\text{nucl}}(\bar{\mathbf{r}}_i) \right| \psi_i(\bar{\mathbf{r}}_i\sigma_i) \right\rangle \\ + \sum_{i,j} \left[\left\langle \delta\psi_i(\bar{\mathbf{r}}_i\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{e^2}{|\bar{\mathbf{r}}_{ij}|} \right| \psi_i(\bar{\mathbf{r}}_i\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \right\rangle - \left\langle \delta\psi_i(\bar{\mathbf{r}}_i\sigma_i) \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{e^2}{|\bar{\mathbf{r}}_{ij}|} \right| \psi_j(\bar{\mathbf{r}}_i\sigma_i) \psi_i(\bar{\mathbf{r}}_j\sigma_j) \right\rangle \right] \\ = \varepsilon_{ij} \langle \delta\psi_i(\bar{\mathbf{r}}_i\sigma_i) | \psi_j(\bar{\mathbf{r}}_j\sigma_j) \rangle \\ \Rightarrow \left(\frac{\bar{\mathbf{p}}_i^2}{2m} + V_{\text{nucl}}(\bar{\mathbf{r}}_i) \right) \psi_i(\bar{\mathbf{r}}_i\sigma_i) + \sum_j \left[\left\langle \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{e^2}{|\bar{\mathbf{r}}_{ij}|} \right| \psi_j(\bar{\mathbf{r}}_j\sigma_j) \right\rangle \psi_i(\bar{\mathbf{r}}_i\sigma_i) - \left\langle \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{e^2}{|\bar{\mathbf{r}}_{ij}|} \right| \psi_j(\bar{\mathbf{r}}_i\sigma_i) \psi_i(\bar{\mathbf{r}}_j\sigma_j) \right\rangle \right] \\ = \varepsilon_{ij} \psi_j(\bar{\mathbf{r}}_j\sigma_j) \end{aligned}$$

Define operators:

$$\begin{aligned} V_{\text{Coul}}(\bar{\mathbf{r}})\psi_i(\bar{\mathbf{r}}) &= \sum_j \left\langle \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{e^2}{|\bar{\mathbf{r}}_{ij}|} \right| \psi_j(\bar{\mathbf{r}}_j\sigma_j) \right\rangle \\ &= \left[\sum_j \int \psi_j^*(\bar{\mathbf{r}}_j\sigma_j) \frac{e^2}{|\bar{\mathbf{r}} - \bar{\mathbf{r}}_j|} \psi_j(\bar{\mathbf{r}}_j\sigma_j) d^3\bar{\mathbf{r}}_j \right] \psi_i(\bar{\mathbf{r}}) \\ V_{\text{exch}}(\bar{\mathbf{r}})\psi_i(\bar{\mathbf{r}}) &= - \sum_j \left\langle \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{e^2}{|\bar{\mathbf{r}}_{ij}|} \right| \psi_j(\bar{\mathbf{r}}_i\sigma_i) \psi_i(\bar{\mathbf{r}}_j\sigma_j) \right\rangle \quad (= - \sum_j \left\langle \psi_j(\bar{\mathbf{r}}_j\sigma_j) \left| \frac{e^2}{|\bar{\mathbf{r}}_{ij}|} \right| \psi_j(\bar{\mathbf{r}}_j\sigma_j) \right\rangle \psi_j(\bar{\mathbf{r}}_i\sigma_i)) \\ &= - \sum_j \int \psi_j(\bar{\mathbf{r}}_j\sigma_j) \frac{e^2}{|\bar{\mathbf{r}} - \bar{\mathbf{r}}_j|} \psi_j(\bar{\mathbf{r}}\sigma) \psi_i(\bar{\mathbf{r}}_j\sigma_j) d^3\bar{\mathbf{r}}_j \\ &= - \sum_j \psi_j(\bar{\mathbf{r}}\sigma) \int \psi_j(\bar{\mathbf{r}}_j\sigma_j) \frac{e^2}{|\bar{\mathbf{r}} - \bar{\mathbf{r}}_j|} \psi_i(\bar{\mathbf{r}}_j\sigma_j) d^3\bar{\mathbf{r}}_j \end{aligned}$$

Above equation reduces to a single electron equation:

$$\left(\frac{\bar{\mathbf{p}}_i^2}{2m} + V_{\text{nucl}}(\bar{\mathbf{r}}_i) + V_{\text{Coul}}(\bar{\mathbf{r}}_i) - V_{\text{exch}}(\bar{\mathbf{r}}_i) \right) \psi_i(\bar{\mathbf{r}}_i\sigma_i) = \varepsilon_{ij} \psi_i(\bar{\mathbf{r}}_i\sigma_i)$$

Diagonalize ε so that $\varepsilon_{ij} = \varepsilon_i \delta_{ij}$, we have the Hartree-Fock equation:

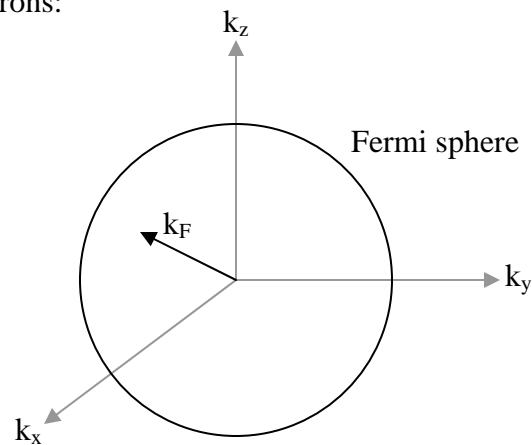
$$\left(\frac{\bar{\mathbf{p}}_i^2}{2m} + V_{\text{nucl}}(\bar{\mathbf{r}}_i) + V_{\text{Coul}}(\bar{\mathbf{r}}_i) - V_{\text{exch}}(\bar{\mathbf{r}}_i) \right) \psi_i(\bar{\mathbf{r}}_i\sigma_i) = \varepsilon_i \psi_i(\bar{\mathbf{r}}_i\sigma_i)$$

III. Free electron

1. Screening of nuclei potential by inner electrons $\Rightarrow V_{\text{nucl}} = 0$.
2. Low electron density, screening by free electrons (Thomas-Fermi screening) and the rareness of electron-electron scattering $\Rightarrow V_{\text{Coul}} = V_{\text{exch}} = 0$.
3. For free electrons:

$$\left(\frac{\vec{p}_i^2}{2m} \right) \psi_i(\vec{r}_i, \sigma_i) = \varepsilon_i \psi_i(\vec{r}_i, \sigma_i) \Rightarrow \psi_i(\vec{r}_i, \sigma_i) = e^{i\vec{k} \cdot \vec{r}}$$

4. For free electrons:



Determination of Fermi energy E_F :

$$2 \times \frac{\frac{4}{3} \pi k_F^3}{8\pi^3} = \frac{N}{V} \Rightarrow \frac{k_F^3}{3\pi^3} = n$$

Dispersion relation:

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

Density of state:

$$2 \times \frac{4\pi k^2 dk}{8\pi^3} = D(E) dE \Rightarrow D(E) = V \pi^2 k^2 \frac{dk}{dE}$$

Temperature effect:

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

Note that $\mu(0)=E_F$.

IV. Central equation

1. A crystal possesses lattice symmetry, and hence there must be some potential for the electron with the same periodicity, no matter how small is the potential (in case of nearly free electron). The one electron Schrodinger equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

where V is the periodic potential.

2. Bloch's theorem.

The solution of the one electron Schrodinger equation is always in the form:

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$$

where $u_{\vec{k}}(\mathbf{r})$ is a periodic function that has the same periodicity as the lattice:

$$u_{\vec{k}}(\mathbf{r}+\mathbf{R}) = u_{\vec{k}}(\mathbf{r})$$

Note that $\psi_{\vec{k}}(\mathbf{r})$ does *not* have the same periodicity as the lattice because $\psi_{\vec{k}}(\mathbf{r}) \neq \psi_{\vec{k}}(\mathbf{r}+\mathbf{R})$. Instead,

$$\psi_{\vec{k}}(\vec{r} + \vec{R}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot(\vec{r}+\vec{R})} = e^{i\vec{k}\cdot\vec{R}} u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}} = e^{i\vec{k}\cdot\vec{R}} \psi_{\vec{k}}(\vec{r})$$

This equation is considered as Bloch's theorem also (in another form).

3. Because of the periodicity, $e^{i\mathbf{K}\cdot\mathbf{r}}$ forms a complete orthogonal set of functions. Any function with the same periodicity as the lattice can be expressed as a linear combination of $e^{i\mathbf{K}\cdot\mathbf{r}}$:

$$V(\vec{r}) = \sum_{\vec{K}} V_{\vec{K}} e^{i\vec{K}\cdot\vec{r}} \Rightarrow V_{\vec{K}} = \frac{1}{V} \int_{\text{Cell}} V(\vec{r}) e^{-i\vec{K}\cdot\vec{r}} d^3\vec{r}$$

4. The one electron Schrodinger equation can be reduced to the *Central equation*:

$$\left(\frac{\hbar^2 \mathbf{k}^2}{2m} - E \right) C(\vec{k}) + \sum_{\vec{K}} V_{\vec{K}} C(\vec{k} - \vec{K}) = 0$$

Central equation relates $C(\mathbf{k})$ and $C(\mathbf{k}+\mathbf{K})$ for all reciprocal vectors \mathbf{K} . There is one central equation for each allowed value of \mathbf{k} . The dispersion relation of electron can be obtained by requiring the determinant of this set of linear equations to be zero (for a non-trivial solution).

5. $\psi_{\vec{k}}(\mathbf{r})$ in terms of $C(\mathbf{k})$:

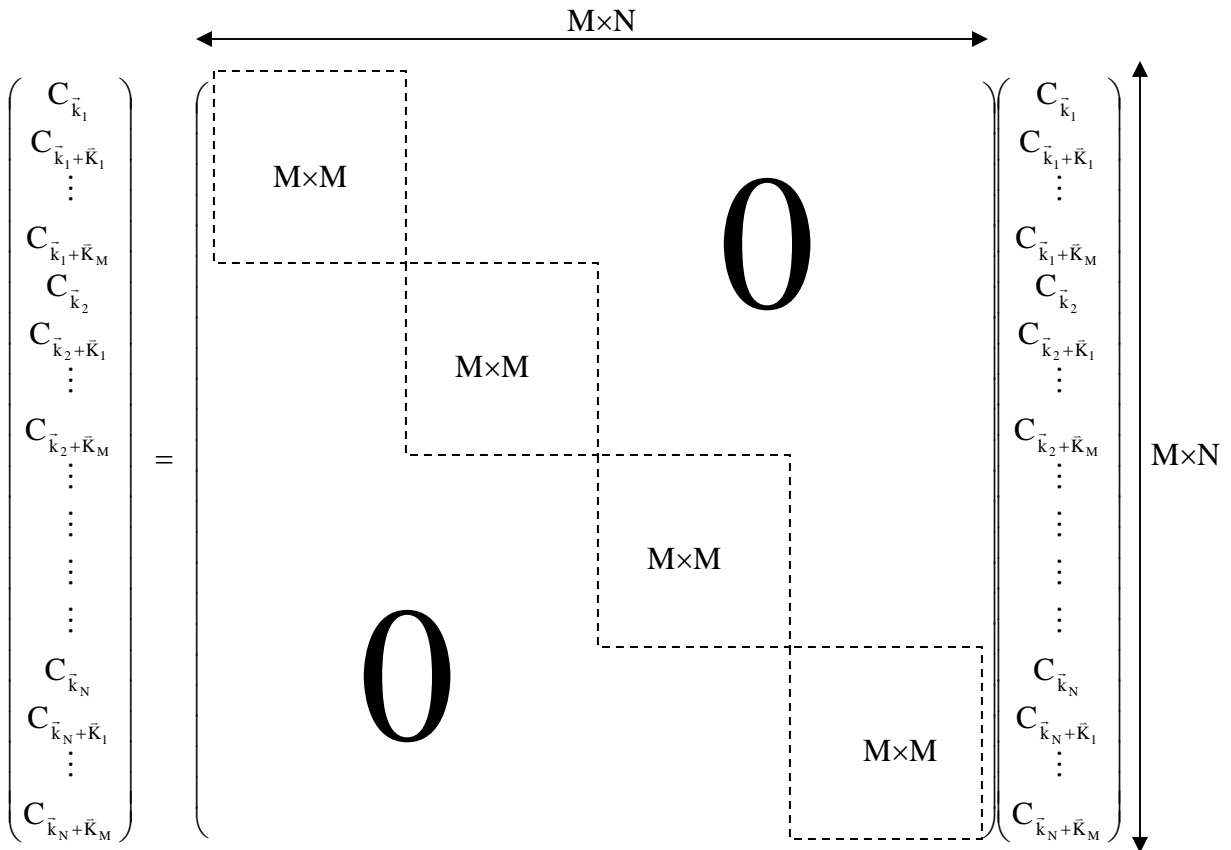
$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{K}} C(\vec{k} - \vec{K}) e^{-i\vec{K}\cdot\vec{r}} e^{-i\vec{k}\cdot\vec{r}}$$

Compare with Bloch's theorem, we know that

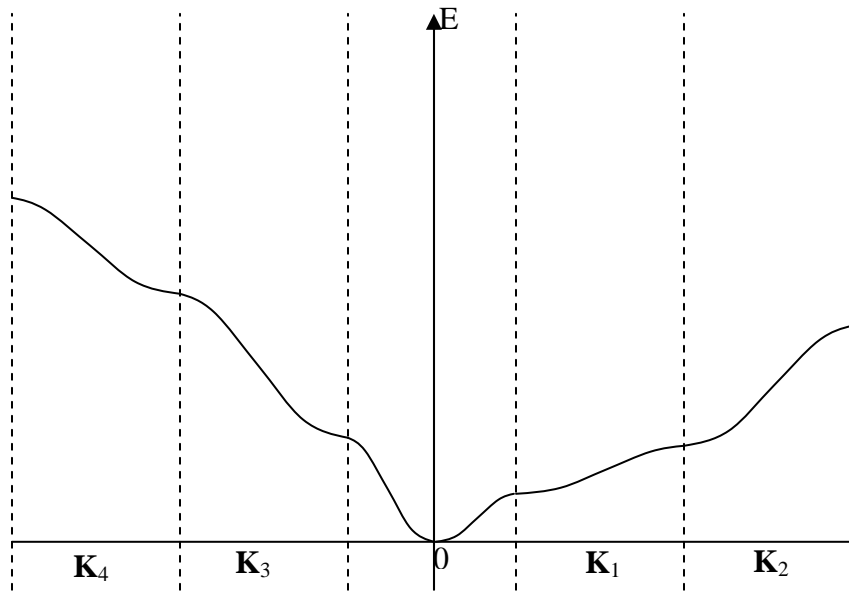
$$\sum_{\bar{\mathbf{K}}} C(\bar{\mathbf{k}} - \bar{\mathbf{K}}) e^{-i\bar{\mathbf{K}} \cdot \bar{\mathbf{r}}} = u_{\bar{\mathbf{k}}}(\bar{\mathbf{r}}) \text{ and it has the same periodicity as the lattice :}$$

$$u_{\bar{\mathbf{k}}}(\bar{\mathbf{r}} + \bar{\mathbf{R}}) = \sum_{\bar{\mathbf{K}}} C(\bar{\mathbf{k}} - \bar{\mathbf{K}}) e^{-i\bar{\mathbf{K}} \cdot (\bar{\mathbf{r}} + \bar{\mathbf{R}})} = \sum_{\bar{\mathbf{K}}} C(\bar{\mathbf{k}} - \bar{\mathbf{K}}) e^{-i\bar{\mathbf{K}} \cdot \bar{\mathbf{r}}} e^{-i\bar{\mathbf{K}} \cdot \bar{\mathbf{R}}} = \sum_{\bar{\mathbf{K}}} C(\bar{\mathbf{k}} - \bar{\mathbf{K}}) e^{-i\bar{\mathbf{K}} \cdot \bar{\mathbf{r}}} = u_{\bar{\mathbf{k}}}(\bar{\mathbf{r}})$$

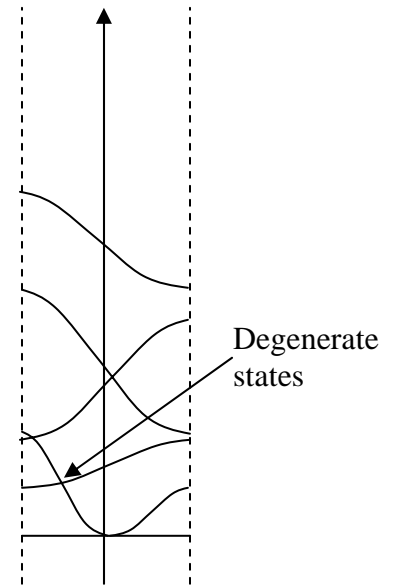
6. Now look at the Central equation, there is one equation for each value of \mathbf{k} ($-\infty < \mathbf{k} < \infty$). However, only $\mathbf{k}, \mathbf{k} + \mathbf{K}, \mathbf{k} + \mathbf{K}', \mathbf{k} + \mathbf{K}'', \dots$ are related together within the same group of equation. For the sake of discussion, let us assume there are N real space lattice points and M reciprocal space lattice points ($N, M \rightarrow \infty$). There is a total number of $N \times M$ central equations for the $N \times M$ unknown $C(\mathbf{k})$. However, since only $\mathbf{k}, \mathbf{k} + \mathbf{K}, \mathbf{k} + \mathbf{K}', \mathbf{k} + \mathbf{K}'', \dots$ (M of them) will appear in the same central equation (M of them), hence the $N \times M$ central linear equation system is actually block diagonalized into $M \times M$ blocks and there are N of these blocks.



7. This block diagonalization allows us (and *more reasonable*) to present the dispersion relationship of single electron in the reduced zone scheme: instead of using the $N \times M$ \mathbf{k} ($-\infty < \mathbf{k} < \infty$) values to index the solution (extended zone scheme), we can use \mathbf{k} (limited to the first Brillouin zone, N of them) and \mathbf{K} (M of them) to index the solution (reduced zone scheme). It is more often to use n ($=1, 2, \dots, M$) instead of \mathbf{K} in labeling the solution.



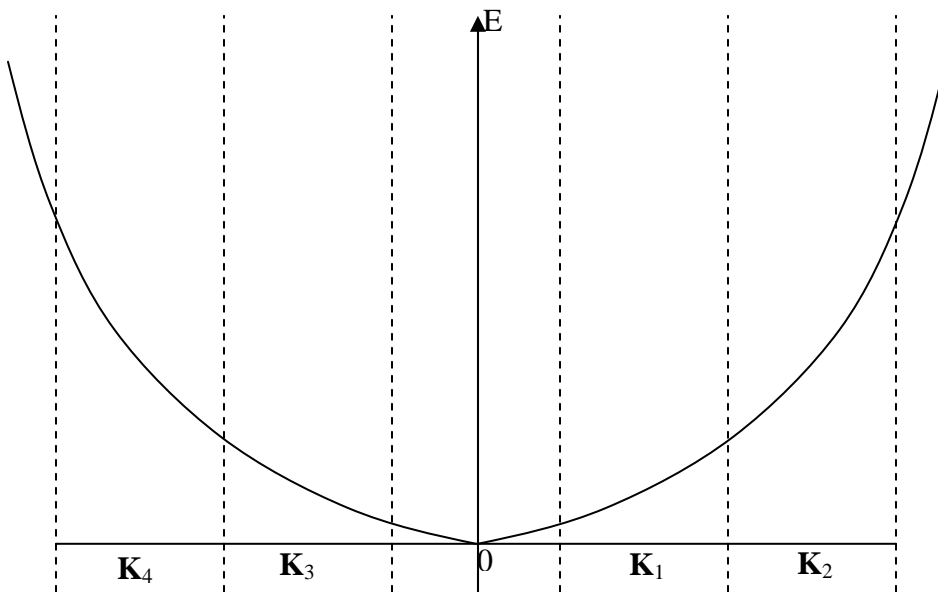
Extended zone scheme



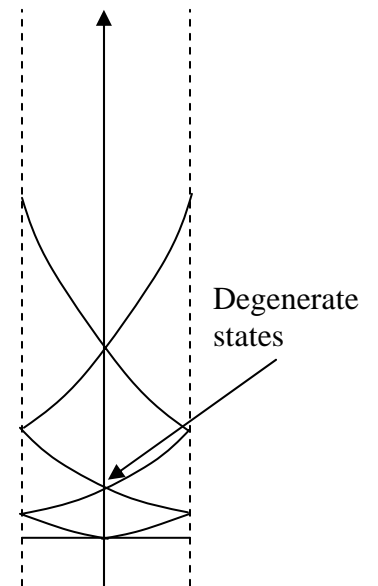
Reduced zone scheme

V. Nearly free electron model

1. *One dimensional* free electrons “superimposed” on the reciprocal lattice space:

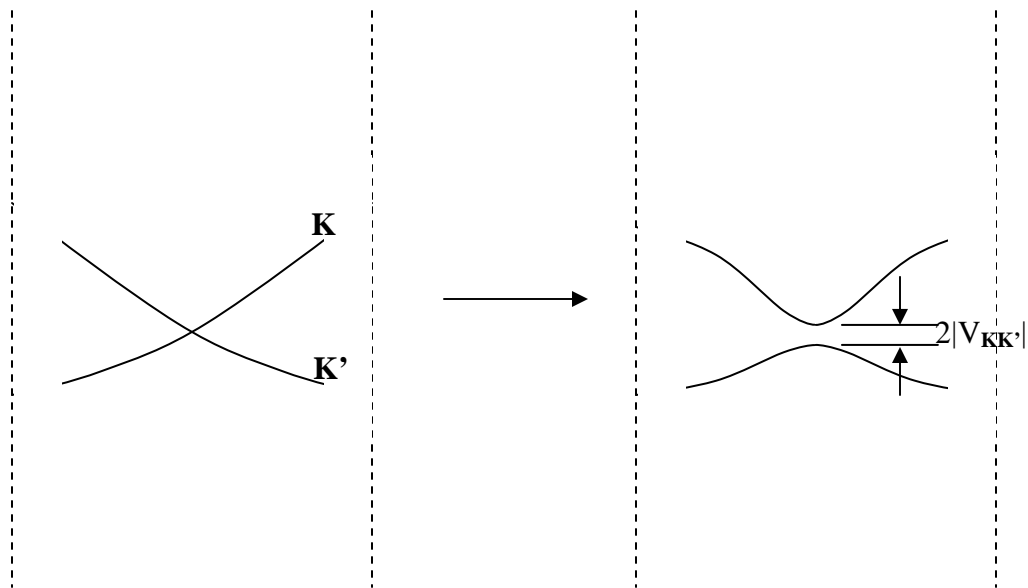


Extended zone scheme



Reduced zone scheme

2. If there is no potential, the electron will be perfectly free, but there will be no periodicity either. Hence, for the existence of lattice periodicity, there must be some potential, no matter how weak, possessing the same periodicity as the lattice.
3. If the potential is very weak, the dispersion relationship for the single electron should be very similar to that of free electron and the wave function of the electron should look like the plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$.
4. In reduced zone scheme, degenerate states will occur (see figures above). Bragg's scattering will remove the degeneracy and create *band gap*.



For this reason, it is not practical to label the band with reciprocal vector \mathbf{K} .

5. Sketching Fermi surfaces

- (i) Construct enough Brillouin zone to contain the Fermi sphere (i.e. construction in extended zone scheme).
- (ii) Draw the Fermi sphere to hold all electrons

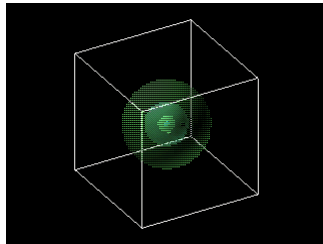
$$\frac{\frac{4}{3}\pi k_F^3}{8\pi^3} \times 2_{\text{spin}} = N$$

V

- (iii) Rearrange different zone region into one piece (reduced zone scheme) \Rightarrow possible to have several Fermi surfaces.
- (iv) "Round off" corners. By crystal symmetry, Fermi surface always perpendicular to zone boundary.

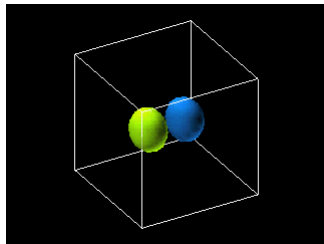
VI. Tight binding model

1. Also known as Linear Combination of Atomic Orbital (LACO).
2. This model starts from isolated atoms and atoms can “share” electrons by overlap of atomic orbital. Model works fine for the d-bands of transition metals and also valance bands of insulators.
3. Atomic orbital:
s orbital ($l=0$ with $m_z=0$), can hold two electrons.

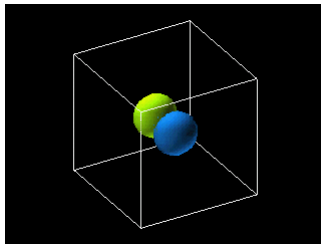


Group notation: a_{1g} (a=non-degenerate, g= inversion symmetry)

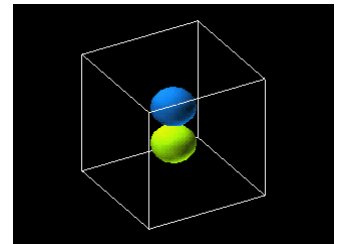
p orbital ($l=1$ with $m_z=0, \pm 1$), can hold 6 electrons.



p_x



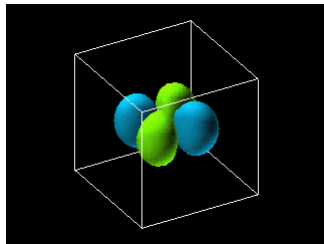
p_y



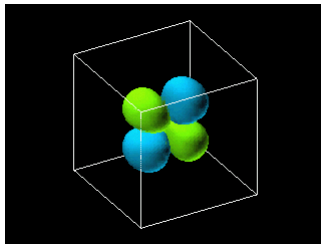
p_z

\ Group notation: t_{1u} (t=triple degeneracies)

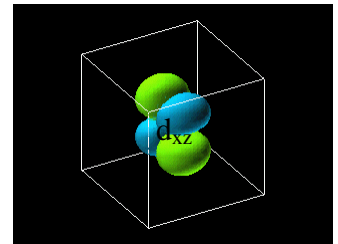
d orbital ($l=2$ with $m_z=0, \pm 1, \pm 2$), can hold 10 electrons.



d_{xy}

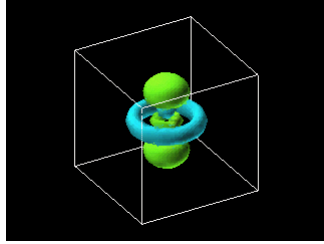


d_{xz}

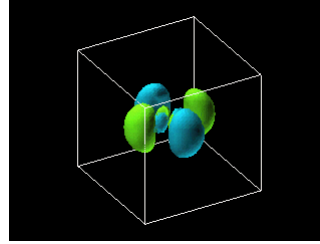


d_{xz}

Group notation: t_{2g} (t=triple degeneracies)



d_z^2



$d_x^2 - y^2$

Group notation: e_g (e=double degeneracies)

4. Mixint of different orbital \Rightarrow Hybridization. E.g. s-d hybridization.

$$5. \quad E_{\vec{k}} = \underbrace{\int \varphi^*(\vec{r})H\varphi(\vec{r})d^3\vec{r}}_{-\alpha} + \underbrace{\int \varphi^*(\vec{r} - \vec{\rho})H\varphi(\vec{r})d^3\vec{r}}_{-\gamma} \sum_{nn} e^{-i\vec{k}\cdot\vec{\rho}}$$

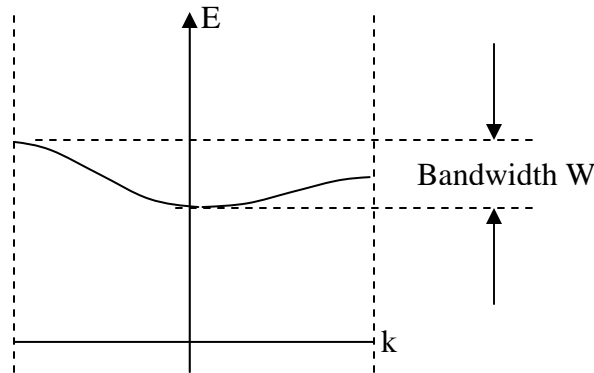
where nn=nearest neighbors and ρ is the vector pointing to the nearest neighbor vector.

For example, there are six nearest neighbors for simple cubic.

$$\rho = (\pm a, 0, 0), (0, \pm a, 0), (0, 0, \pm a).$$

$$\begin{aligned} \therefore E_{\vec{k}} &= -\alpha - \gamma [e^{-ik_x a} + e^{ik_x a} + e^{-ik_y a} + e^{ik_y a} + e^{-ik_z a} + e^{ik_z a}] \\ &= -\alpha - 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a) \end{aligned}$$

6. Band width:

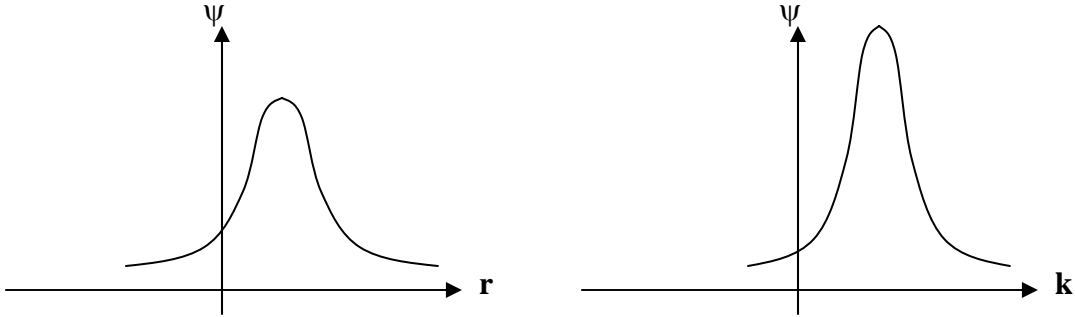


Narrow band with small bandwidth \Leftrightarrow Higher effective mass m^* \Leftrightarrow Lower mobility.

A material with a very narrow bandwidth is an insulator (Mott insulator). A metal-insulator (Mott) transition by adjusting the bandwidth is called Mott transition. One way to achieve Mott transition is to increase the atomic separation a and reduce the overlap of atomic orbitals.

VII. Semiclassical model

1. A single particle in k-space (occupying a unique state) will produce a wave $u(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$ in real space. Similarly, a single particle in real space is a wave in k-space. In semi-classical model, a compromise is made so that the single electron wave function is “Gaussian” like in both real space and k-space:



In this way the electron is “particle like” in both real space and k-space. Physical quantities like position and velocity can be measured by the mean of the Gaussian functions.

2. Equations of motion:

$$\bar{\mathbf{v}} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E$$

$$\bar{\mathbf{F}} = \dot{\bar{\mathbf{p}}} = \hbar \dot{\mathbf{k}}$$

For example, one-dimensional free electrons case,

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow \nabla_{\mathbf{k}} E = \frac{dE}{dk} = \frac{\hbar^2 k}{m} = \frac{\hbar p}{m} = \hbar v$$

In the presence of electric and magnetic field,

$$\bar{\mathbf{F}} = -e(\bar{\mathbf{E}} + \bar{\mathbf{v}} \times \bar{\mathbf{B}}) \Rightarrow \hbar \dot{\mathbf{k}} = -e(\bar{\mathbf{E}} + \bar{\mathbf{v}} \times \bar{\mathbf{B}})$$

3. Effective mass of an electron at state \mathbf{k} :

The effective mass is actually a tensor $[m^*(\mathbf{k})]$ with its inverse defined as

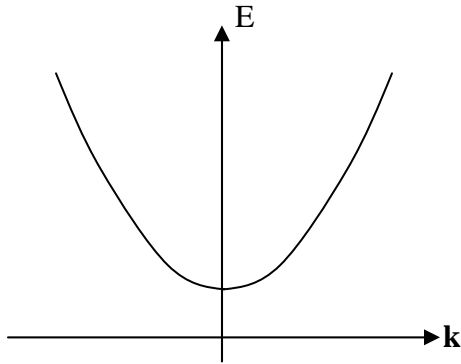
$$[m^*(\bar{\mathbf{k}})^{-1}]_{ij} = \pm \frac{1}{\hbar^2} \frac{\partial^2 E(\bar{\mathbf{k}})}{\partial k_i \partial k_j}$$

Example: For 1-D free electron,

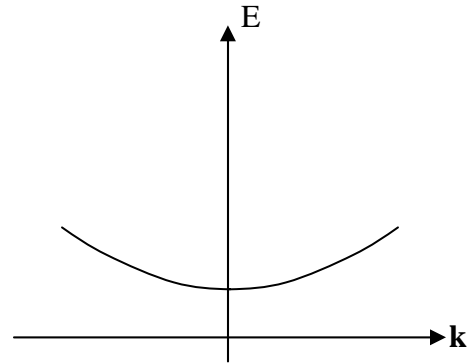
$$\frac{1}{\hbar^2} \frac{\partial^2 E(\bar{\mathbf{k}})}{\partial k_i \partial k_j} = \frac{1}{\hbar^2} \frac{\partial^2}{\partial k^2} \left(\frac{\hbar^2 k^2}{2m} \right) = \frac{1}{\hbar^2} \frac{\hbar^2}{m} = \frac{1}{m}$$

Notes:

- (i) There are two signs for the mass tensor. Positive sign is for *electron* and negative sign is for *hole*.
- (ii) Near the extremums of the energy band, m^{-1} is a measure of the parabolic curvature.



Larger $m^{-1} \Rightarrow$ smaller m



Smaller $m^{-1} \Rightarrow$ larger m
 \therefore narrow band \Rightarrow larger m

$$\begin{aligned}
 4. \quad \bar{v} &= \frac{1}{\hbar} \nabla_{\bar{k}} E \Rightarrow v_i = \frac{1}{\hbar} \frac{\partial E(\bar{k})}{\partial k_i} \hat{i} \quad (i = x, y, z) \\
 &\Rightarrow \dot{v}_i = \sum_j \frac{1}{\hbar} \frac{\partial^2 E(\bar{k})}{\partial k_i \partial k_j} \frac{\partial k_j}{\partial t} \hat{i} \\
 &\Rightarrow \dot{v}_i = \hbar M^{-1}_{ij} \dot{k}_j \\
 &\Rightarrow M_{ji} \dot{v}_i = \hbar \dot{k}_j
 \end{aligned}$$

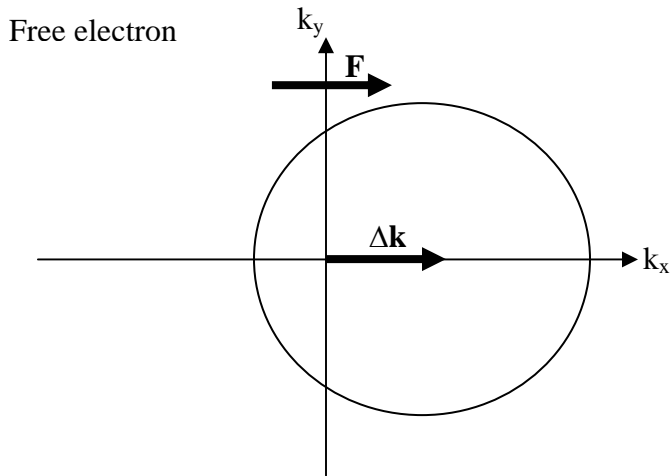
Therefore, we have in real space :

$$\bar{F} = \dot{\bar{p}} = \hbar \dot{\bar{k}} \Rightarrow F_j = M_{ji} \dot{v}_i$$

If the mass tensor is diagonalized, $\bar{F} = M \dot{\bar{v}}$

- 5. Semiclassical model does not allow interband transition. i.e., n remains constant for a particular electron.
- 6. The equations of motion apply only to an electron in the time *between* two collisions. Immediately after a collision, the electron will be scattered in random direction (Drude model) and the equations of motion will be followed again until the next collision.
- 7. Effect of external force:

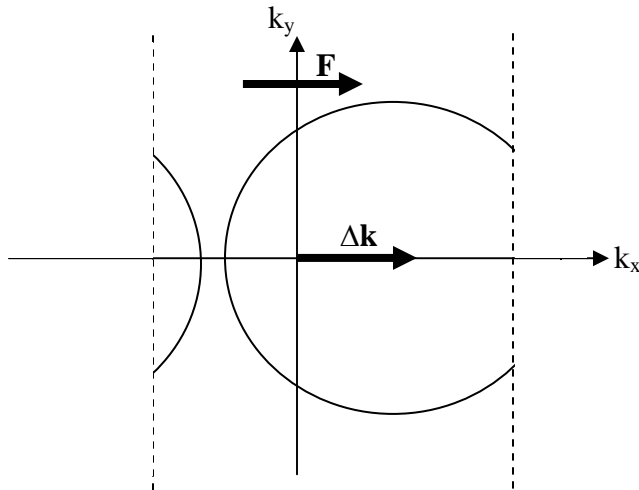
If there is no collision (i.e. no resistance)



The Fermi sphere will translate across the d-space:

$$\begin{aligned} \vec{F} = \dot{\vec{p}} = \hbar \dot{\vec{k}} &\Rightarrow \dot{\vec{k}} = \frac{\vec{F}}{\hbar} \Rightarrow \Delta \vec{k} = \int \frac{\vec{F}}{\hbar} dt \\ &= \frac{\vec{F}t}{\hbar} \quad \text{if force is constant} \end{aligned}$$

Un-free electron

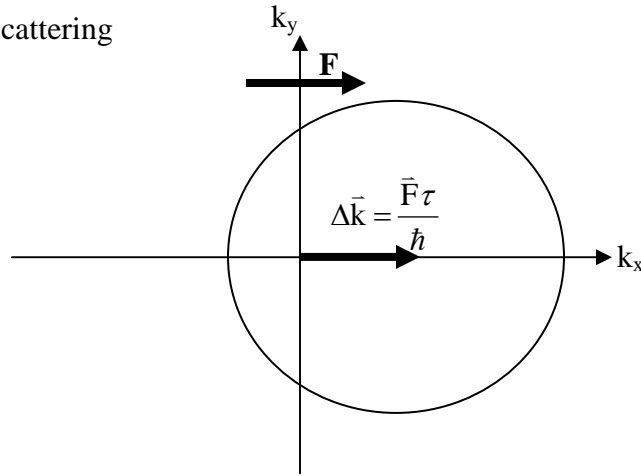


No interband transition \Rightarrow the Fermi surface will “oscillate” and remain in the first Brillouin zone. Over time, it will “disappear” at the zone boundary but reappear immediately at the opposite zone boundary as shown in the above figure.

If there is collision (as in all real cases):

The Fermi surface will remain stationary in k-space. On average, the sphere has only a time of τ (relaxation time) to translate across the k-space.

Scattering

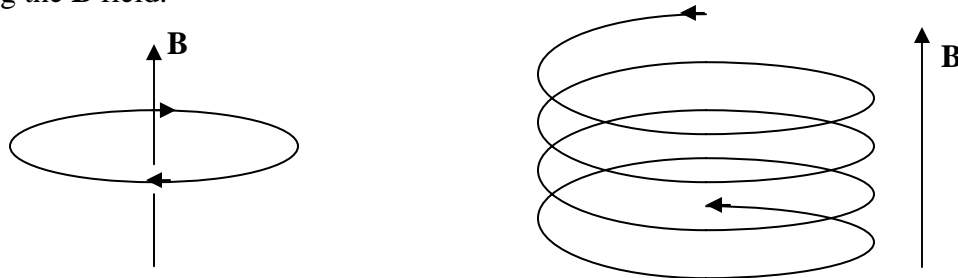


The equation of motion has to be modified accordingly:

$$\vec{F} = \hbar \dot{\vec{k}} \quad \rightarrow \quad \vec{F} = \hbar \left(\frac{d}{dt} + \frac{1}{\tau} \right) \dot{\vec{k}}$$

VIII. Electrons in magnetic field

1. Consider an electron moving in a *constant* magnetic field without electric field.
2. In real space, the electron moves either in circle perpendicular to the **B** field, or spiral along the **B** field.



If the mass tensor is diagonalized, with equal mass in all directions,

$$-e\vec{v} \times \vec{B} = m \left(\frac{d}{dt} + \frac{1}{\tau} \right) \vec{v}$$

$$\frac{d}{dt} \vec{v} = 0 \text{ for steady case.}$$

$$\therefore v_x = -\frac{eB}{m} \tau v_y, \quad v_y = -\frac{eB}{m} \tau v_x, \quad v_z = 0$$

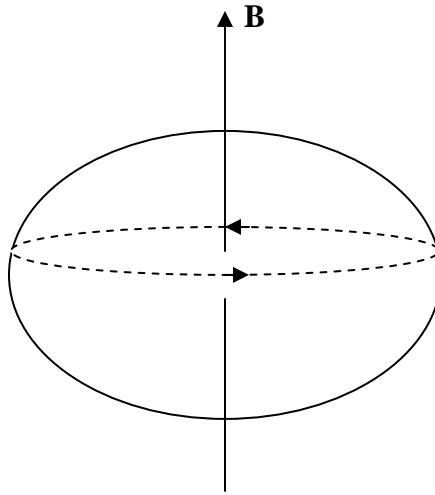
$$\omega_c = \frac{eB}{m} \text{ is the cyclotron frequency.}$$

ω_c is the frequency of the circular trajectory. Note that the trajectory is possible only between collisions.

3. In k-space, equation of motion:

$$\begin{aligned} \hbar \dot{\vec{k}} &= -e\vec{v} \times \vec{B} \\ \Rightarrow \hbar \dot{\vec{k}} &= -e\vec{r} \times \vec{B} \\ \Rightarrow \dot{\vec{k}} &= -\frac{e}{\hbar} \vec{r} \times \vec{B} \\ \therefore \vec{k} &\perp \vec{B} \end{aligned}$$

The trajectory in k-space is a path on equal energy surface and perpendicular to the \mathbf{B} field.

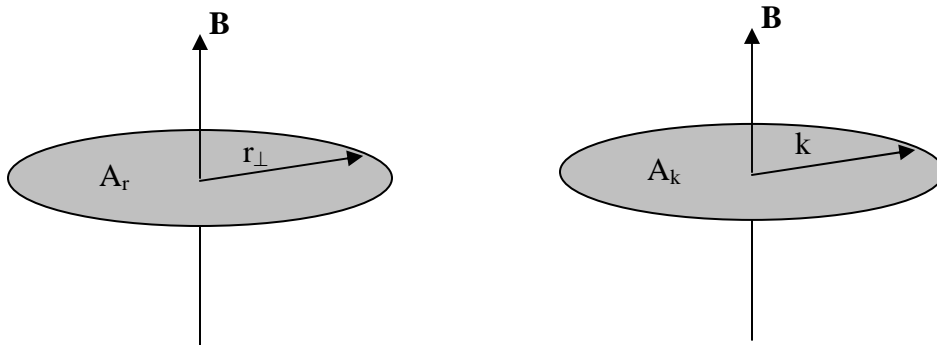


Note that the trajectory does not need to be closed.

4. If r_{\perp} is component of \mathbf{r} perpendicular to \mathbf{B} ,

$$\vec{k} \parallel \vec{r}_{\perp} \quad \text{and} \quad |\vec{k}| = \frac{e |\vec{r}_{\perp}| |\vec{B}|}{\hbar}$$

If the particle is tracing closed orbit in both real space (with an area A_r) and k-space (with an area A_k):



$$A_r \propto r_{\perp}^2 \quad \text{and} \quad A_k \propto k^2 \quad \Rightarrow \quad \frac{A_k}{A_r} = \left(\frac{eB}{\hbar} \right)^2$$

IX. Resistivity

1. Electrical resistivity is caused by inelastic collisions of electrons. Drude model assumes $\langle \mathbf{v} \rangle = 0$ immediately after a collision and we have:

$$\sigma = \frac{ne^2\tau}{m^*}$$

2. τ is the relaxation time, equals to the average time duration between two collisions. Hence, if l is the mean free path,

$$l = v_F\tau$$

For typical materials, $v_F = 10^8 \text{ cm/s} = 10^6 \text{ m/s}$. If $l = 1000 \text{ Angstroms} = 10^{-7} \text{ m}$ then $\tau = 10^{-7}/10^6 = 10^{-13} \text{ s}$.

3. Origin of electrical resistivity:

- (i) Collision with phonon -- dominant at high temperatures (e.g. room temperature).
- (ii) impurity -- dominant at low temperatures.
- (iii) lattice imperfection -- dominant at low temperatures.
- (iv) sample boundary -- dominant at low temperatures.

If τ_L is the relaxation time for phonon scattering, and τ_i is the relaxation time for impurities and defects etc.

$$\frac{1}{\tau} = \frac{1}{\tau_L} + \frac{1}{\tau_i}$$

4. Mathiessen's rule:

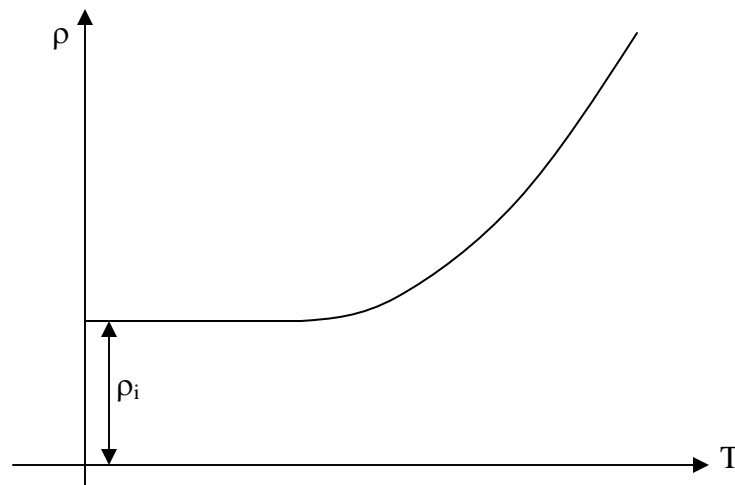
Separate sources of resistivity, such as phonon and impurities, sum linearly to produce the total resistivity of a sample just as resistors in a series sum linearly:

$$\rho \propto \frac{1}{\sigma} \Rightarrow \rho_{\text{Total}} = \rho_1 + \rho_2 + \dots$$

5. In most cases,

$$\rho = \rho_L + \rho_i$$

ρ_L decreases with temperature while ρ_i remains constant,



6. Residual resistivity ratio (RRR) is defined as:

$$\text{RRR} = \frac{\text{Resistivity at room temperature (300K)}}{\text{Resistivity at 0K (or 4.2K)}}$$

RRR can be used as an indication on the purity of the sample:

$$\text{RRR} = \frac{\rho(300\text{K})}{\rho(\text{or } 4.2\text{K})} = \frac{\rho_i + \rho_L(300\text{K})}{\rho_i} = 1 + \frac{\rho_L(300\text{K})}{\rho_i}$$

For a purer sample, ρ_i is smaller and hence RRR is greater. RRR can be 10^6 for some very pure metal, but ~ 1 for some alloys.

7. Mathiessen's rule \Rightarrow Resistivity \propto impurity sample. If n_i = impurity concentration,

$$\rho_i(0\text{K}) \propto n_i \Rightarrow \frac{\rho_i(0\text{K})}{n_i} = \text{constant}$$

As a rough rule:

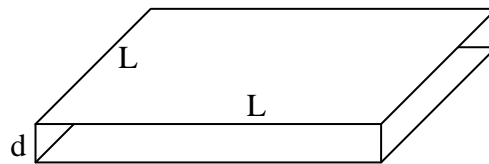
$$\frac{\rho_i(0\text{K}) \text{ in } \mu\Omega\text{-cm}}{n_i \text{ in } \% \text{ atom}} = 1$$

For example:

For example, $\rho(300\text{K})$ for a copper sample is $1.7 \times 10^{-6} \mu\Omega\text{-cm}$. If $\text{RRR} = 1000$, then $\rho(0\text{K}) \sim 1.7 \times 10^{-3} \mu\Omega\text{-cm}$.

$$\frac{\rho_i(0\text{K}) \text{ in } \mu\Omega\text{-cm}}{n_i \text{ in } \% \text{ atom}} = 1 \Rightarrow n_i \text{ in } \% \text{ atom} \approx 1.7 \times 10^{-3} \% \text{ or } 1.7 \times 10^{-5} \text{ (17 ppm)}$$

8. Surface resistance, or more appropriately square or sheet resistance R_s . This is the resistance measured between opposite edges of a square sheet:

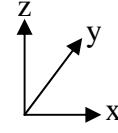
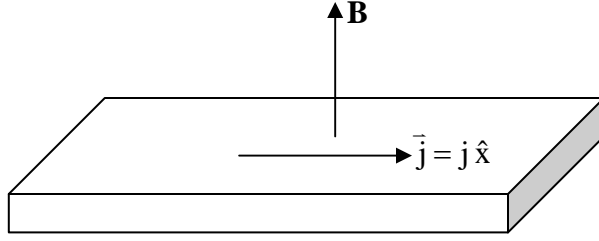


$$R_s = \rho \frac{L}{A} = \rho \frac{L}{Ld} = \frac{\rho}{d}$$

R_s is independent of the dimension of the sheet. Surface resistance is commonly used in semiconductor and thin film measurements.

X. Hall effect

1. Consider a constant homogeneous field B applied perpendicular to the sample plane:



$$-e\vec{E} - e\vec{v} \times \vec{B} = m \left(\frac{d}{dt} + \frac{1}{\tau} \right) \vec{v}$$

$$\frac{d}{dt} \vec{v} = 0 \text{ for steady case :}$$

$$v_x = -\frac{e\tau}{m} E_x - \omega_c \tau v_y$$

$$v_y = -\frac{e\tau}{m} E_y - \omega_c \tau v_x$$

$$v_z = -\frac{e\tau}{m} E_z$$

$$\text{where } \omega_c = \frac{eB}{m} = \text{cyclotron frequency}$$

$$\text{Also, } \vec{j} = j \hat{x} \Rightarrow v_y = v_z = 0$$

$$v_z = 0 \Rightarrow E_z = 0$$

$$v_y = 0 \Rightarrow v_x = -\frac{e\tau}{m} E_x$$

$$\text{and } -\frac{e\tau}{m} E_y - \omega_c \tau v_x = 0$$

$$\therefore -\frac{e\tau}{m} E_y - \omega_c \tau \left(-\frac{e\tau}{m} E_x \right) = 0$$

$$\Rightarrow E_y = -\omega_c \tau E_x = -\frac{eB\tau}{m} E_x$$

2. Hall conductivity σ_H is defined as $j_x = \sigma_H E_y$. The more common Hall resistivity is $R_H = 1/\sigma_H = E_y/j_x$.

$$\rho_H = \frac{E_y}{j} = -\frac{eB\tau}{m} \frac{E_x}{j}$$

$$\text{But } j = \sigma E_x = \frac{ne^2\tau}{m} E_x$$

$$\therefore \rho_H = -\frac{eB\tau}{m} \frac{m}{ne^2\tau} = -\frac{B}{ne}$$

3. Hall coefficient R_H is defined as

$$R_H = \frac{\rho_H}{B}$$

$$\therefore R_H = -\frac{1}{ne}$$

R_H depends only on the carrier density n . R_H can be positive or negative, depends on the sign of the carrier charge.

4. Hall effect is important in the determination of carrier density, and also the sign of the charges. Note that many metals have positive (hole) carrier charge.