Lecture Notes

Introduction to Strongly Correlated Electron Systems

WS 2014/ 2015

Mohsen Abd-Elmeguid

II. Institute of Physics, University of Cologne, Germany

Introduction to strongly correlated electron systems

I. Introduction
Brief summary of electrons in solids, origin of strong electron correlations

II. Classes of strongly correlated electron systems

(a) Transition metal compounds: 3d-electrons
- Hubbard model, Mott insulator, metal-insulator transition
- Spin, charge, and orbital degrees of freedom and ordering phenomena, selected materials

(b) Heavy fermion systems: 4f (5f) – electrons
- The Kondo effect, heavy fermion systems, non-Fermi liquid behavior,
- Quantum phase transitions, unconventional superconductivity, selected materials

(c) Nanoscale structures:
- Quantum confinement, unusual properties for potential applications

III. Pressure effect on the ground state properties:
- Recent experimental results on heavy fermions and transition metal compounds

IV. Summary and open discussion

Some comments on electrons in Solids:

Theoretical description using **two different approachs/ approximations** without taking into account electon-electron correlations:

- The nearly-free electron model (itinerant electrons in very weak periodic potential)

- The tight-binding model (electrons localized on an atomic site but weakly coupled to all other atoms----use Linear Combination of Atomic Orbitals, LCAO)

Both models qualitatively yield the same results and are well known to most of you in details from the lectures on Solid State Physics by Prof. M. Grüninger and Pd Dr. T. Lorenz .

To remind you, I just will go briefly through the two models and stress on some relevant points!

Free electron model:

the electrons move in a constant electrostatic potential *U* within the crystal. All the details of the crystal structure is lost when this assumption is made. Consider a metal with a shape of cube with edge length of *L*, **Ψ and *E* can be found by solving Schrödinger equation:**

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \quad \text{, since } U{=}0$$

periodic boundary conditions: $\quad \psi(x+L, y+L, z+L) = \psi(x, y, z)$
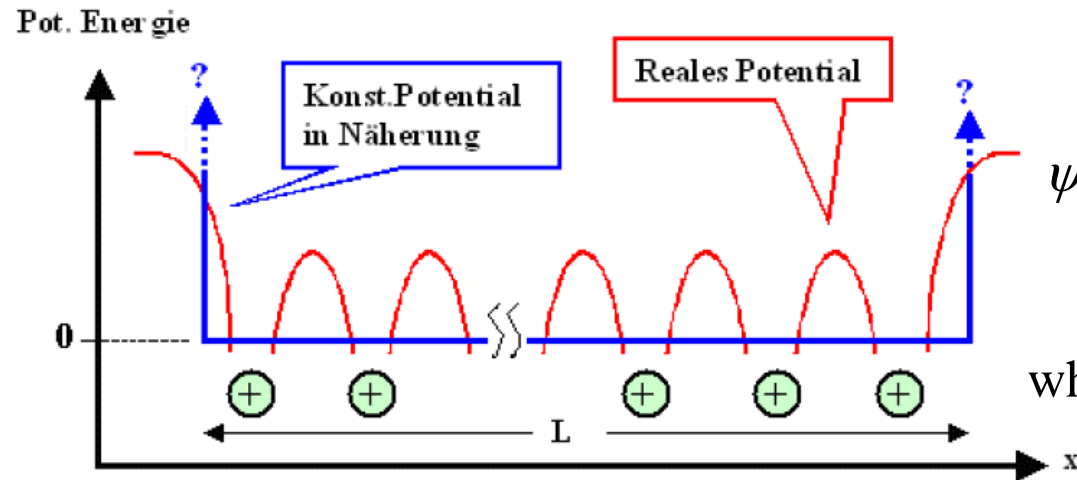
The solutions are plane waves

$$\psi(x, y, z) = \underbrace{\frac{1}{\sqrt{V}}}e^{i\vec{k}\vec{r}} = \frac{1}{\sqrt{V}}e^{i(k_x x + k_y y + k_z z)}$$

Normalization constant

where *V* is the volume of the cube, $V{=}L^3$

- The wave function $\Psi(x,y,z)$ corresponds to an energy of

$$E = \frac{\hbar^2 k^2}{2m}$$ $\longrightarrow$ $$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$$

and momentum $$p = \hbar(k_x, k_y, k_z)$$

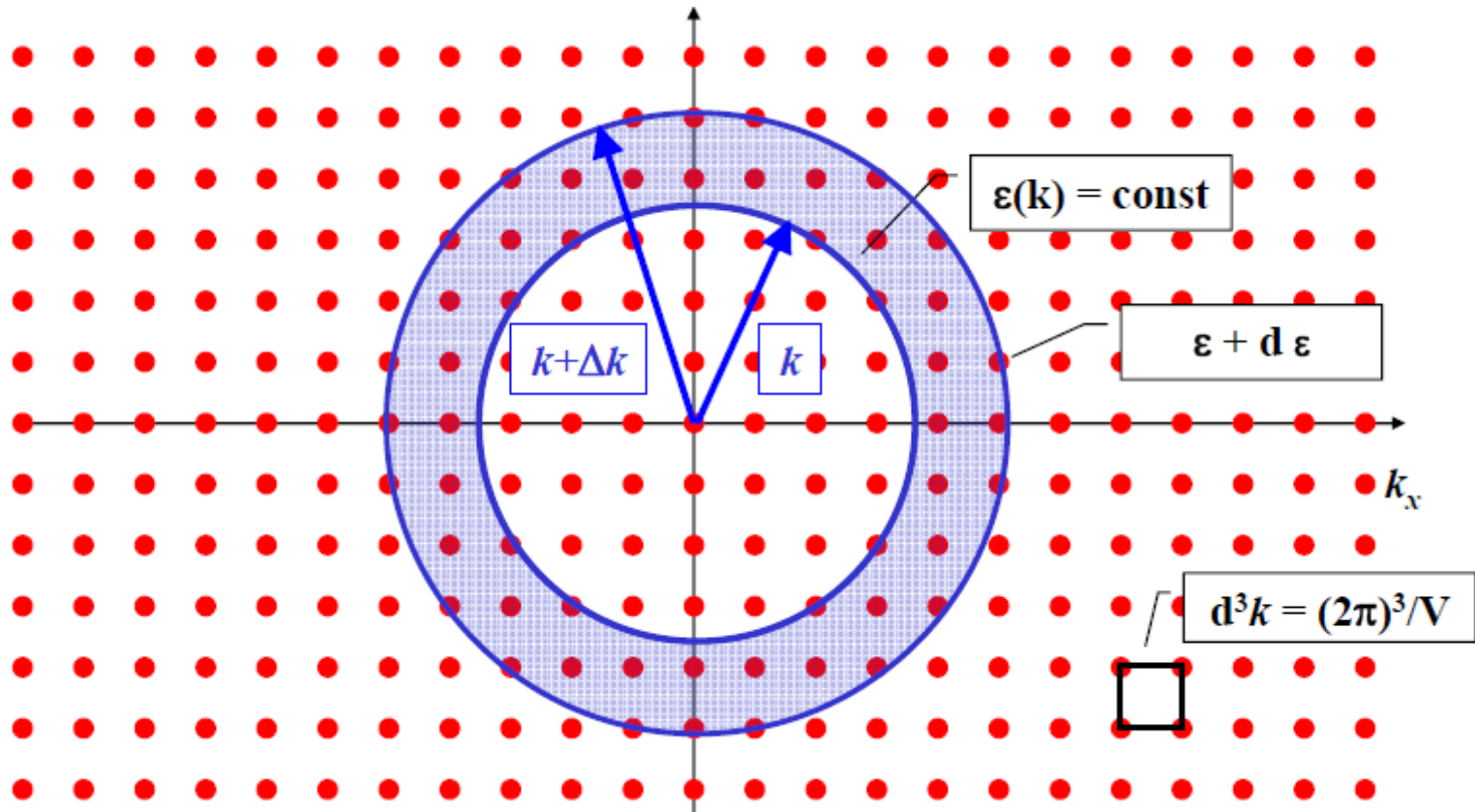periodic boundary conditions only allow discrete wave vectors:

$$k_x = \frac{2\pi n_x}{L} \quad k_y = \frac{2\pi n_y}{L} \quad k_z = \frac{2\pi n_z}{L}$$

$$n_x, n_y, n_z = 0 \pm 1, \pm 2, \pm 3, ...$$

Consequence:
We obtain discrete wave vectors and discrete energies
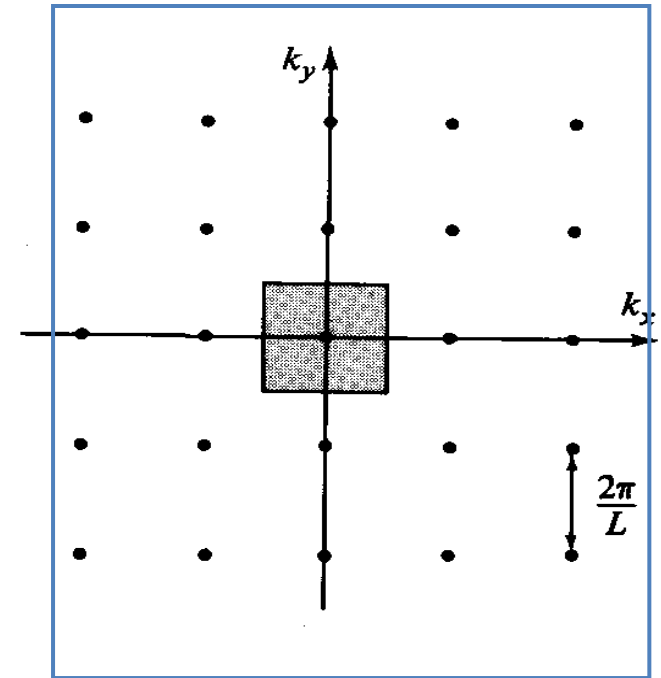
Quantized electronic states in the k-space

Density of states in k-space $D(k)$

Number of states per volume in k-space

volume in k-space is $\left(\dfrac{2\pi}{L}\right)^3$

k-space

➡ density of states in k-space is:

two possible electron states, spin up and spin down

$$D(k) = \frac{2}{\left(2\pi / L\right)^3} = \frac{V}{4\pi^3}$$

Density of States in energy space $D(E)$

We often need to know the <u>density of electron states</u>, which is the <u>number of states per unit energy</u>:

The differential number of electron states in a range of energy dE or wavevector dk is:

$$dN = D(E)dE = D(k)dk$$

This allows:

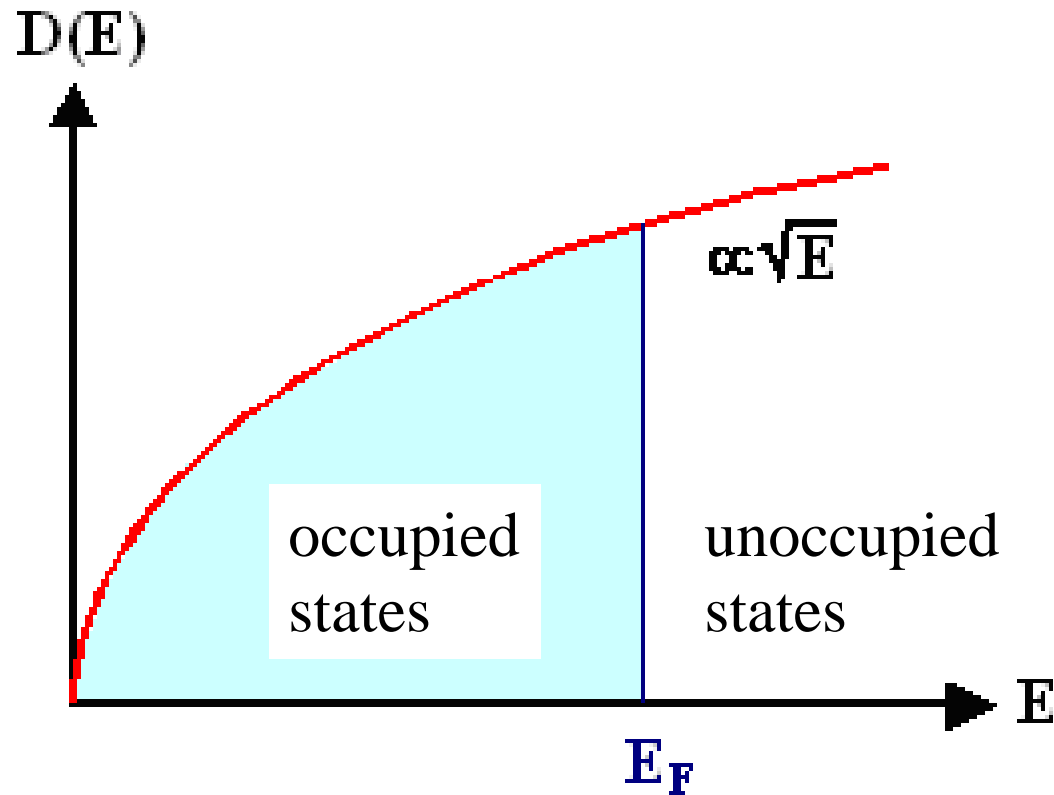$$D(E) = D(k)\frac{dk}{dE} = \frac{D(k)}{dE/dk} = \frac{V/4\pi^3}{\hbar^2 k/m} = \frac{mV}{\hbar^2 4\pi^3 k}$$

Now using the general relation:

$$k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

we get:

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

Density of States in energy space

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

Ground state of the free electron gas (T=0)

- Electrons are fermions (s=±1/2) and obey Pauli exclusion principle; each state can accommodate only one electron.

- The lowest-energy state of N free electrons is therefore obtained by filling the N states of lowest energy.

- Thus all states are filled up to an energy E_F, **Fermi energy**, obtained by integrating density of states between 0 and E_F should equal N. Hence

$$D(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

$$N = \int_0^{E_F} D(E)d(E) = \int_0^{E_F} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}d(E)$$
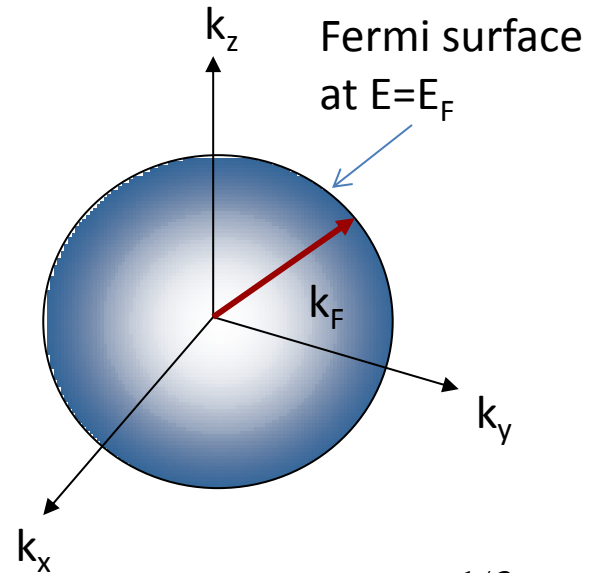
Solve for E_F (Fermi energy);

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \longrightarrow E_F = \frac{\hbar^2 k_F^2}{2m} \longrightarrow k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

The occupied states are inside the Fermi sphere in k-space , the radius is Fermi wave number k_F.

Density of states at the Fermi level $D(E_F)$

This is the most important quantity, as it is related to all the physical properties

$$D(E_F) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{1/2} \qquad \textbf{with} \qquad E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$D(E_F) = \frac{3}{2}\frac{N}{E_F} = \frac{3}{2}\left(\frac{N}{K_B T_F}\right)$$

Energy per electron in the ground state Fermi gas T=0

$$\overline{E} = \frac{3}{5} E_F = \frac{3}{5} K_B T_F$$

Compare with classical gas at T=0
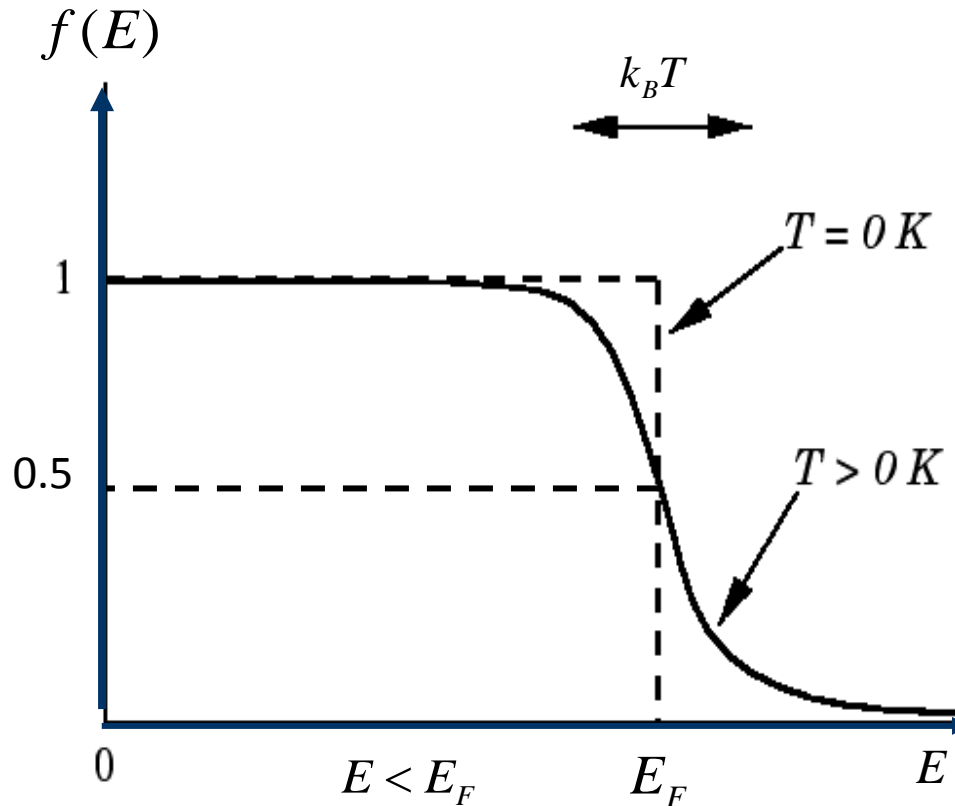
$$\overline{E} = \frac{3}{2} K_B T \qquad \overline{E} \rightarrow 0 \,!$$

Fermi-Dirac distribution Function at T=0 and at a finite temperatures

At a temperature T the probability of occupation of an electron state of energy E is given by the Fermi-Dirac distribution function:

$$f(E) = \frac{1}{e^{(E-E_F)/k_BT} - 1}$$

$f(E)$

k_BT

$T = 0$: $f(E) = 1$ for $E < E_F$
$\qquad \qquad = 0$ for $E > E_F$

$f(E = E_F) = \frac{1}{2}$ for all T

$T = 0\,K$

$T > 0\,K$

1

0.5

0    $E < E_F$ E_F E

only electrons with energies within ~ K_BT of E_F will be able to contribute to thermal processes, transport etc.
Note that: T/T_F $T/T_F \sim 10^{-2}$!

Specific heat of free electron gas

so at temperature T the total energy is:

$$E_{el} = \int_0^\infty E f(E) D(E)\, dE = \int_0^\infty \frac{E D(E)}{e^{(E-E_F)/k_B T} - 1}\, dE$$

and the electronic heat capacity is:

$$C_{el} = \frac{dE_{el}}{dT} = \frac{1}{k_B T^2} \int_0^\infty \frac{E D(E)(E-E_F) e^{(E-E_F)/k_B T}}{\left(e^{(E-E_F)/k_B T} - 1\right)^2}\, dE$$

$$\longrightarrow \boxed{C_{el} = \frac{\pi^2}{3} k_B{}^2 D(E_F) T = \gamma T} \longrightarrow \boxed{C_{el} = \gamma T}$$

$\boxed{\gamma}$ is Sommerfeld coefficient of the heat capacity; $\boxed{C_{el} \propto T}$ $\boxed{and \propto D(E_F)}$

The equation for C_{el} is also valid for electrons in periodic potential using corresponding $D(E_F)$
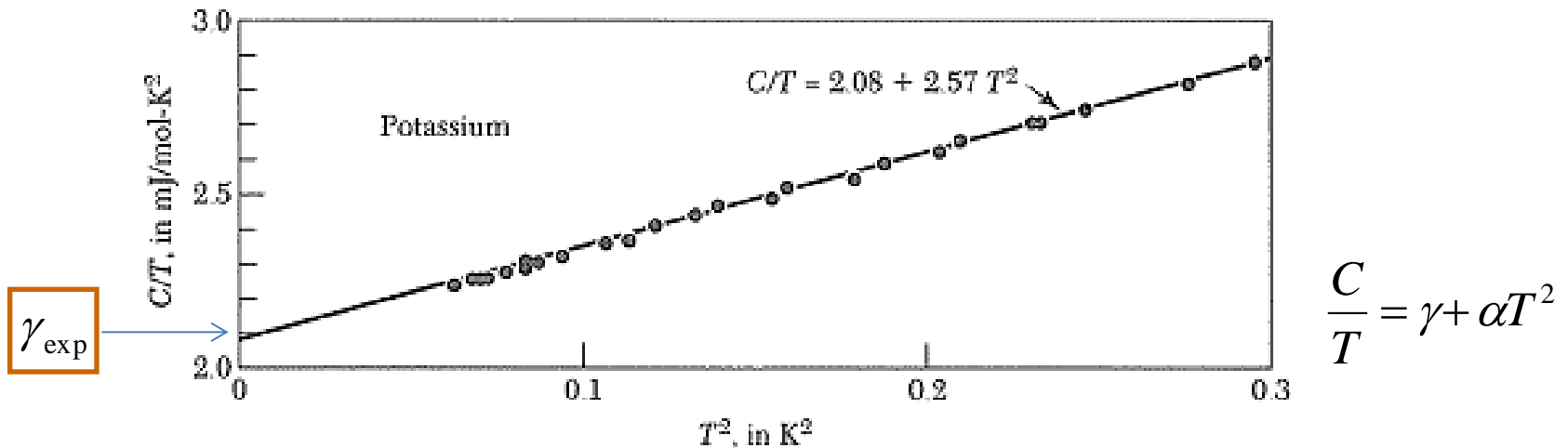
and we know that $\boxed{D(E_F) = \frac{3}{2} \frac{N}{E_F} = \frac{3N}{2} \frac{2m}{\hbar^2 K_F^2}}$ $\longrightarrow$ $\boxed{C_{el} \propto m.T}$

$$\boxed{C_{el} = \frac{\pi^2}{2} N K_B \frac{T}{T_F}}$$, Specific heat per volume $\longrightarrow$ $\boxed{C_{el} = \frac{\pi^2}{2} n k_B \frac{T}{T_F}}$ $n = \frac{N}{V}$

The heat capacity of a metal has <u>two contributions</u>. For a metal at low temperatures we can write the <u>total</u> heat capacity:

$$C(T) = C_{el} + C_{lattice} = \gamma T + \alpha T^3$$

<u>total</u> heat capacity at very low temperatures

$C/T = 2.08 + 2.57\ T^2$

Potassium

γ_{exp}

$$\frac{C}{T} = \gamma + \alpha T^2$$

per mole:

$$\gamma_{free} = \frac{\pi^2}{3} K_B^2 D(E_F) = \frac{\pi^2 K_B^2 m N_0 z}{\hbar^2 (3\pi^2 N / V)^{2/3}}$$

N_0 Avogadro s number and z number of conduction electrons per formula unit

The effective mass of electrons and density of states

$$D(E_F) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{\ 1/2} \qquad C_{el} = \frac{\pi^2}{3}k_B^{\ 2}D(E_F)T = \gamma T \quad , \text{ hence } \boxed{\gamma \propto m}$$

For free electrons γ calculated per mole:

$$\gamma_{th} = \frac{\pi^2}{3}k_B^2 D(E_F) = \frac{\pi^2 k_B^2 m N_0 z}{\hbar^2 (3\pi^2 N/V)^{2/3}}$$

N_0 Avogadro s number and z number of conduction electrons per formula unit

Bloch theorem for non-interacting electrons in a periodic potential

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

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

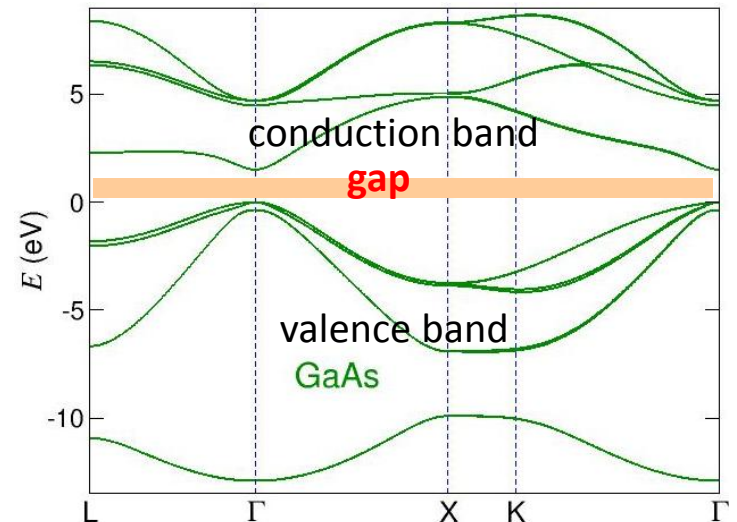**R is a Bravais lattice vector!**

… where $U(\vec{r})$ is a function with the periodicity of the lattice …

Bloch's theorem tells us that eigenstates have the form

$$\psi(\vec{r})=e^{i\vec{k}\cdot\vec{r}}U(\vec{r})$$

Energy eigenvalues $E_n(\vec{k})$ **Band structure!**

conduction band
gap
valence band
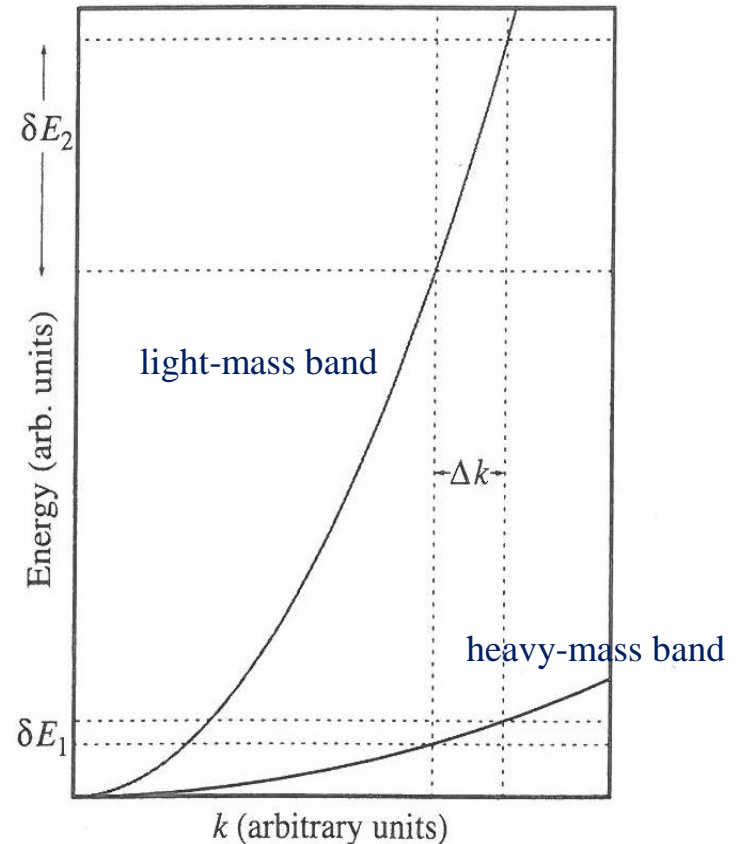GaAs

Some comments to the effective mass of electrons

The effective mass of Bloch electrons

The motion of electrons is modified by the crystal potential through which it moves

$$m^* = \left(\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \right)^{-1}$$

1/ curvature of the band is proportional to m^*

Heavy effective mass implies high density of states D(E) and high γ and vice versa ⟹

Electrons in a crystal are accelerated in response to an external force just as though they were free electrons with effective mass m^*

light-mass band

heavy-mass band

δE_2

δE_1

Energy (arb. units)

$\leftarrow \Delta k \rightarrow$

k (arbitrary units)

The effective mass of electrons and density of states

$$D(E_F) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{1/2}$$

$$C_{el} = \frac{\pi^2}{3} k_B^2 D(E_F) T = \gamma T \quad , \text{ hence } \quad \boxed{\gamma \propto m}$$

For free electrons γ calculated per mole:

$$\gamma_{th} = \frac{\pi^2}{3} k_B^2 D(E_F) = \frac{\pi^2 k_B^2 m N_0 z}{\hbar^2 (3\pi^2 N/V)^{2/3}}$$

N_0 Avogadro s number and z number of conduction electrons per formula unit

comparison of γ_{th} with experimental γ values

m^*

$$\frac{m^*}{m} \equiv \frac{\gamma}{\gamma_{th}}$$

Metal	γ	γ_{th}	Metal	γ	Metal	γ
Li	1.63	0.749	Fe	5.0	$CeAl_3$	1600
Na	1.38	1.094	Co	4.7	$CeCu_6$	1500
K	2.08	1.668	Ni	7.1	$CeCu_2Si_2$	1100
Cu	0.69	0.505	La	10	$CeNi_2Sn_2$	600
Ag	0.64	0.645	Ce	21	UBe_{13}	1100
Au	0.69	0.642	Er	13	U_2Zn_{17}	500
Al	1.35	0.912	Pt	6.8	YbBiPt	8000
Ga	0.60	1.025	Mn	14	$PrInAg_2$	6500

$\gamma / \gamma_{th} \approx 1 - 1.5$

$\gamma / \gamma_{th} \approx 10 - 30$

$\boxed{\gamma / \gamma_{th} \approx 100 - 1000}$

mainly s-electrons,
broad bands

partially filled d-bands

heavy fermion compounds 4 f (5f)-orbitals strong electron-electron correlations SCES

Why m^* is so large in some 4f and 5f electron system?

No answer from the band theory (one electron approximation),
neglecting electron-electron interactions. This will be discussed in Chapter II (b).

Effective mass of localized and extended density of states (see Board!)

a large value of the Sommerfeld coefficient indicates that heavy fermion materials have a high density of states at the Fermi Energy.
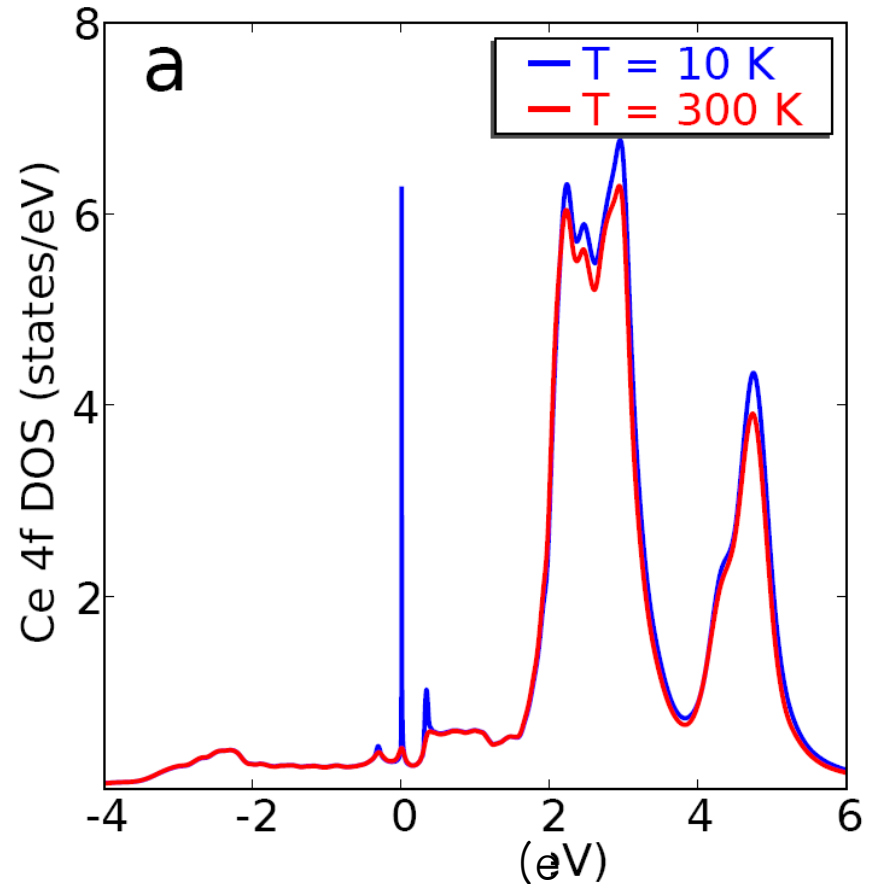
J. H. Shim, KH, and G. Kotliar Science 318, 1618 (2007).

Some comments on electrons in Solids:

Theoretical description using **two different approachs/ approximations** without taking into account electon-electron correlations:

- The nearly-free electron model (itinerant electrons in very weak periodic potential)

- The tight-binding model (electrons localized on an atomic site but weakly coupled to all other atoms----use Linear Combination of Atomic Orbitals, LCAO)

Both models qualitatively yield the same results and are well known to most of you from the lectures on Solid State Physics by Prof. M. Grüninger and Pd Dr. T. Lorenz.

To remind you, I just will go briefly through the two models and stress on some relevant points!

The tight-binding model

Basic idea:

The full Hamiltonian of the system is approximated by using the Hamiltonians of isolated atoms, each one centered at a lattice point.

The eigenfunctions are assumed to have amplitudes that go to zero as distances approach the lattice constant.

The assumption is that any necessary corrections to the atomic potential will be small.

The solution to the Schrodinger equation for this type of single electron system, which is time-independent, is assumed to be a linear combination of atomic orbitals.

Now see Board!

The tight – binding model

- Electrons (inner shells) are strongly localized and mainly see the atomic potential

  $\Rightarrow$ use Linear Combination of Atomic Orbitals (LCAO)

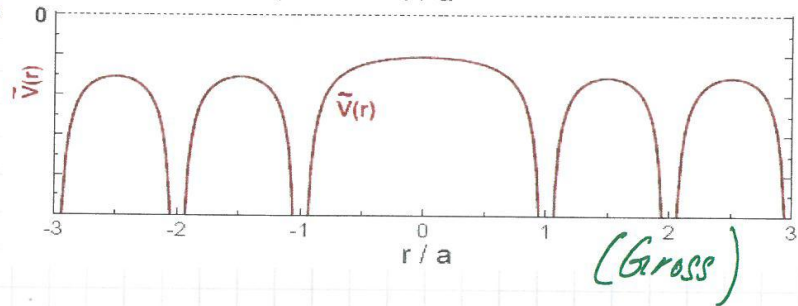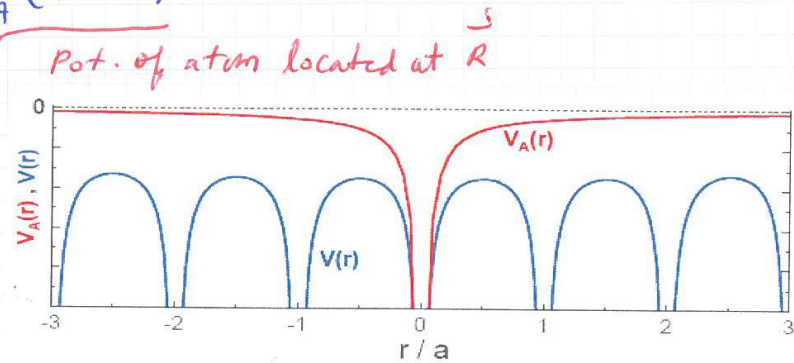- The atomic wave function of level i ϕ_A^i at site $\vec{R}$ ($\vec{R}$ site of Bravais lattice) is defined by

$$\mathcal{H}_A(\vec{r}-\vec{R}) \cdot \phi_A^i(\vec{r}-\vec{R}) = E_A^i \phi_A^i(\vec{r}-\vec{R}) \quad\underline{\qquad} \quad \boxed{(7.7)}$$

$$\Rightarrow \quad \mathcal{H}_A(\vec{r}-\vec{R}) = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + \underline{V_A(\vec{r}-\vec{R})}$$
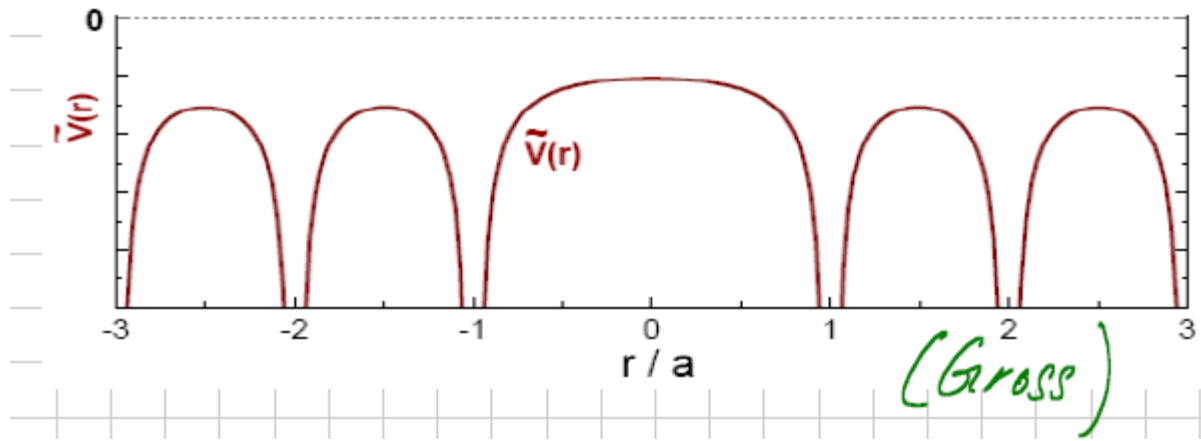
Pot. of atom located at $\vec{R}$
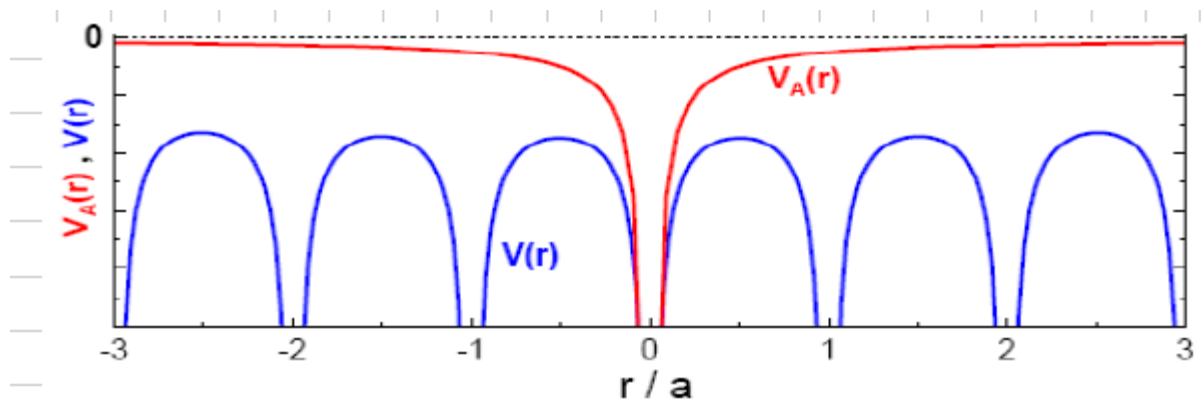
- Lattice periodic potential

$$V(\vec{r}) = \sum_{\vec{R'}} V_A(\vec{r}-\vec{R'})$$

$$= V_A(\vec{r}-\vec{R}) + \underline{\sum_{\vec{R'} \neq \vec{R}} V_A(\vec{r}-\vec{R'})}$$

$$= \tilde{V}(\vec{r}-\vec{R})$$

$\Rightarrow$ lattice : single atom at $\vec{R}$ + rest !

(Gross)

$V_A(r)$, $V(r)$

$V_A(r)$

$V(r)$

r / a

$\tilde{V}(r)$

$\tilde{V}(r)$

r / a

(Gross)

Hamiltonian for single electron : $\boxed{\mathcal{H} = \mathcal{H}_A + \tilde{V}(\vec{r} - \vec{R})}$

approx. :
electrons see mainly the atomic
pot. $\rightarrow \tilde{V}(\vec{r} - \vec{R})$ is a
perturbation !

tight binding Wave functions :

for any strength of the periodic pot. , Wave functions have to fulfill the Bloch theorem

$$\Phi_{\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k}\vec{R}} \Phi_{\vec{k}}(\vec{r})$$

use linear combination of $\phi(\vec{r} - \vec{R})$ for all $\vec{R}$

$$\sim \boxed{\Phi_{\vec{k}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \phi^i_A(\vec{r} - \vec{R})}$$ Tight-binding Wf   ⓐ

satisfy the Bloch condition , whilst displaying the atomic character of the levels

$\sim$ with $\mathcal{H}\Psi_{\vec{k}}(\vec{r}) = E(\vec{k})\Psi_{\vec{k}}(\vec{r})$ and $\mathcal{H} = \mathcal{H}_A + \tilde{V}(\vec{r} - \vec{R})$, $\Phi_{\vec{k}}(\vec{r})$ from ⓐ

$$\Rightarrow \boxed{\mathcal{H}(\Psi_{\vec{k}}(\vec{r}) = \left\{\mathcal{H}_A + \bar{V}(\vec{r} - \vec{R})\right\}\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi^i_A(\vec{r} - \vec{R}) = \underline{E(\vec{k})}\,\Psi_{\vec{k}}(\vec{r})} \quad —\, Ⓐ$$

Band structure !

To evaluate $E(\vec{k})$, we multiply Ⓐ by $\phi^*_A(\vec{r})$ and integrate over all $\vec{r}$

(see details of calculation in lectures (Grüninger , Lorenz)

eqs. (A) becomes

$$\Rightarrow \int \phi_A^*(\vec{r}) \mathcal{H}_A \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi_A(\vec{r}-\vec{R}) \, d^3r + \int \phi_A^*(\vec{r}) \tilde{V}(r) \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi_A(\vec{r}-\vec{R}) \, d^3r$$

$$\underbrace{\text{I} \Rightarrow E_A^i}_{} \qquad \underbrace{\text{II} \Rightarrow \text{Bands}!}_{}$$

$$= \underbrace{\int \phi_A^*(\vec{r}) \, E(\vec{k}) \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi_A(\vec{r}-\vec{R}) \, d^3r}_{\text{III} \Rightarrow E(\vec{k})}$$

Integral I yields E_A^i , Integral III gives $E(\vec{k})$ $\left[\int \text{with } \vec{R}=0 \text{ is } \gg \text{ all others as} \atop \phi(\vec{r}) \text{ is so short range}\right]$

Integral II is the one which gives rise to the bands :

for a simple cubic crystal with $\vec{a}_1 = a\,\vec{e}_1$, $\vec{a}_2 = b\,\vec{e}_2$ and $\vec{a}_3 = c\,\vec{e}_3$ (e_j are the mutually $\perp$ Cartesian unit vectors)

with 6 nearest neighbors and considering s – orbit

Integral II $\rightarrow$ is non-negligible only for the on-site ($\vec{R}=0$) and nearest –neighbor values of $\vec{R}$

i.e $R = \pm a\,\vec{e}_1 , \pm b\,\vec{e}_2 , \pm c\,\vec{e}_3 \Rightarrow \int (\text{II})$ thus splits into discrete terms !

$$\underbrace{\int \phi_A^*(\vec{r}) \tilde{V}(\vec{r}) \phi_A(\vec{r}) \, d^3r}_{A} + \left(e^{ik_x a} + e^{-ik_x a}\right) \int \phi_A^*(\vec{r}) \tilde{V}(\vec{r}) \phi_A(\vec{r}+\vec{a}_1) \, d^3r$$

$$+ \left(e^{ik_y b} + e^{-ik_y b}\right) \int \phi_A^*(\vec{r}) \tilde{V}(\vec{r}) \phi_A(\vec{r}+\vec{a}_2) \, d^3r$$

$$+ \left(e^{ik_z c} + e^{-ik_z c}\right) \int - - - - \phi_A(\vec{r}+\vec{a}_3) \, d^3r$$

$$\Rightarrow \boxed{E(\vec{k}) = E_A^i - A - 2t_x \cos(k_x a) - 2t_y \cos(k_y b) - 2t_z \cos(k_z c)} \quad \text{——(B)}$$

t_x, t_y, t_z hopping integrals

atomic level

binding energy

(electrons at site $\vec{R}$ feel
the attraction potential
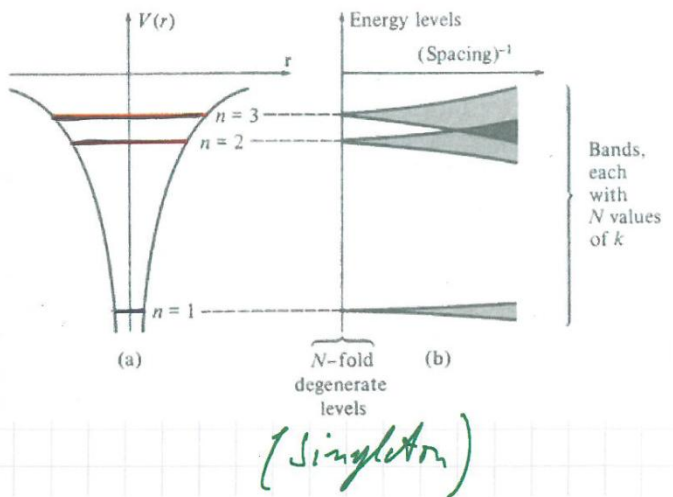$\tilde{V}(\vec{r}-\vec{R})$ of all other ions

Bandwidth $W = 12t$ in 3D cubic lattice

($\cos$ from -1 to $+1$)

— dispersion results from finite overlap (hopping)
in general:

$$\Rightarrow t \sim \langle \phi_A^i (r-\vec{R}') | \tilde{V} | \phi_A^i (r-\vec{R}) \rangle$$

$\vec{R}'$ nearest neighbor

Schematic representation of formation of TB bands

(a)   N-fold degenerate levels   (b)

(Singleton)

notes: Band width depends on the spatial extent
of wf, interatomic distance, and on
the number of nearest neighbors (nn)

$$W \approx 2zt \qquad z = 2 \text{ for } 1D$$

no. of nn

eqs. ⓑ for 1D

$$\Rightarrow \boxed{E(k) \approx E_A - 2t \cos k_x x} \quad \text{(B')}$$

Effective mass and hopping integral :

from eqs. Ⓑ :   For small k $\Rightarrow$ $\cos(k_f a) \simeq 1 - \frac{1}{2}(k_x a)^2$

$$\Rightarrow E(\vec{k}) = E_A^i - A - 6t + t a^2 k^2$$

$\underbrace{E_A^i - A - 6t}_{\text{constant !}}$

$$\Rightarrow E(\vec{k}) \simeq t a^2 k^2 \qquad \left(E(k) = \frac{\hbar^2 k^2}{2m_{eff}} \quad \text{free electrons !}\right)$$

$$\Rightarrow t a^2 k^2 = \frac{\hbar^2 k^2}{2 m_{eff}}$$

$$\Rightarrow \boxed{m_{eff} = \frac{\hbar^2}{2 t a_2}} \quad \text{or} \quad E(\vec{k}) = E_0 + \frac{\hbar}{2 m_{eff}} k^2$$

$$\text{TB-model}$$

note :

(1) for $t > 0$ or $t < 0$ $\rightarrow$ m can be +ve or -ve

(2) if t small $\rightarrow$ overlap small $\Rightarrow$ narrow band , $\Rightarrow$ large effective mass

$\quad$ " t large — for large $\Rightarrow$ broad bands $\qquad\qquad$ f electrons heavy fermion

$\qquad \rightarrow$ t small $\Rightarrow$ difficult for electron to hope , m_{eff} large ①

Electron Density of States: LCAO