# Electronic structure of Solids I





A free electron model is the simplest way to represent the electronic structure of solids such as metals.

Although the free electron model is a great oversimplification of the reality, is able to describe many important properties of conductors.

### *Fermi Gas :*

- Valence electrons are considered to travel freely throughout the crystal, neglecting the interaction of electrons with ions of the lattice and the interaction between electrons
- Pauli principle is taken into account.



*Enrico Fermi (1901 – 1954)*



*1D-conductor = "particle in a 1D-box"*

 $\text{trace in a 1D-box } H \quad (x) \quad E \quad (x)$ 

We assume that an electron of mass m is confined to a length L by infinite potential barriers. I that an electron of mass in is commed to a length L by immite<br>arriers.

$$
H\psi_n(x) = \frac{p^2}{2m}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_n(x) = E_n\psi_n(x).
$$



#### Free electron gas model  $S^{\text{S}}$  important property of the free electron gas is that it should meet that it should meet the Pauli exclusion principle, which leads to important consequences. Which leads to important consequences. The consequences of th We consider first a free electron gas in one dimension. We assume that an electron of mass *m* is We consider first a free electron gas in one dimension. We assume that an electron of mass *m* is

#### We consider first a free electron gas in one dimension. We assume that an electron of mass *m* is confined to a length *L* by infinite potential barriers. The wavefunction ( ) *<sup>n</sup>* <sup>ψ</sup> *x* of the electron is a  $H(x)$  *H*  $\left(x\right)$  *E*  $\left(x\right)$   $\left(x\right)$  $H = \begin{pmatrix} H \\ T \end{pmatrix} = \begin{pmatrix} x \\ F \end{pmatrix} = \begin{pmatrix} x \\ T \end{pmatrix}$  (x) Since w can assume that the potential lies at zero, the Hamiltonian *H* includes only the kinetic

confined to a length *L* by infinite potential barriers. The wavefunction ( ) *<sup>n</sup>* <sup>ψ</sup> *x* of the electron is a

Since w can assume that the potential lies at zero, the Hamiltonian *H* includes only the kinetic

 $\int_{a}$  *h*  $\int_{a}$  *H*<sub>*n*</sub>  $\int_{a}$  *E*  $\int_{a}$  *x*  $\int$  $\begin{pmatrix} \lambda & \lambda \\ \lambda & \lambda \end{pmatrix}$  ( $\lambda$ *n*)<br>lectron of **Mass** m is confined to karlength L by infinite  $2m$ *1D-conductor* = "particle in a 1D-box" We assume that an electron of mass m is confined to a length L by infinite potential barriers.  $\gamma$   $(r)$ 2 (and in the control of the same is confined to the depth of  $\lim_{x\to a} \frac{d}{dx}$  is  $\lim_{x\to a} \frac{d}{dx}$  in the same in the same is  $\lim_{x\to a} \frac{d}{dx}$  in the same in the same in the same is  $\lim_{x\to a} \frac{d}{dx}$  in the same in the *d d d (x) d d (x) d d d d d x d d z i z E d x d z i x z z i x i z x i z x i z x i x x i x x i x x i x x x x x x m m dx*  $H(x)$   $(x)$   $(x)$   $(x)$   $(y)$   $(x)$   $(y)$   $(x)$   $(x)$  takes of  $f(x)$  and  $f(x)$  and  $f(x)$  is configurate takes of  $f(x)$  by  $f(x)$  finite  $2v \cdot v \cdot \frac{1}{b}$ <sup>2</sup> ( ) ( ) ( ) ( ) <sup>2</sup> <sup>2</sup> *<sup>n</sup> <sup>n</sup> <sup>n</sup> <sup>n</sup> <sup>n</sup> <sup>p</sup> <sup>d</sup> <sup>H</sup> <sup>x</sup> <sup>x</sup> <sup>x</sup> <sup>E</sup> <sup>x</sup> m m* is confined to the  $\hbar$   $\begin{array}{cc} H & (x) & E \\ (x) & E & (x) \end{array}$ <br>  $\hbar$   $\begin{array}{cc} H & (x) & E \\ (y) & E & (x) \end{array}$ Note that this is a one-electron equation, which means that we neglect the electron-electron  $\frac{H_{\text{max}}}{2m}$  are discretion of  $\frac{H_{\text{max}}}{2m}$  and  $\frac{H_{\text{max}}}{2m}$  are defining  $\frac{H_{\text{max}}}{2m}$ 

**One dimension**

$$
H\psi_n(x) = \frac{p^2}{2m} \psi_n(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n(x) = E_n \psi_n(x).
$$
  
(x)

*SOLUTIONS :*



# **Fermi energy** (for a system of N electrons)

Free electron gas model

One need to accomodate N electrons in the various quantum states of the particle in a box. usually described by the *distribution function, f*(*E*), which is defined as the probability that the level EXPERIMENT EXPERIENCE FILLING FILLING STATE START FILLING START FILL

The highest occupied state = Fermi level





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solid is characterized by two quantum numbers that are *n* and *ms*, where *n* describes the

orbital (  $x$  ) **n**  $\rightarrow$   $(x)$  , and  $\rightarrow$  the spin momentum of the spin momentum on a spin momentum on a quantization axis.

Electron spin is equal to S=1/2, so that there (2S+1)=2 possible spin states with *ms* = ±½.

Therefore, each orbital labeled by the quantum number *n* can accommodate two electrons,



Periodic boundary conditions = we assume that the crystal is infinite in  $x$ ,  $y$  and  $z$  $\alpha$  odic boundary conditions = we assume that the crystal is infinite in x  $\alpha$  and z  $\mathcal{I}$  many cases, however, it convenient to introduce periodic boundary conditions, as we did for  $\mathcal{I}$ 

$$
\mathbf{r} = \exp(\mathbf{k} \cdot \mathbf{r})
$$
  
\n
$$
\psi(x + L_v^+ y, z) = \psi(x, y, z) \qquad \text{if } v \in \mathbb{R} \text{ and } v \in \mathbb{R} \text{
$$

The solution of the Schrödinger equation which satisfies these boundary conditions, called Born  $\frac{1}{l}$ von Karman periodic conditions, has the form of a traveling plane wave: bilation of the *Schrödinger* equation wave all structures these boundary conditions,  $L^{\text{out}}$  Kannan perform conditions, has the form of a traveling plane wave: solution of the Schrödinger equation which satisfies these boundary conditions,<br>*i*d Born <sub>7</sub> von Karman periodic conditions, has the form of a traveling plane wave:  $L$ <sup>*L*</sup>  $L$   $L$   $L$   $L$   $L$   $L$ ution of the Schrodinger equation wang satisfies these boundary conditions,<br>Born - von Karman periodic conditions, has the form of a traveling plane wave:

$$
\psi_{\mathbf{K}}(\mathbf{r}) = A \exp(i\mathbf{k} \cdot \mathbf{r})
$$
With a quantized wave vector **k**:

$$
(\mathbf{r}) = \exp(\mathbf{k} \cdot \mathbf{r})
$$

(*x, y* + *L, z*) = (*x, y, z*)

$$
E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2mL} = \frac{\hbar^2}{2m} \left( k_x^2 + k_y^2 + k_z^2 \right) \qquad \frac{\pi n_z}{2m}
$$
\n
$$
E_{\mathbf{k}} = \frac{2\pi n_z}{2m} = \frac{\hbar^2 k^2}{2m} \left( k_x^2 + k_y^2 + k_z^2 \right) \qquad \frac{\pi n_z}{2m}
$$
\nQuantization of electronic energy

$$
Quant Z
$$
  
Quantization of electronic energy

 $\mathbf{p} = -i\hbar \nabla$ 

where *nx*, *ny*, and *nz* are positive or negative integers.  $\hbar$   $\hbar$ 2 <del>2</del> 2 2  $h$   $h$   $h$  $\hbar$  ,  $\hbar$ 

## Free electron gas model

and another one being "spin down"

However, electrons are identical fermions and obey Pauli exclusion principal, so only two of them can occupy any particular state (two because of the spin, one being "spin up"

satisfies these boundary conditions has the form of the traveling plane wave:

and similarly for the *y* and *z* coordinates. The solution of the Schrödinger equation (7.7) which

3D-conductor = particle in periodic 
$$
bo(\mathbf{r}) = \exp(\mathbf{k} \cdot \mathbf{r})
$$

*2.1. ETAT FONDAMENTAL A` <sup>T</sup>* = 0 *<sup>K</sup>* **Fermi wave-vector** <sup>5</sup>  $e-vector$ </u>

ground state,

In the ground state, a system of N electrons occupies states with lowest possible energies.

Therefore all the occupied states lies inside the sphere of radius  $k_F$ (Fermi sphere)



$$
E_{\rm k} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left( k_x^2 + k_y^2 + k_z^2 \right)
$$





proque est donn´ee par *V/*8⇡<sup>3</sup>. Dans le cas o`u *V* est grand, le r´eseau de points

#### $Fermi$  *temperature*

and another one being "spin down"

 $k_z$ 

Fermi Surface

 $k_F$   $k_y$ 

If the electrons were distinguishable particles or bosons they all would have been in the

However, electrons are identical fermions and obey Pauli exclusion principal, so only two of the m can occupy any particular state (two because of the spin up"s  $\sim$ 

by

l<br>I







Fermi-Dirac distribution : how to fill the quantum states with electrons?  $p<sub>z</sub>$ , and  $p<sub>z</sub>$ , at  $p<sub>z</sub>$ , at  $p<sub>z</sub>$ , and  $p<sub>z</sub>$ , at  $p<sub>z</sub>$ , and  $p<sub>z</sub>$ , and



 $E = F$ <br> $E_F$  ( $E_F$ ) (1.5) (1.5) (1.5) (1.5) (1.5) Recall in this context that the energy which an electron may absorb thermally is of the order *kBT* ( = empty, and hence when the electrons move to a higher level there is no violation of the exclusion of t distribution at  $\frac{1}{\sqrt{2}}$  = 0°C, except very close to the electrons are excited very close to the electrons are except very close to the electrons are except very close to the electrons are except very close to the elec  $f(E)$  = probability that the level E is occupied by electrons

$$
f(E) = 1
$$
  $\rightarrow$  level completely filled (2 electrons)  
 $f(E) = 0$   $\rightarrow$  level empty

*E*  $E_F$ 

?<br>?<br>?

*E*  $E_F$ 



An important quantity which characterizes electronic properties of a solid is the density of states (DOS), which is the number of electronic states per unit energy range.

Let  $\phi(E)$  be the total number of electronic states of energy  $\lt E$  within a 3D-conductor:

$$
\phi(E) = \frac{V}{3\pi^2} \left(\frac{2mE}{\hbar^2}\right)^{3/2}
$$
  
Then density of states  $g(E)$  is defined as: 
$$
g(E) = \frac{d\phi}{dE}
$$

# Free electron gas model

### *Density of states (DOS)*

Density of states in a 3D-conductor:

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



Normalization:

$$
N = \int_{0}^{E_F} g(E) dE
$$
\n
$$
T = 0 \text{ K}
$$
\n
$$
N = \int_{0}^{+\infty} g(E) f(E, T) dE
$$
\n
$$
T \neq 0 \text{ K}
$$

Where  $f(E, T)$  is the Fermi distribution function.

*Heat capacity of solids – electronic contribution* 

At low temperature  $k_B T \ll E_F$ 

$$
U \qquad ED(E)f(E, \underline{T}) \underset{0}{\overset{+\infty}{E}} E g(E)f(E, T) dE
$$

Each of these *NkBT/EF* electrons has a thermal energy of the order of *kBT*. The total electronic

thermal kinetic energy *U* is of the order of *U*≈(*NkBT/EF*)*kBT*. The electronic heat capacity is

*Cel*=*dU*/*dT*≈*NkB*(*kBT/EF*) and is directly proportional to *T,* in agreement with the experimental

results discussed in the following section. At room temperature *C* is smaller than the classical value

Since only the distribution function depends on Temperature:

$$
C \qquad \qquad \boxed{E\Omega \wr E^{-\frac{dU}{dT}} = \int_{0}^{+\infty} dE g(E) \frac{df(E,T)}{dT} dE}
$$

Using: 
$$
0 = E_F \frac{dN}{dT} = E_F \int_0^L g(E) \frac{df(E, T)}{E} dE \quad , \quad \text{or} \quad \text{where}
$$
\n
$$
C_{el} = \int_0^{+\infty} (E - E_F) g(E) \frac{df(E, T)}{dT} dE
$$
\n
$$
E \qquad E \qquad D \ E \qquad , \quad \text{or} \quad \
$$



At low temperature  $k_B T \ll E_F$ 

 $U$   $ED(E)f(E,T)dE$ *df/dT* is large only at energies which lie close to the Fermi energy:



 $\mathcal{L}_{el} = g(E_F)J_0$ ,  $(\xi - E)E$  *E E E E E E E*  $E \qquad E \qquad D E \qquad D E$   $dE \qquad dT$ So that:  $C_{el} = g(E_F) \int_0^{+\infty} (E - E_F) \frac{df(E,T)}{dT} dE$ 



We also ignore the variation of the chemical potential with temperature and assume that  $\mu = \overline{E}_F$  which is a good approximation at room temperature and below.  $L_F$  which derivation is presented in the appendix  $D = \frac{1}{2}$  of the text book. The text books is  $\frac{1}{2}$  of the text book. The text books is  $\frac{1}{2}$  of the text books. The text books is  $\frac{1}{2}$  of the text books is  $\frac{1}{2}$ 



Additionally, it can be shown that:  $\begin{bmatrix} 0 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \end{bmatrix}$ La largeur de la zone de transition entre la valeur 1 et 0 de *f*(*E*) est  $\mu = E_F$  $\left[1 - \frac{\pi^2}{12} \left(\frac{\text{k}_B T}{E_F}\right)\right]$  $\setminus$ <sup>2</sup>



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And at room temperature  $\mu$  deviates from  $E_F$  by less than 0.01 %



*F <sup>T</sup> <sup>C</sup> Nk* Experimentally the heat eapacity at low temperatures below can be represented as a the heat capacity at low temperatures below can be represented as a  $\frac{1}{2}$  is and phononic contributions: Heat capacity at low temperatures below can be represented as a For the contributions.<br> $C = C_1 + C_2 = \alpha T + \beta T^2$ Experimentally the heat capacity at low temperatures below can be represented as a sum of electronic and phononic contributions:

$$
C = C_{el} + C_{ph} = \alpha T + \beta T^3
$$

where we defined the Fermi temperature / *TF EF <sup>B</sup>* = *k* . This is similar to what we expected to obtain <sup>3</sup> *C* = *Cel* +*Cph* =α*T* + β*T* . (7.33) <sup>3</sup> *C* = *Cel* +*Cph* =α*T* + <sup>β</sup>*T* . (7.33) 1 *µ*

*T*



Experimentally the heat capacity at low temperatures below can be represented as a sum of electronic and phononic contributions:

$$
C = C_{el} + C_{ph} = \alpha T + \beta T^3
$$

