Electronic Materials and Devices

3 Modern theory of solids

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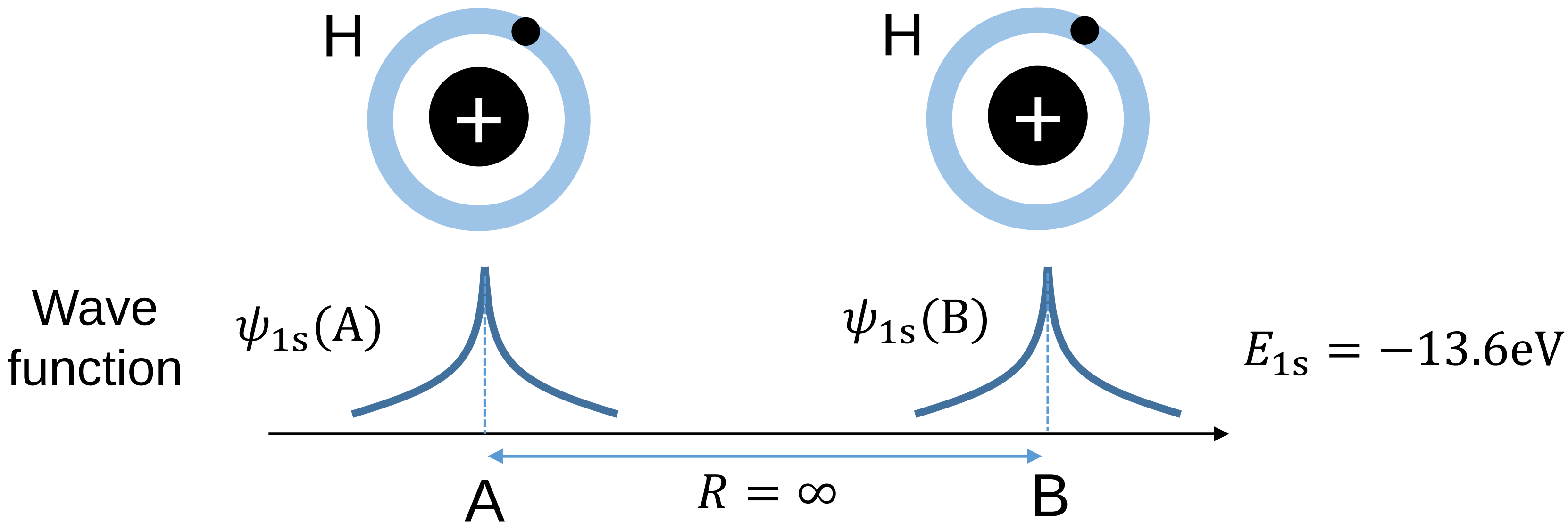
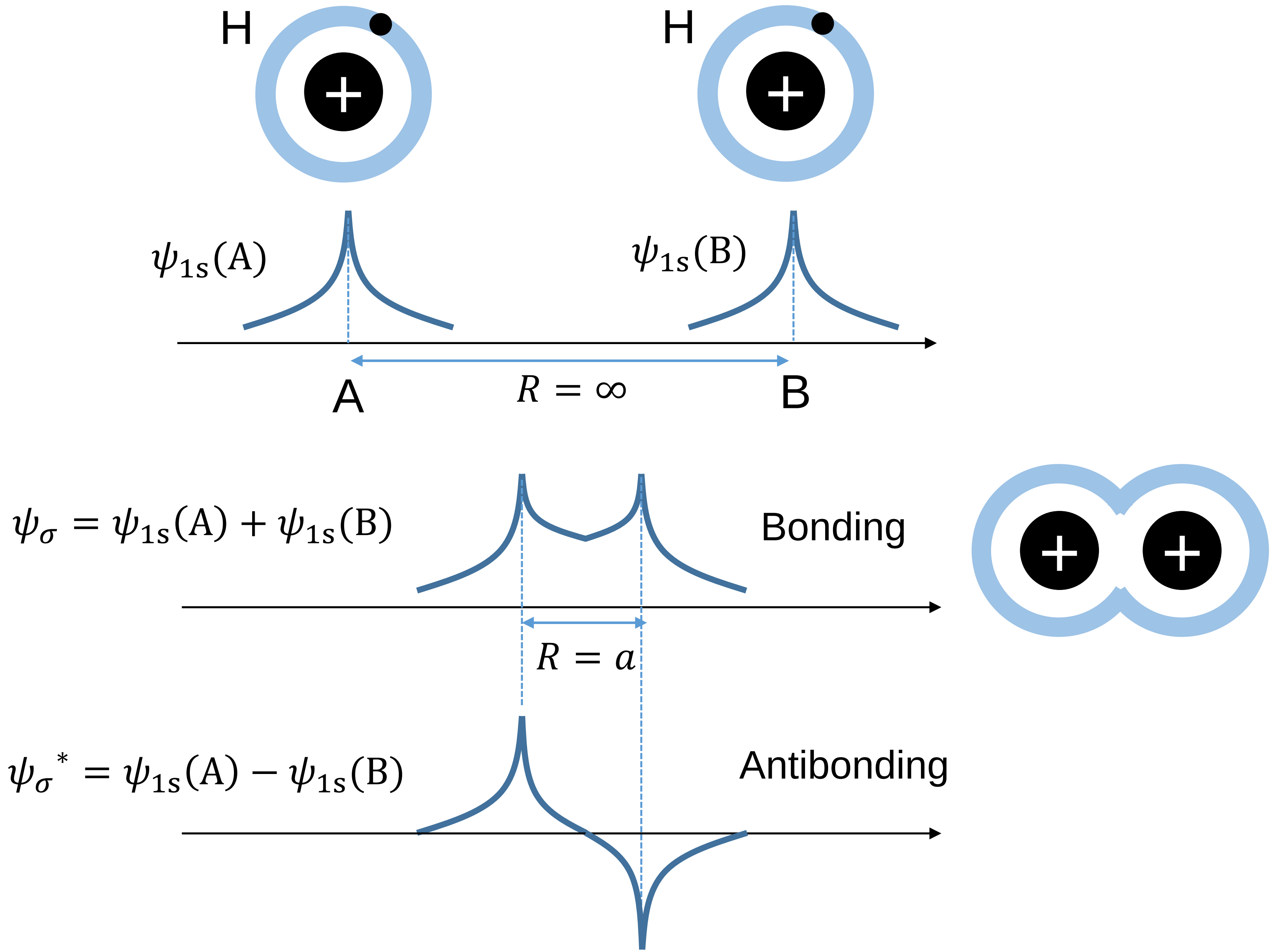
3.7 Hydrogen molecule: molecular orbital theory of bonding

分子轨道成键理论

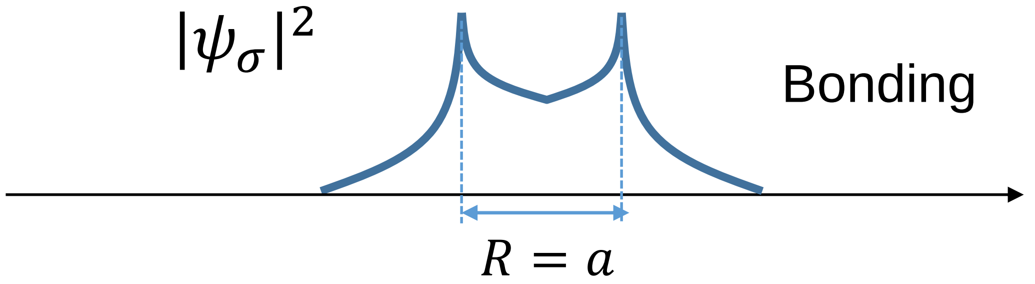


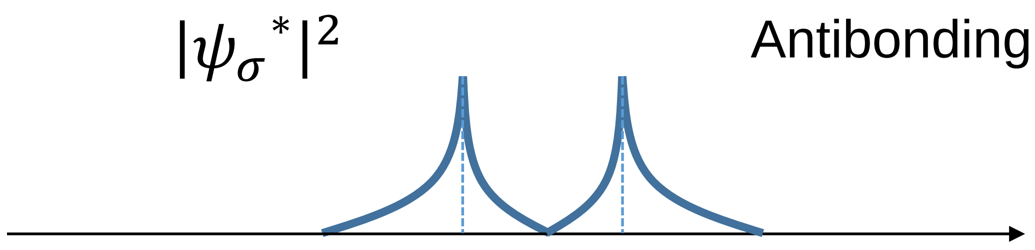
Q: what happens when two hydrogen atoms are brought together?

Linear combination of atomic orbitals 原子轨道线性组合

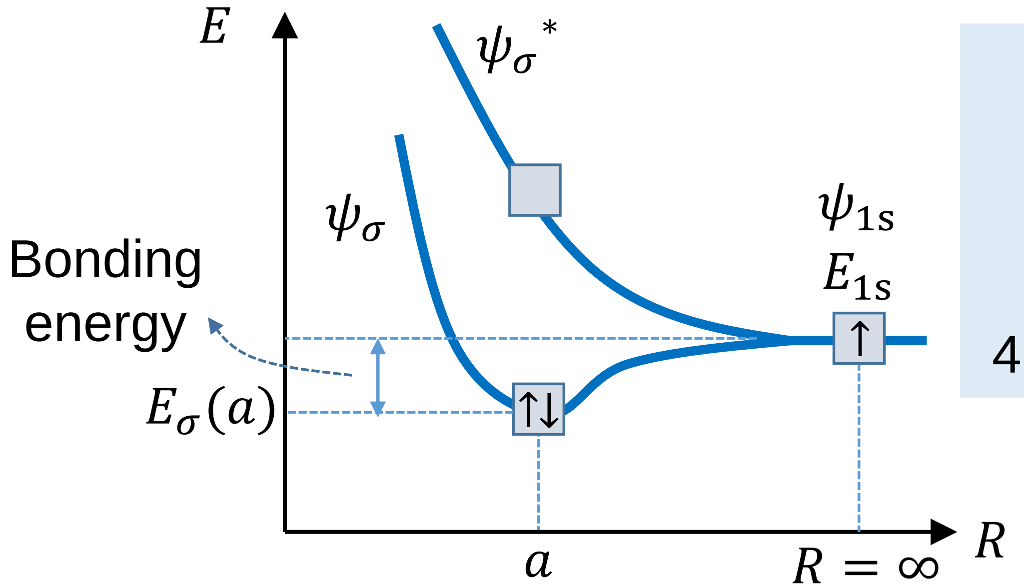


Electron probability distributions for bonding and antibonding orbitals





Energy for bonding and antibonding orbitals

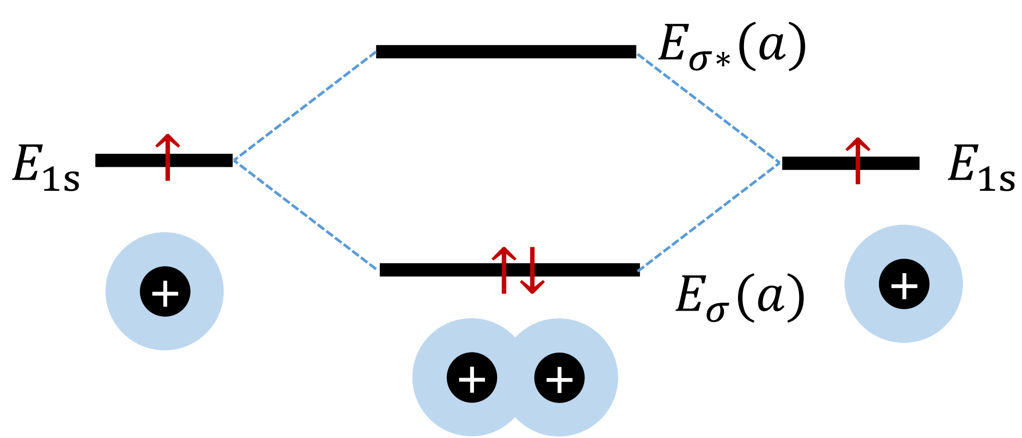


2 H atoms

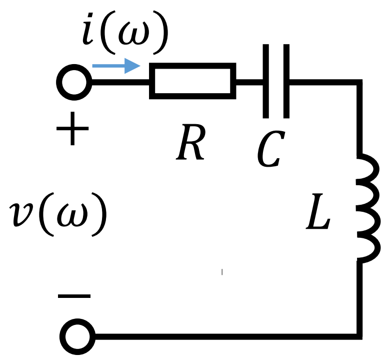
2 Electrons

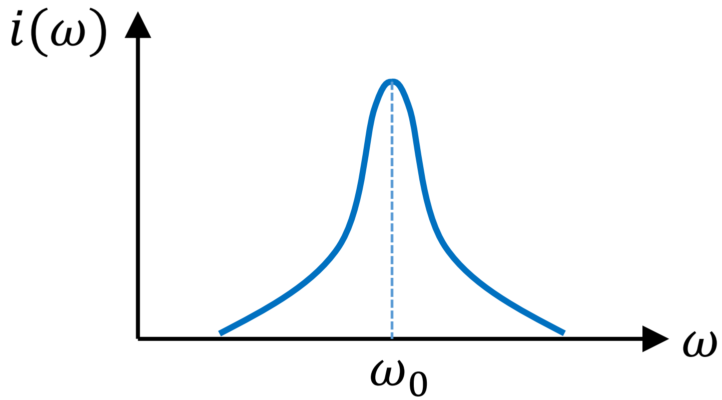
2 Orbitals (1s)

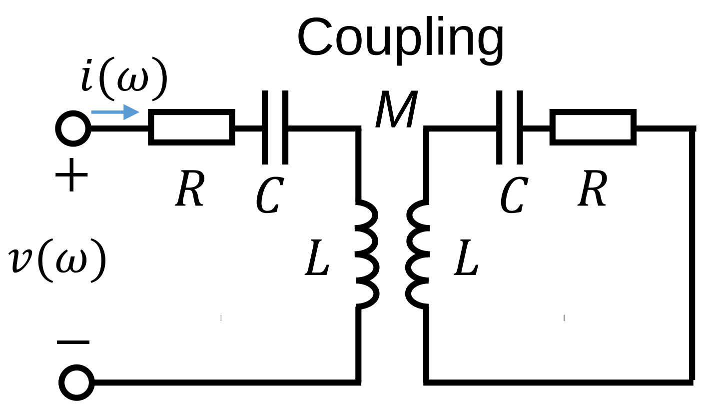
4 States (with spin)

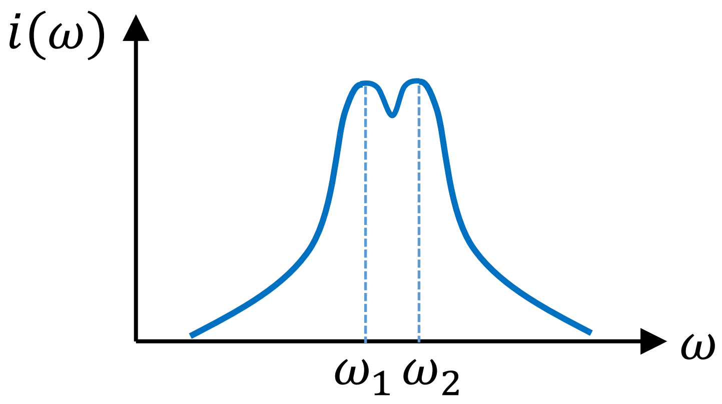


Analogy to RLC resonant circuit





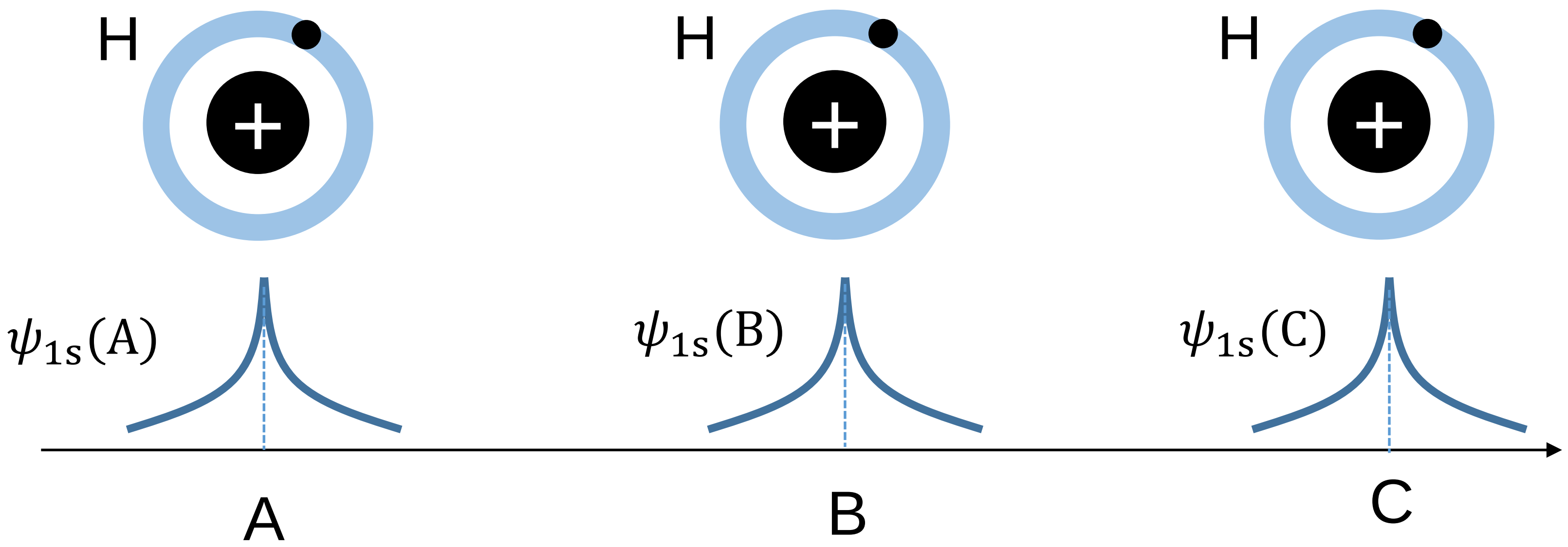




Q: What happens to 2s, and 2p states?

3.8 Band theory of solids 固体能带理论

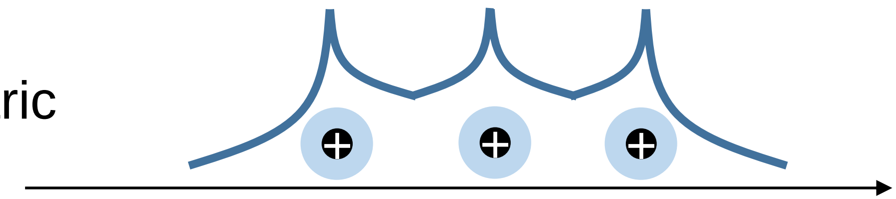
Q: what happens when 3 H atoms are brought together?



The wavefunction must be symmetric or antisymmetric!

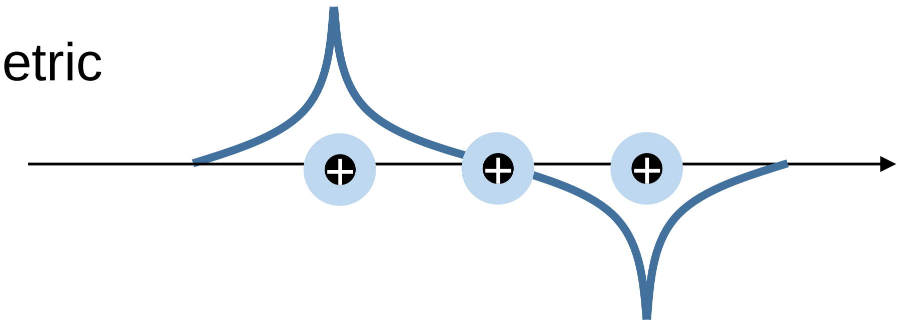
$$\psi_{\mathrm{a}} = \psi_{1\mathrm{s}}(\mathrm{A}) + \psi_{1\mathrm{s}}(\mathrm{B}) + \psi_{1\mathrm{s}}(\mathrm{C})$$

Symmetric



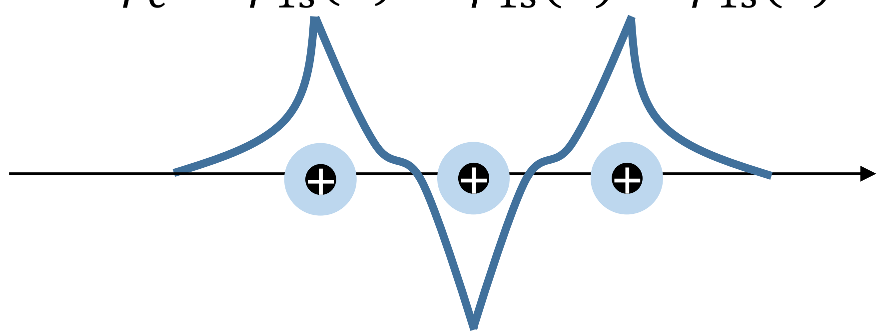
$$\psi_{\mathrm{b}} = \psi_{1\mathrm{s}}(\mathrm{A}) - \psi_{1\mathrm{s}}(\mathrm{C})$$

Antisymmetric

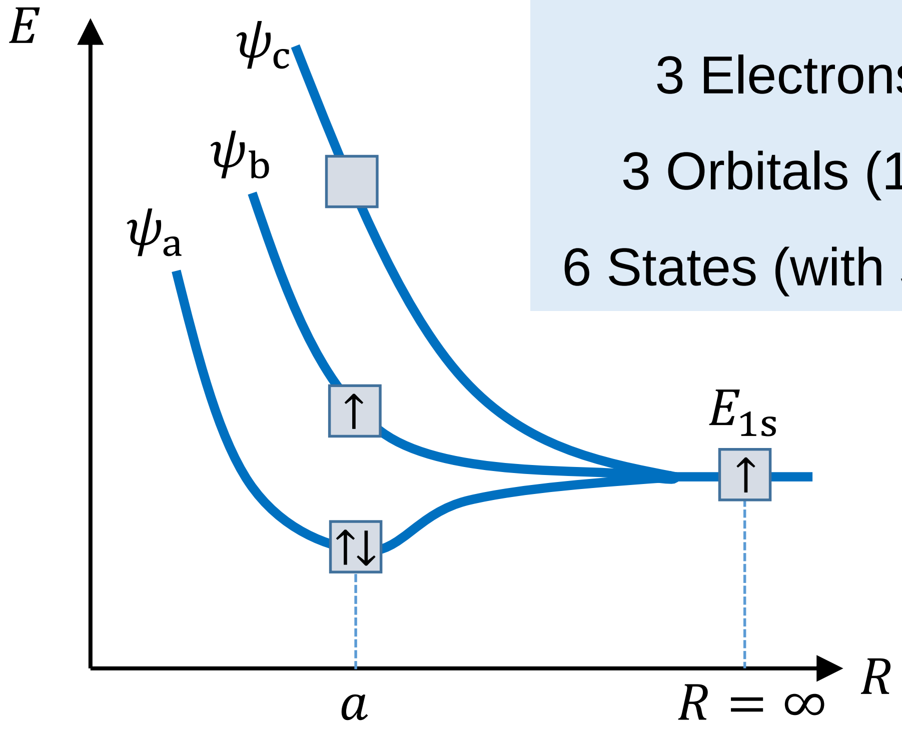


Symmetric

$$\psi_{\mathrm{c}} = \psi_{1\mathrm{s}}(\mathrm{A}) - \psi_{1\mathrm{s}}(\mathrm{B}) + \psi_{1\mathrm{s}}(\mathrm{C})$$



Energy for bonding and antibonding orbitals



3 H atoms

3 Electrons

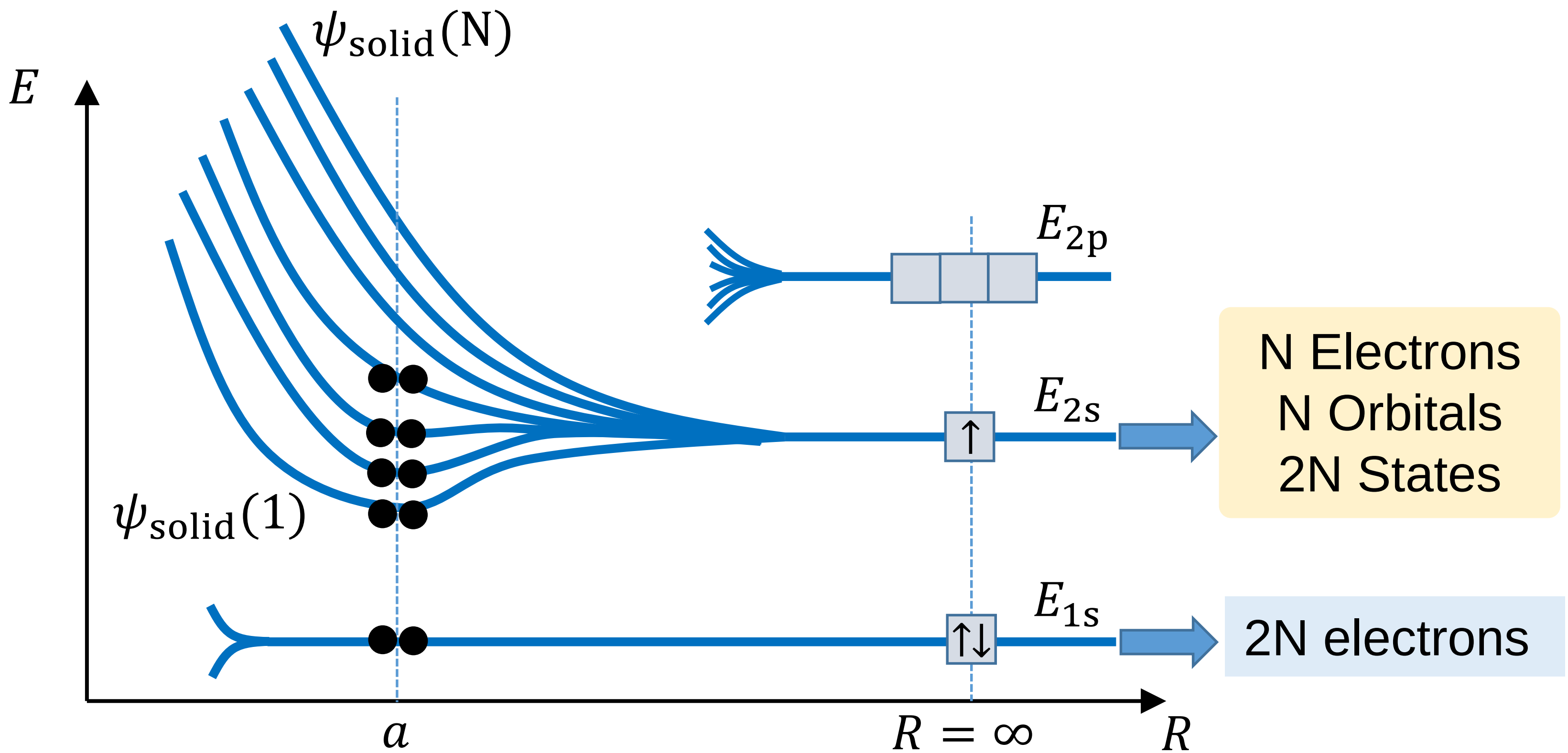
3 Orbitals (1s)

6 States (with spin)

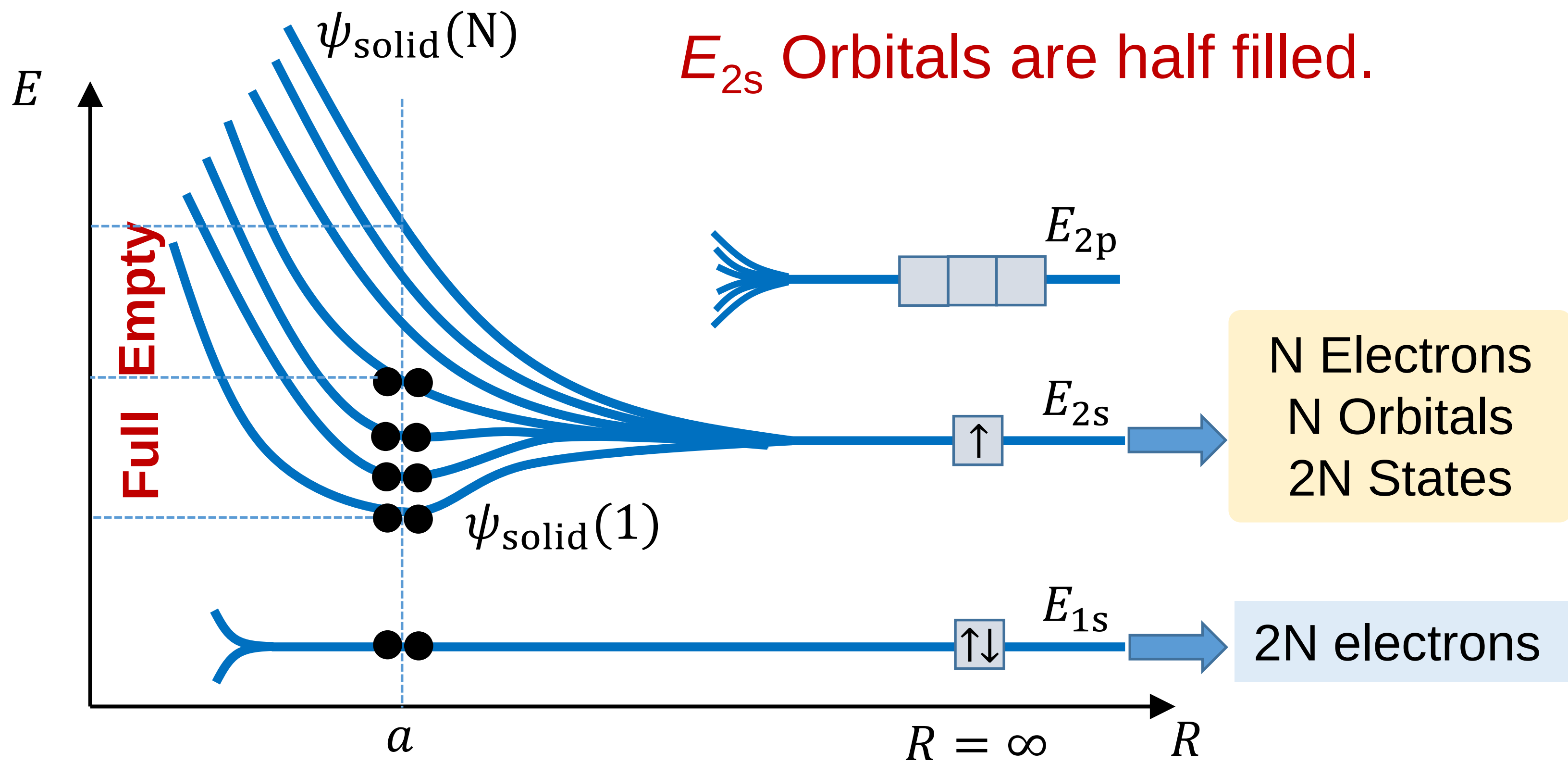
N atoms: Li solid systems

Electronic configuration of Li atoms: $1s^2 2s^1$

The K shell (1s) are fully filled and the splitting of E_{1s} can be neglected.

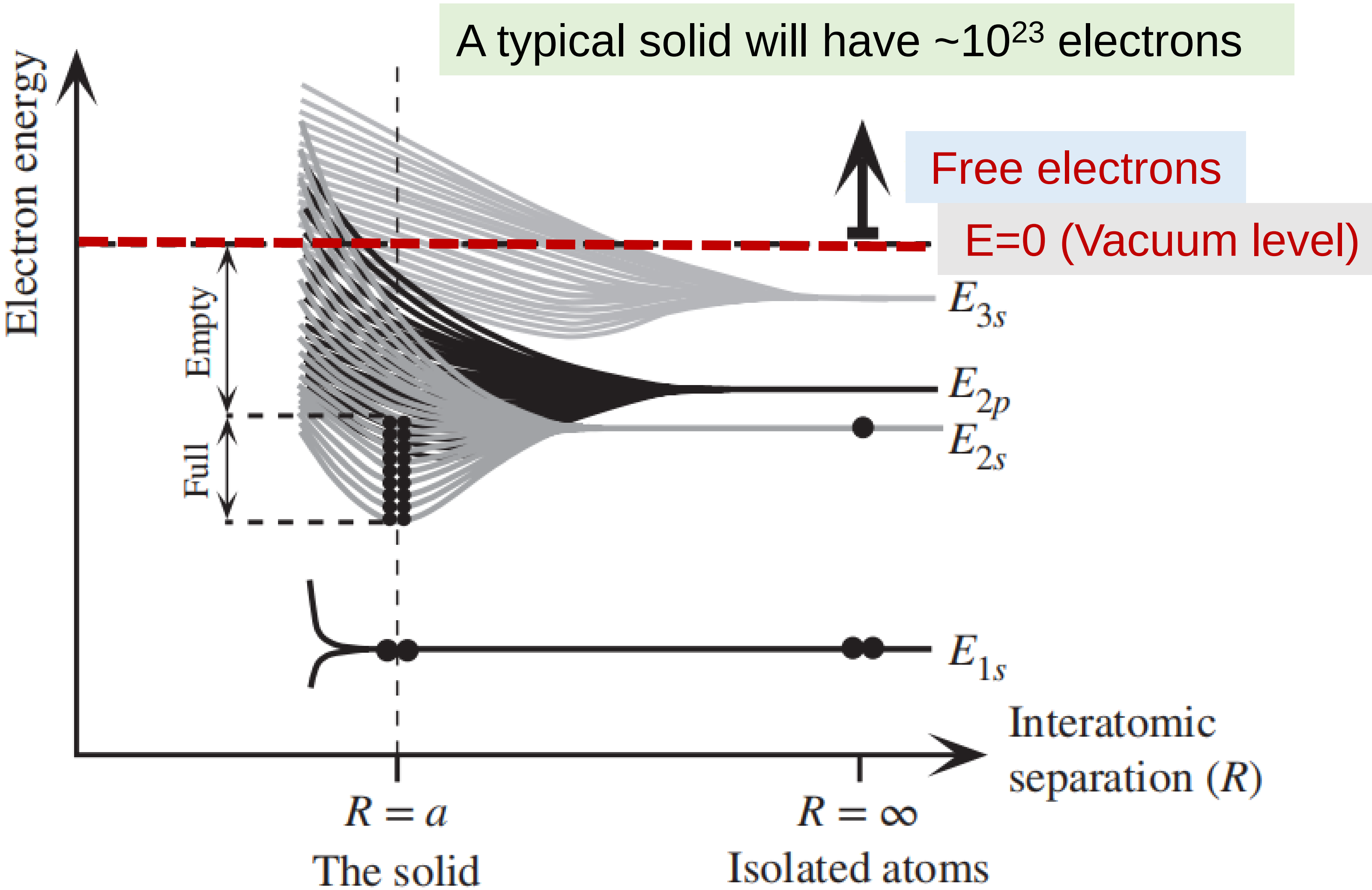


N atoms Li solid systems

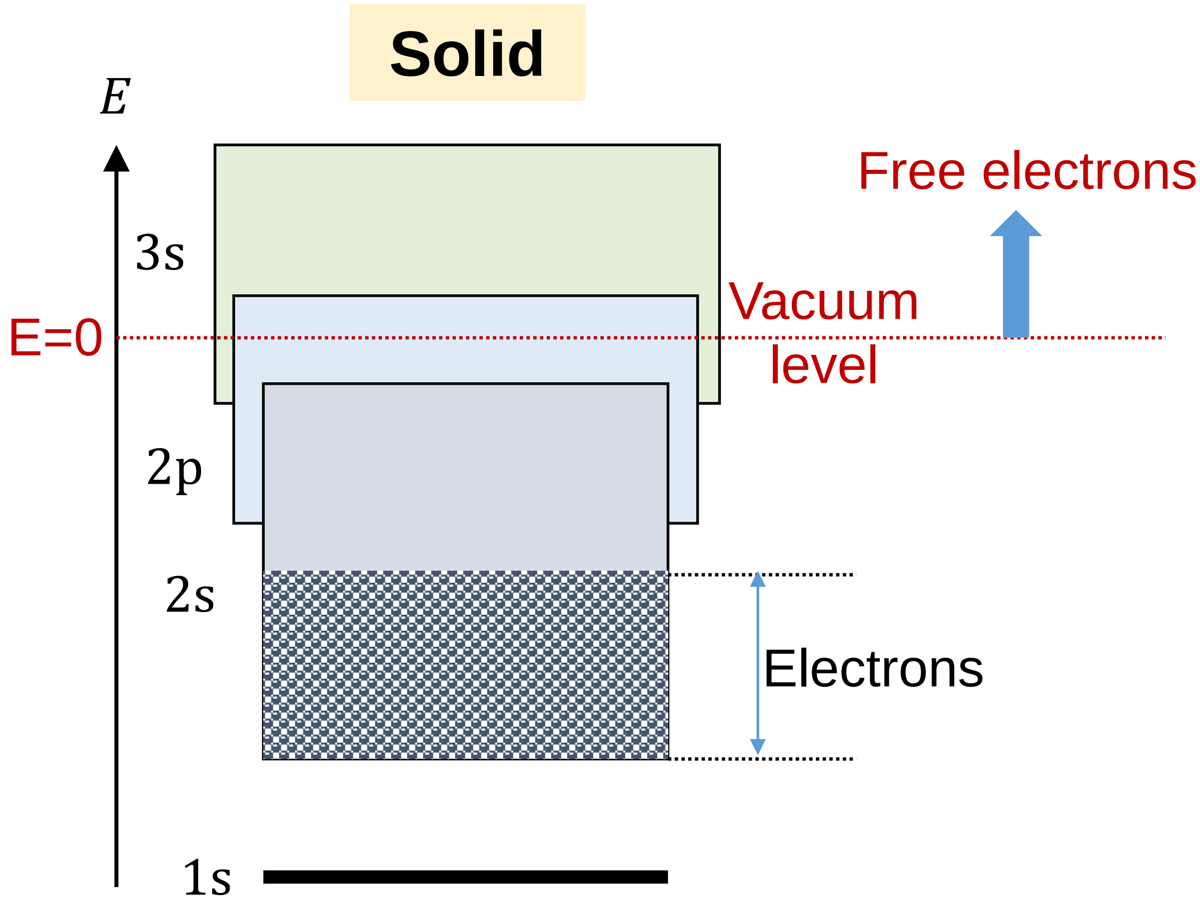


The single 2s energy level splits into N finely separated energy levels, forming an **energy band能带**.

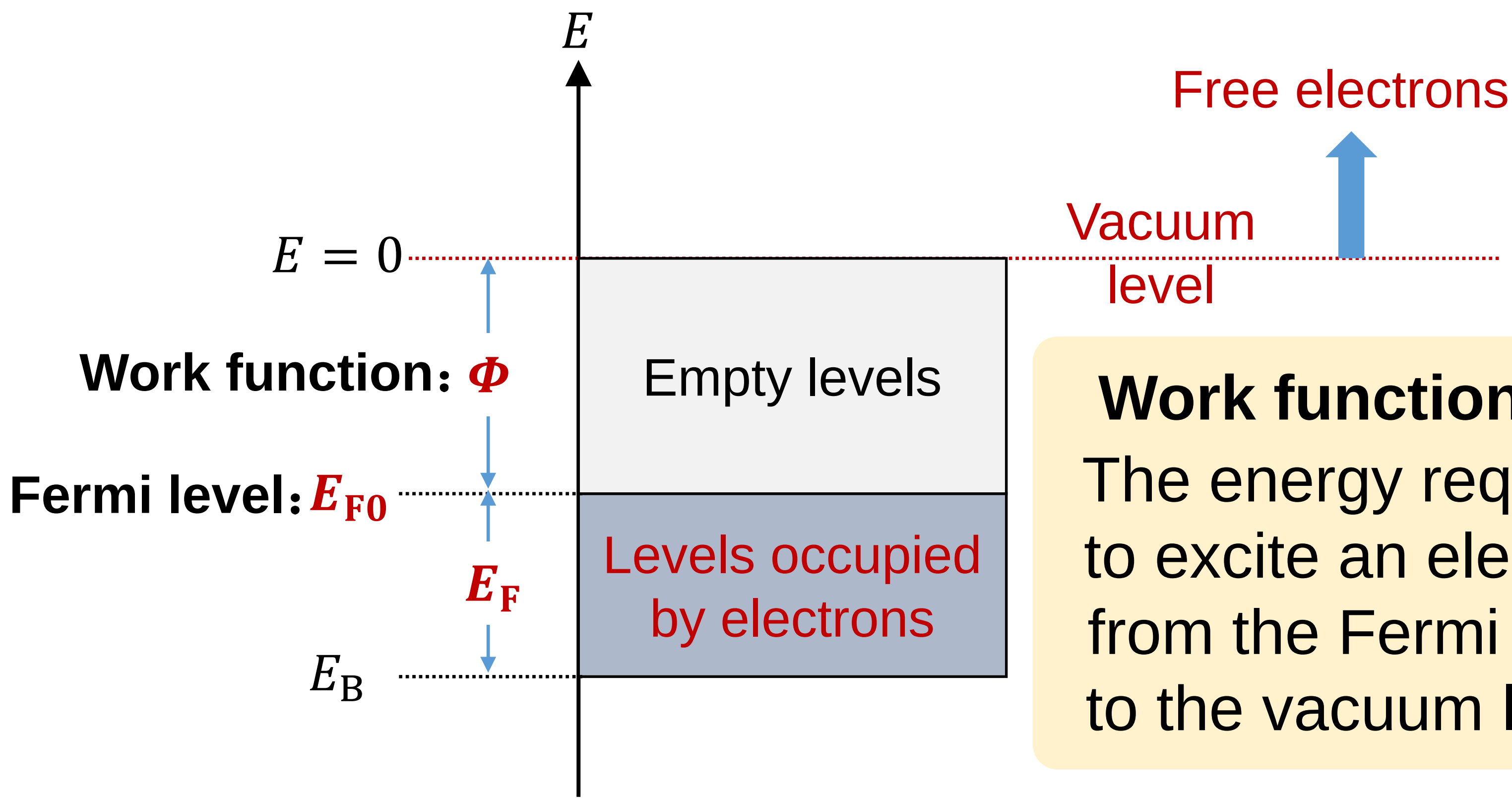
The overlap of energy bands give a single energy band that is only partially full of electrons.



Overlapping energy bands



The overlap of energy bands give a single energy band that is only partially full of electrons.



Work function $\boldsymbol{\Phi}$:
The energy required to excite an electron from the Fermi level to the vacuum level.

This is called **energy band diagram**.

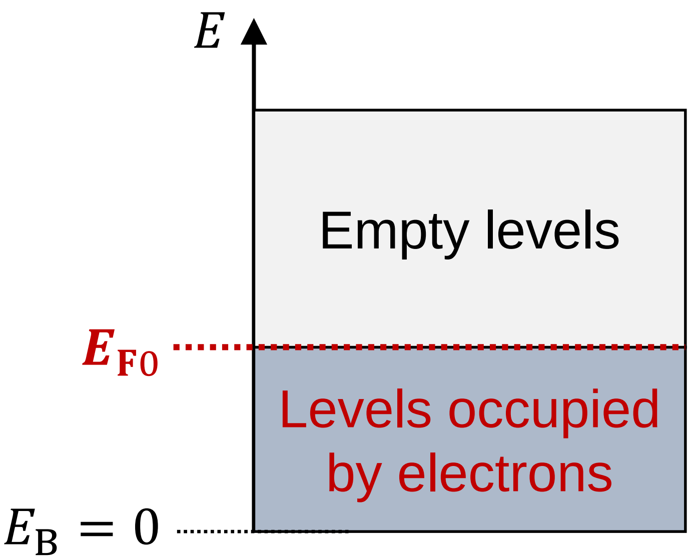
The work function of metals

Metal								
	Ag	Al	Au	Cs	Cu	Li	Mg	Na
$\boldsymbol{\Phi}(\mathrm{eV})$	4.26	4.28	5.1	2.14	4.65	2.9	3.66	2.75
$\boldsymbol{E}_{\mathbf{F0}}(\mathrm{eV})$	5.5	11.7	5.5	1.58	7.0	4.7	7.1	3.2

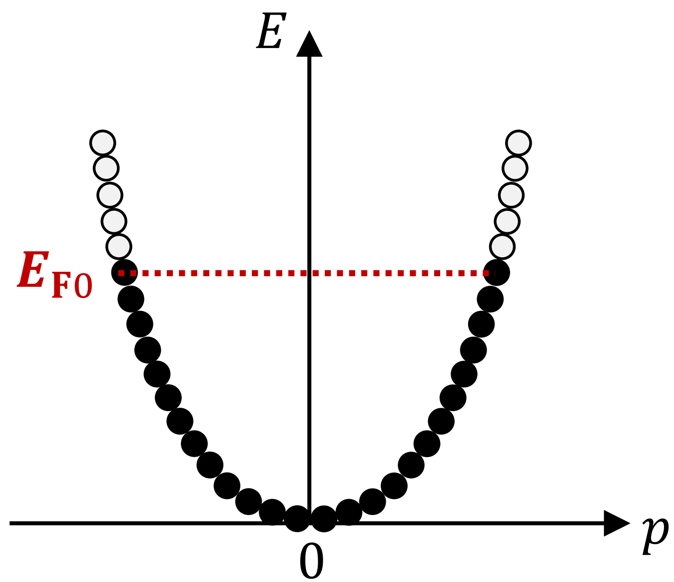
3.9 Properties of electrons in a band (for metals)

Electrons in metals are considered to be "free".

Energy-momentum: $E = \dfrac{p^2}{2m_\mathrm{e}}$

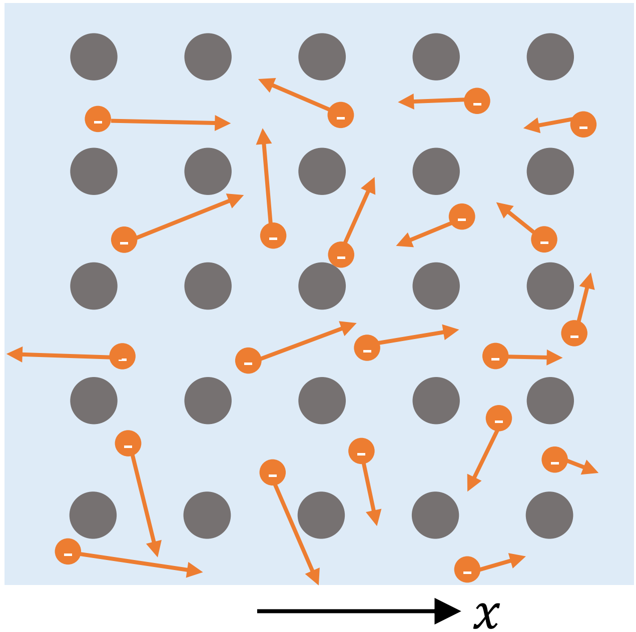


Energy band diagram



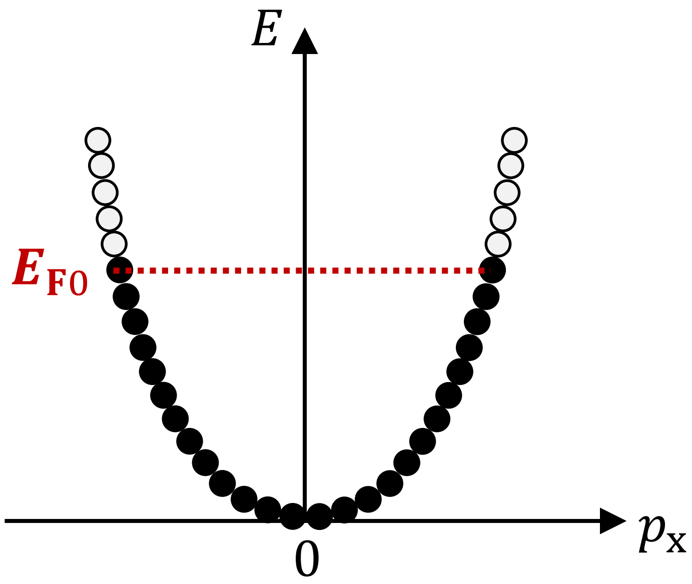
Energy-momentum space

Real space



Chaos!

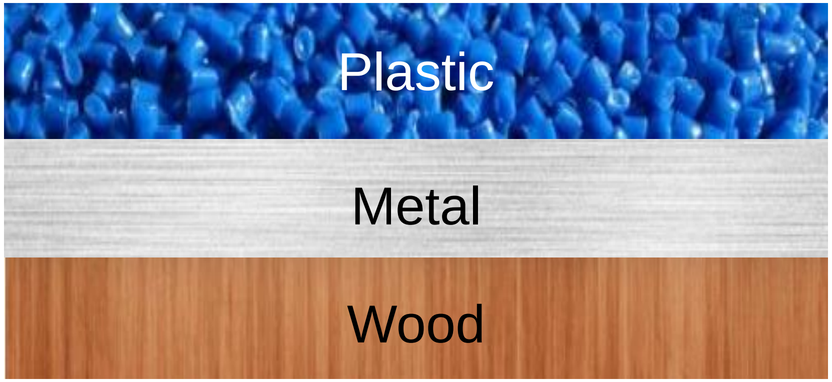
Energy-momentum space



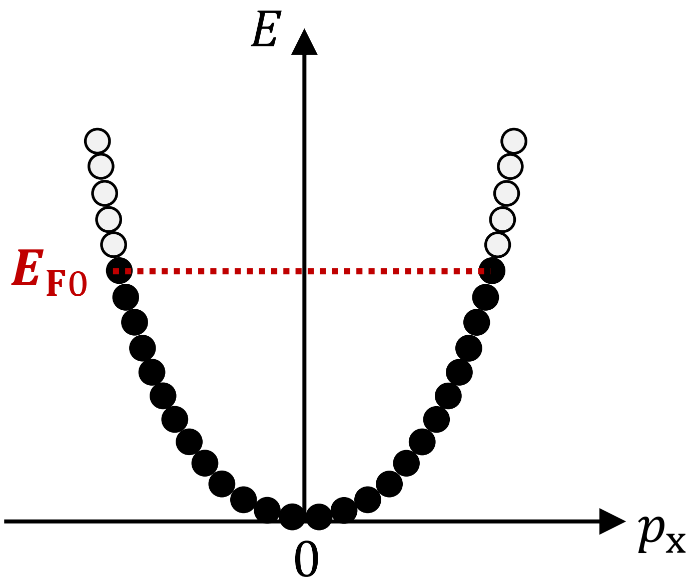
Ordered!

Real space

Energy space

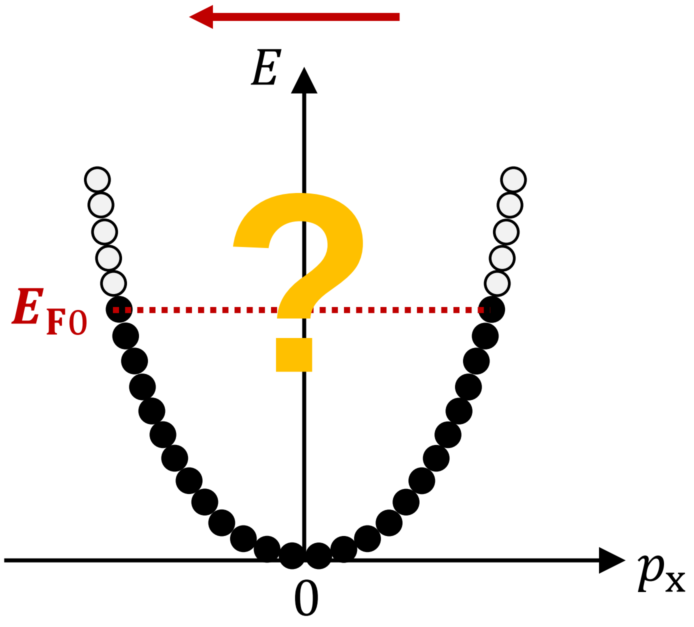


No electric field $E_x = 0$



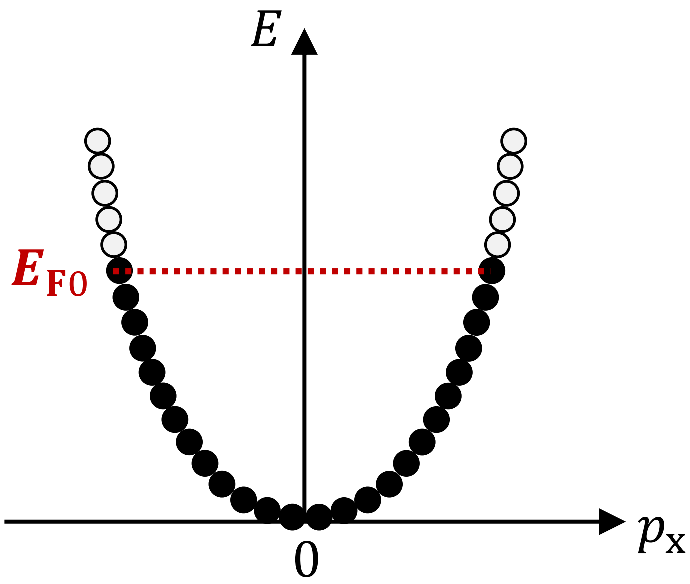
Average momentum in x-direction is zero!

Electric field E_x

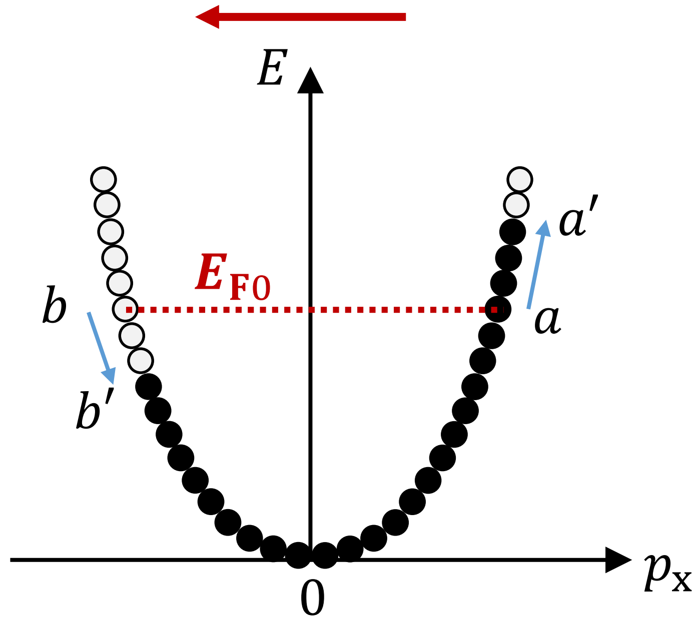


Average momentum in x-direction > zero!

No electric field $E_\mathrm{x} = 0$

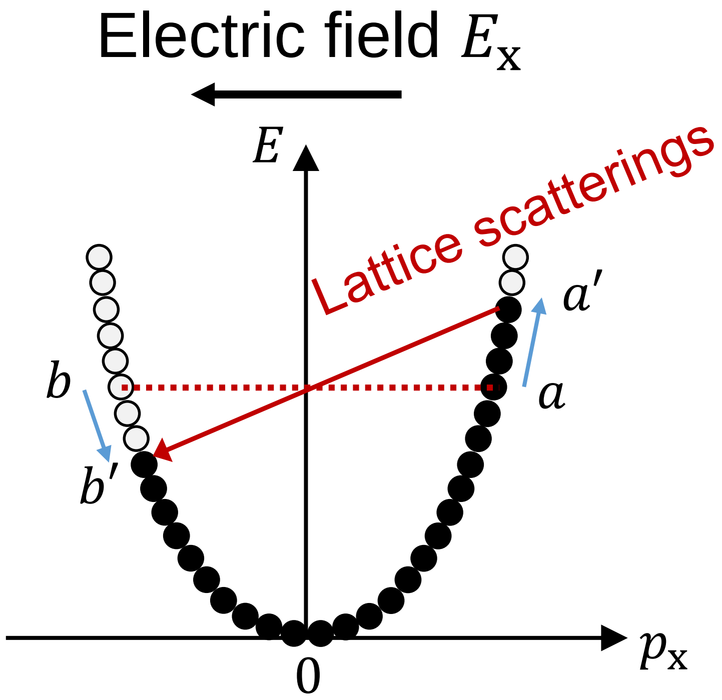


Electric field E_x

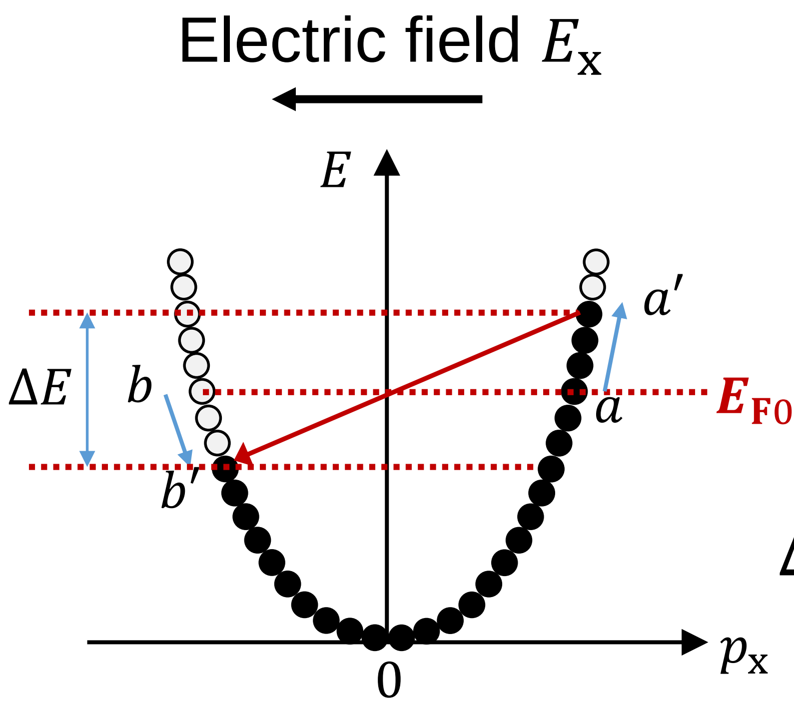


Average momentum in x-direction is zero!

Average momentum in x-direction > zero!



As we know, electrons cannot be accelerated to infinite speed, due to scattering with lattices and impurities.

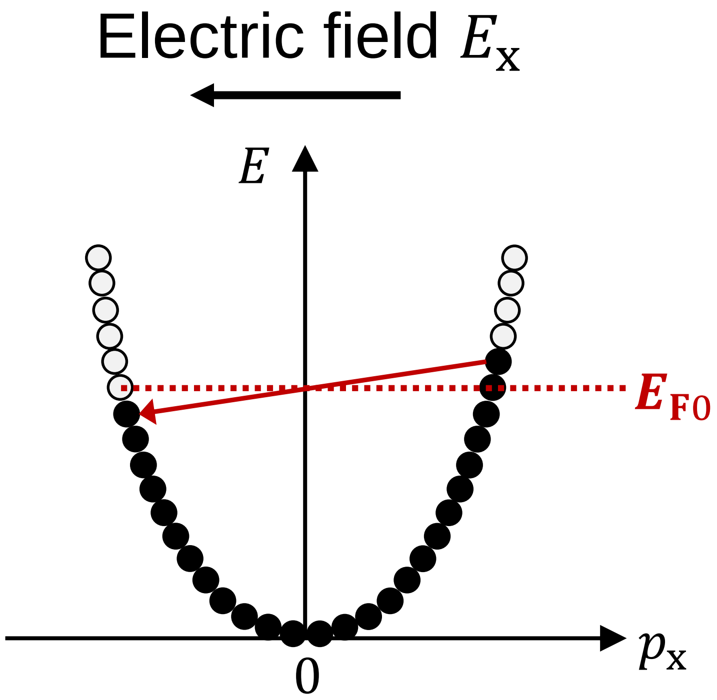


$$\Delta E \ll E_F$$

Below b' level, the average momentum is zero.

Above b' level, the average momentum $\neq$ zero.

We can summarize that **conduction occurs by the drift of electrons at the Fermi level**.

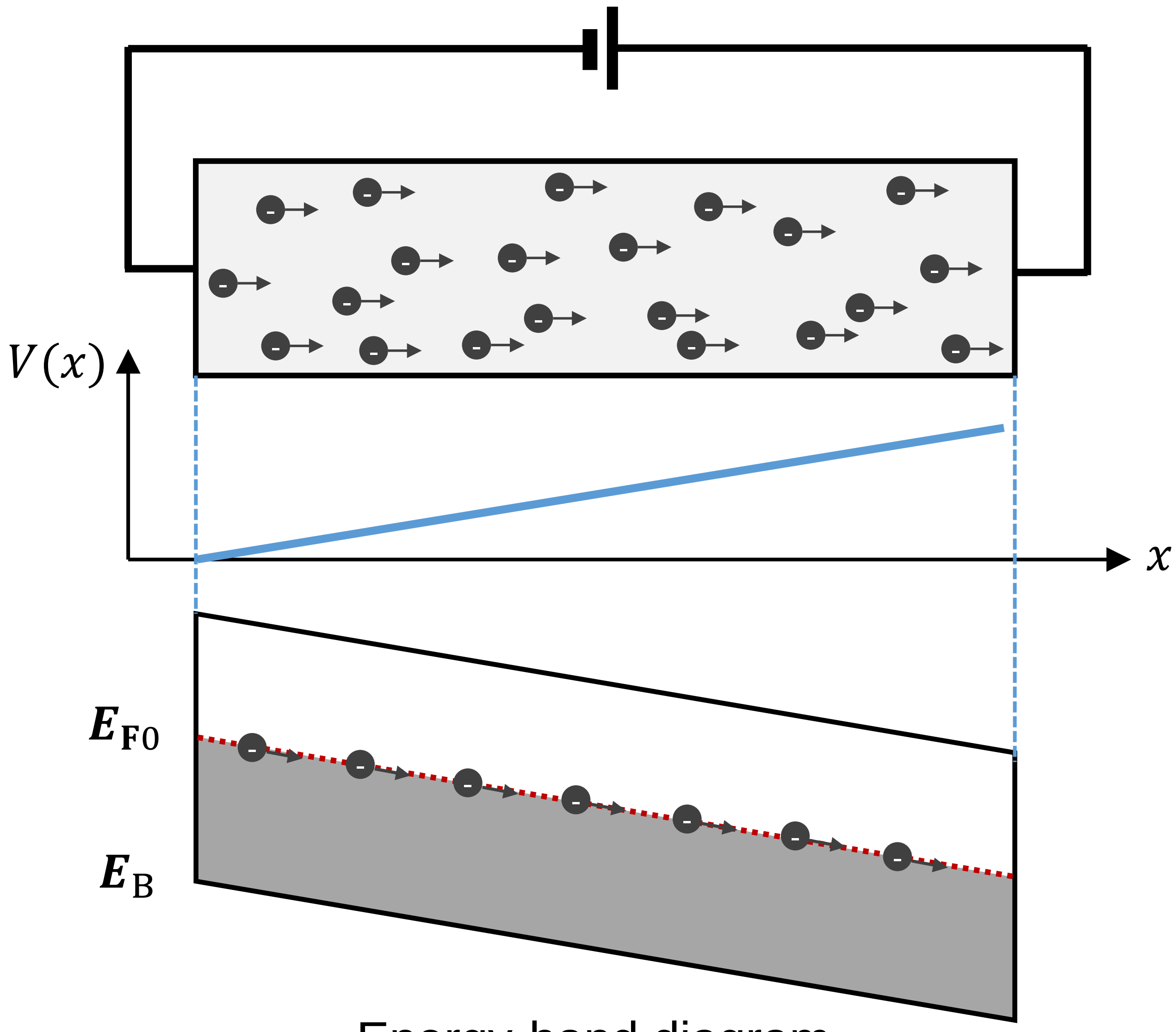


Electron velocity at Fermi level is called the **Fermi velocity v_F**.

$$E_{F0} = \frac{1}{2} m_e v_F^2$$

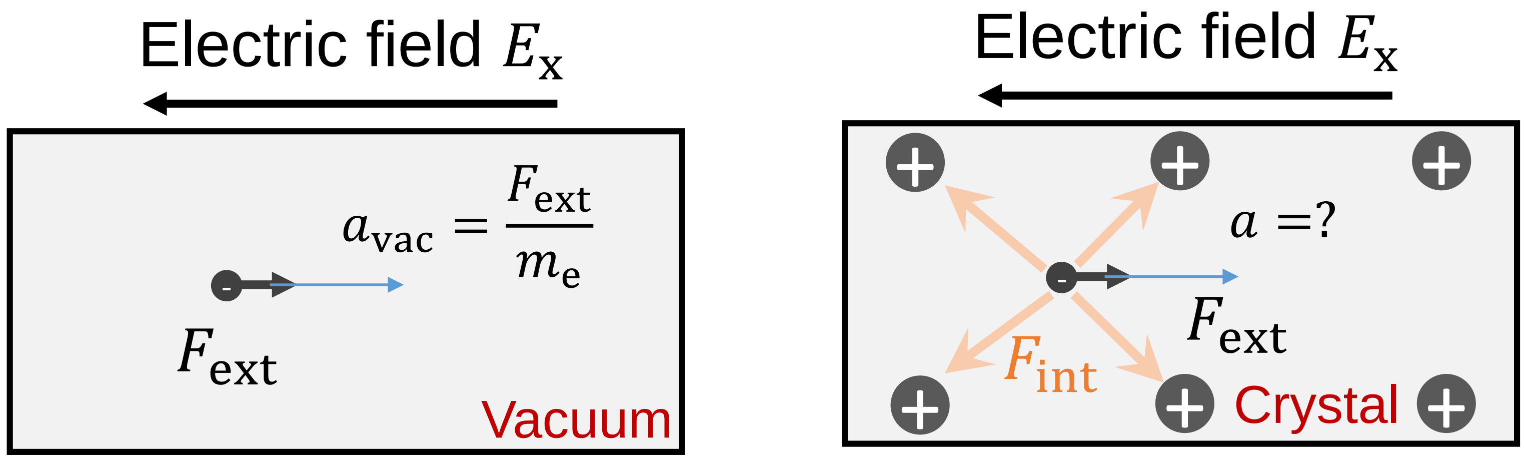
Q: What's the difference between Fermi velocity and drift velocity?

Explain the electrical conduction using energy-band diagram



Energy-band diagram

Effective mass of electrons (for metals and semiconductors)



In crystal: $a_{cryst} = \frac{F_{ext} + F_{int}}{m_e}$

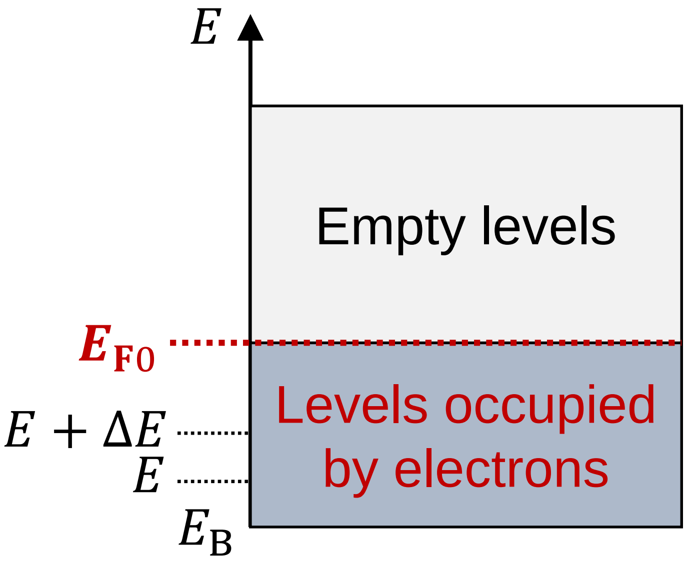
The is F_{int} periodic, and can be solved by Schrodinger equation:

$$a_{cryst} = \frac{F_{ext}}{m_e^*}$$ **Effective mass**

Effective mass of electrons m_e^* in some metals

Metal	Ag	Au	Bi	Cu	Fe	K	Li	Mg	Na	Zn
$\frac{m_e^*}{m_e}$	1.0	1.1	0.008	1.3	12	1.2	2.2	1.3	1.2	0.85

3.10 Density of states 态密度 in an energy band



How many electrons can be filled between E to $E + \Delta E$?

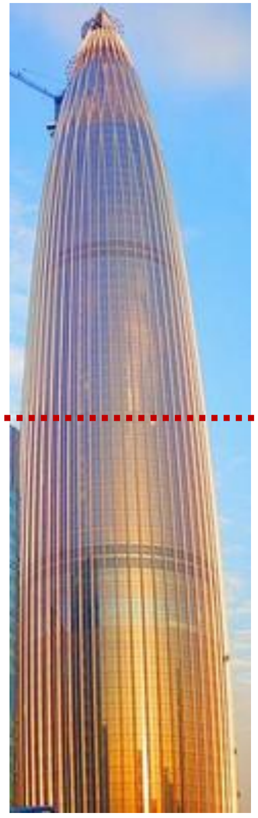
Density of states: the number of states per energy per volume

$g(E)$: $\mathrm{m^{-3}eV^{-1}}$

Q: For empty levels, will there be density of states?

Empty

Filled with guests



Hotel

2 rooms

20 rooms

40 rooms

50 rooms

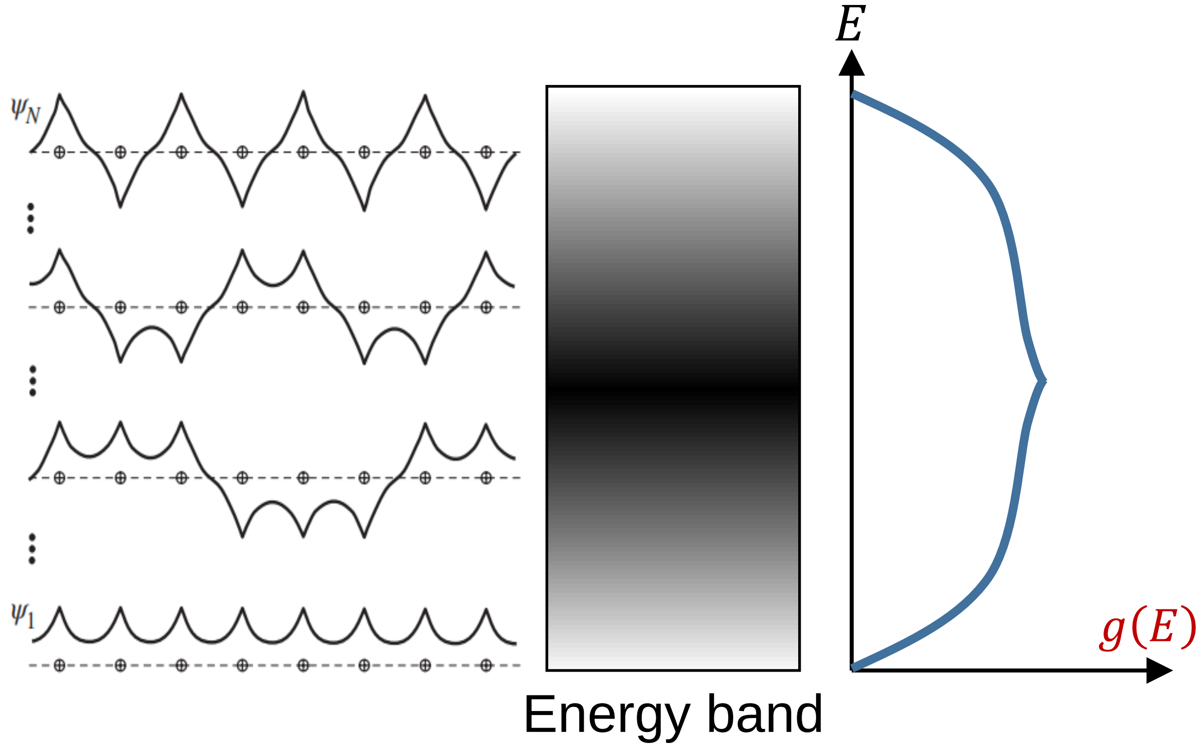
Hotel:	Energy band
Guests:	Electrons
Rooms:	Density of states

Assume we have N atoms ($\psi_A, \psi_B, \psi_C \ldots$) and N electron states ($\psi_1, \psi_2, \ldots, \psi_N$)

$$\psi_N = \psi_A - \psi_B + \psi_C - \psi_D + \cdots$$

$$\vdots$$

$$\psi_1 = \psi_A + \psi_B + \psi_C + \psi_D + \cdots$$



Density of states is highest in the central region of energy band.

Q: What's the value of density of states?

The value of density of states $g(E)$: $\mathrm{m^{-3}eV^{-1}}$

Number of states per volume from 0 to E': $S_\mathrm{v}(E')$?

$$S_\mathrm{v}(E') = \int_0^{E'} g(E)\mathrm{d}E$$

Consider solid crystal as a 3-dimensional quantum well (size: *L* x *L* x *L*):

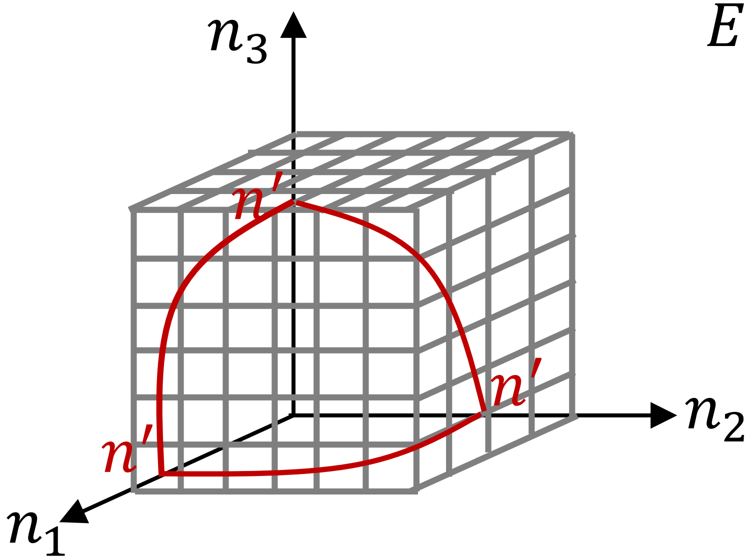
$$E = \frac{h^2}{8mL^2}(n_1^2 + n_2^2 + n_3^2)$$

$$n_1, n_2, n_3 = 1,2,3 \ldots$$

Consider solid crystal as a 3-dimensional quantum well (size: *L* x *L* x *L*):

$$E = \frac{h^2}{8mL^2}(n_1^2 + n_2^2 + n_3^2) \qquad n_1, n_2, n_3 = 1,2,3 \ldots$$

Q: What's the total number of states from 0 to E'?

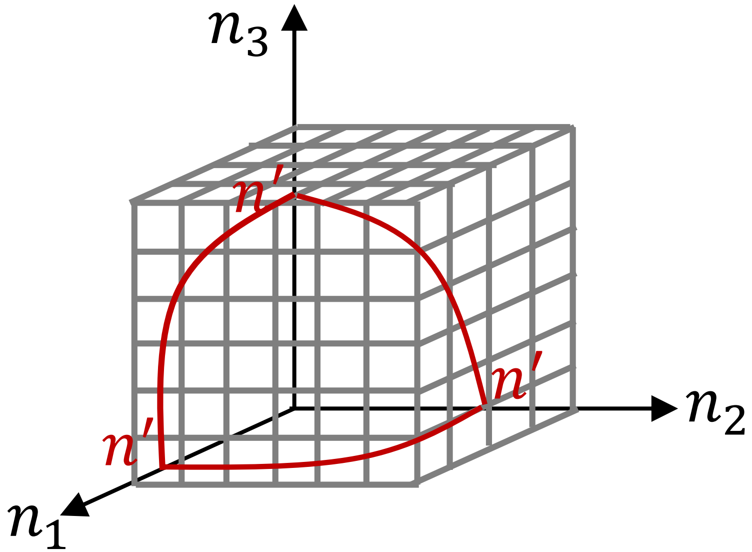


$$E' = \frac{h^2}{8mL^2}n'^2 \Rightarrow n'^2 = \frac{8mL^2E'}{h^2}$$

$$n_1^2 + n_2^2 + n_3^2 \le n'^2$$

$S(E') =$ **2**×Number of unit cells below the spherical surface

Spin up and spin down for each (n_1, n_2, n_3)



$$S(E') = 2 \times \frac{1}{8} \times (\frac{4}{3}\pi n'^3)$$

$$= \frac{1}{3}\pi n'^3$$

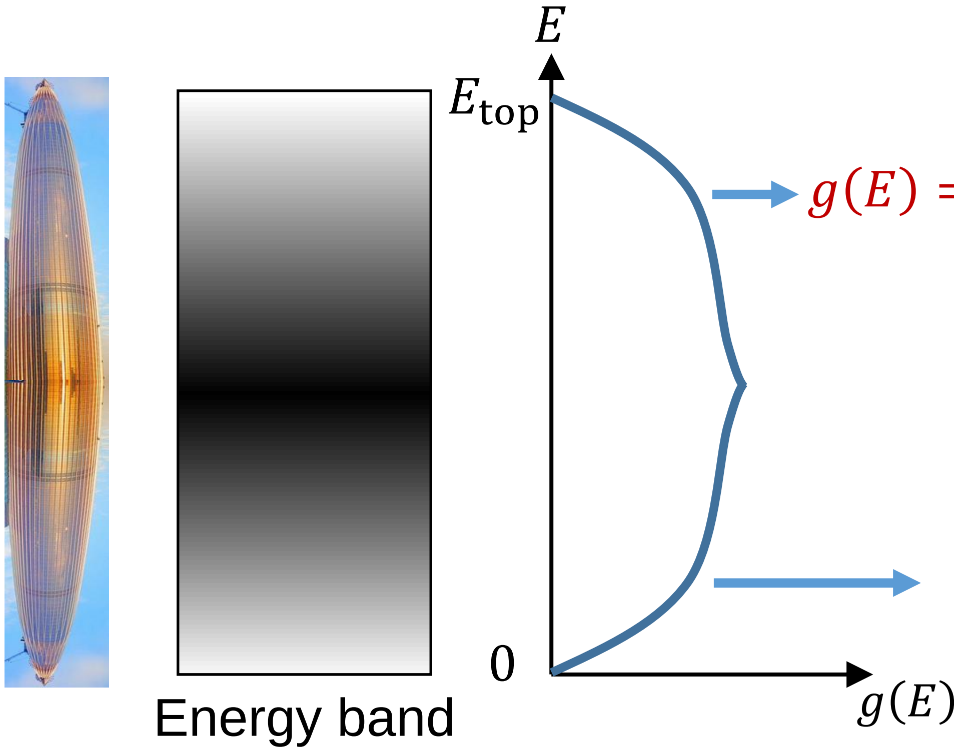
$$= \frac{\pi L^3 (8 m_\mathrm{e} E')^{3/2}}{3h^3}$$

Number of states per volume from 0 to E': $S_\mathrm{v}(E')$

$$S_\mathrm{v}(E') = \frac{\pi (8 m_\mathrm{e} E')^{3/2}}{3h^3}$$

Density of states: $g(E) = \frac{\mathrm{d}S_\mathrm{v}(E)}{\mathrm{d}E}$

$$g(E) = 8\pi\sqrt{2E}\left(\frac{m_\mathrm{e}}{h^2}\right)^{3/2}$$



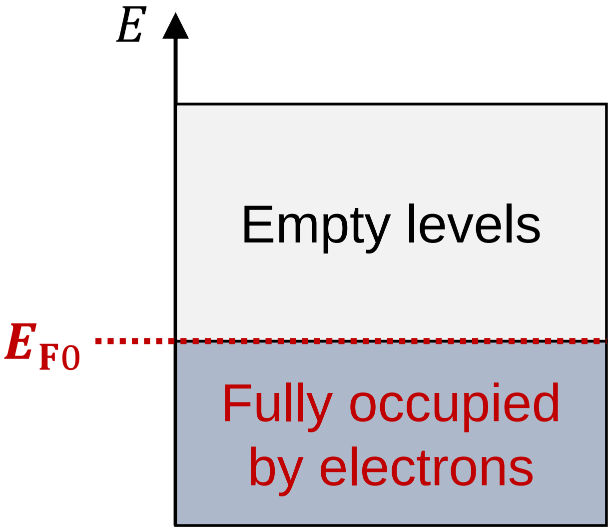
$$g(E) = 8\pi\sqrt{2(E_{\mathrm{top}} - E)}\left(\frac{m_{\mathrm{e}}}{h^2}\right)^{3/2}$$

$$g(E) = 8\pi\sqrt{2E}\left(\frac{m_{\mathrm{e}}}{h^2}\right)^{3/2}$$

$$g(E) = 8\pi\sqrt{2E}\left(\frac{m_{\mathrm{e}}}{h^2}\right)^{3/2} \left\{ \begin{array}{l} \text{is accurate for free electrons.} \\ \text{is good approximation for metals and semiconductors near band edge.} \end{array} \right.$$

- is accurate for free electrons.
- is good approximation for **metals and semiconductors near band edge**.

Q: the relation between carrier concentration/density n and density of states $g(E)$?



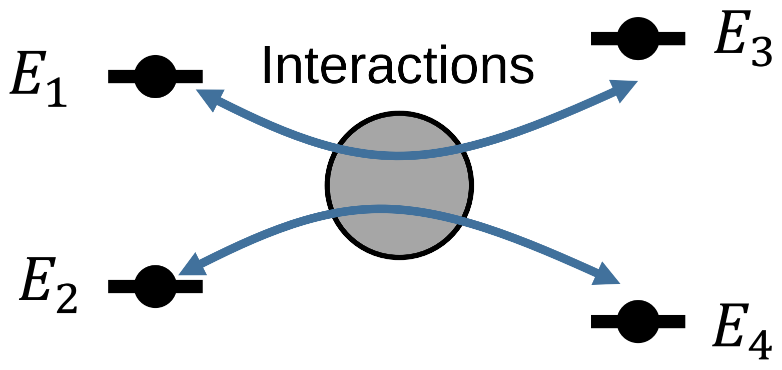
$$n = \int_0^{E_{F0}} g(E)\mathrm{d}E$$

Q: the relation between carrier density n and density of states $g(E)$, if the probability that an energy level is occupied is $f(E)$?

$$n = \int f(E)g(E)\mathrm{d}E$$

3.11 Fermi-Dirac Statistics 费米-狄拉克统计

Classic model: Given a collection of classic particles in random motion and colliding with each other (**ignore Pauli exclusion principle**), the probability of an electron with energy *E* is *P*(E).



In thermal equilibrium (ignore Pauli exclusion principle):

$$P(E_1)P(E_2) = P(E_3)P(E_4)$$

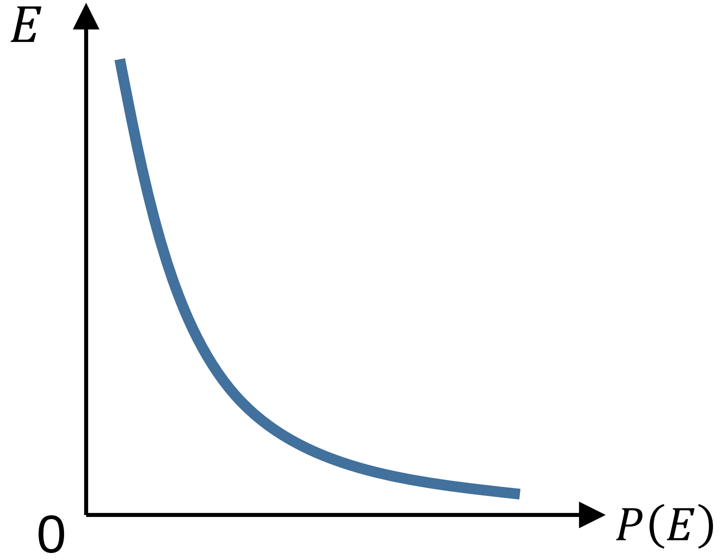
$$E_1 + E_2 = E_3 + E_4$$

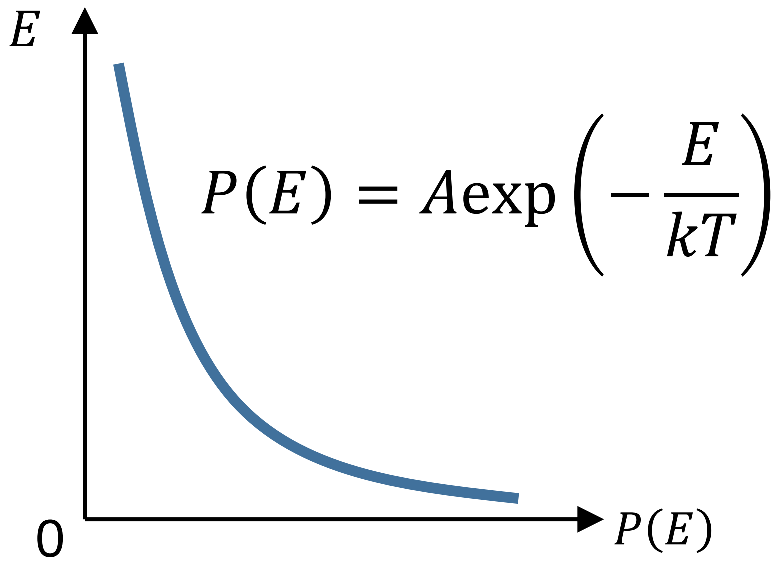
$$\begin{cases} P(E_1)P(E_2) = P(E_3)P(E_4) \\ E_1 + E_2 = E_3 + E_4 \end{cases}$$

$$\Downarrow$$

$$P(E) = A\exp\left(-\frac{E}{kT}\right)$$

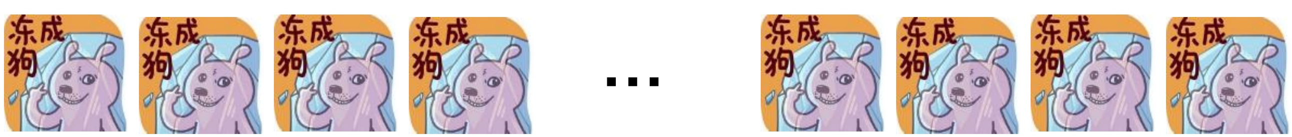
Boltzmann probability function





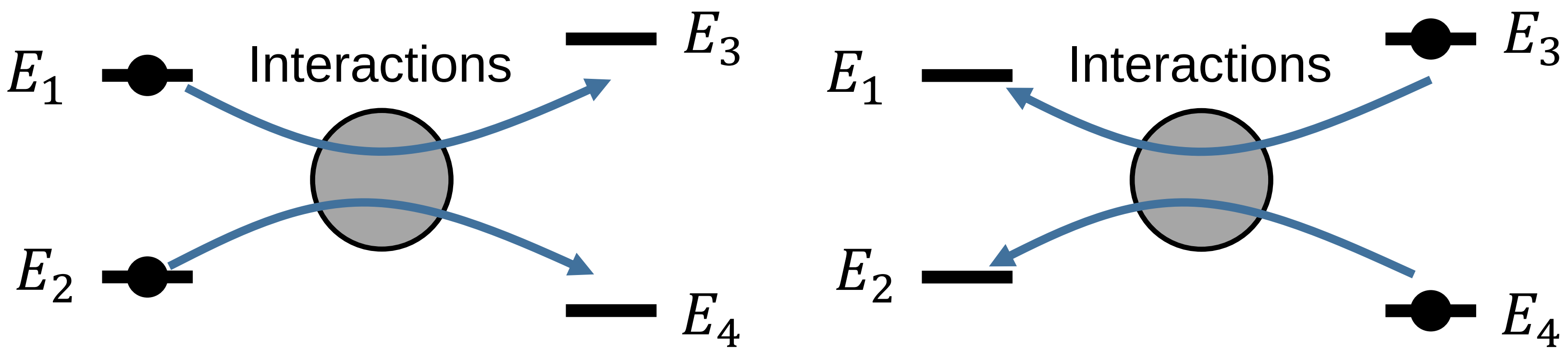
When temperature T→0, all particles are in the lowest energy level E=0.

This is called: Bose-Einstein condensation.



Particles that does not follow Pauli exclusion principles are called Boson 玻色子: photon, phonon…

Fermi-Dirac model: Given a collection of particles in random motion and colliding with each other (**follow Pauli exclusion principle**), the probability of an electron with energy *E* is *f*(E).



In thermal equilibrium (follow Pauli exclusion principle):

$$E_1 + E_2 = E_3 + E_4$$

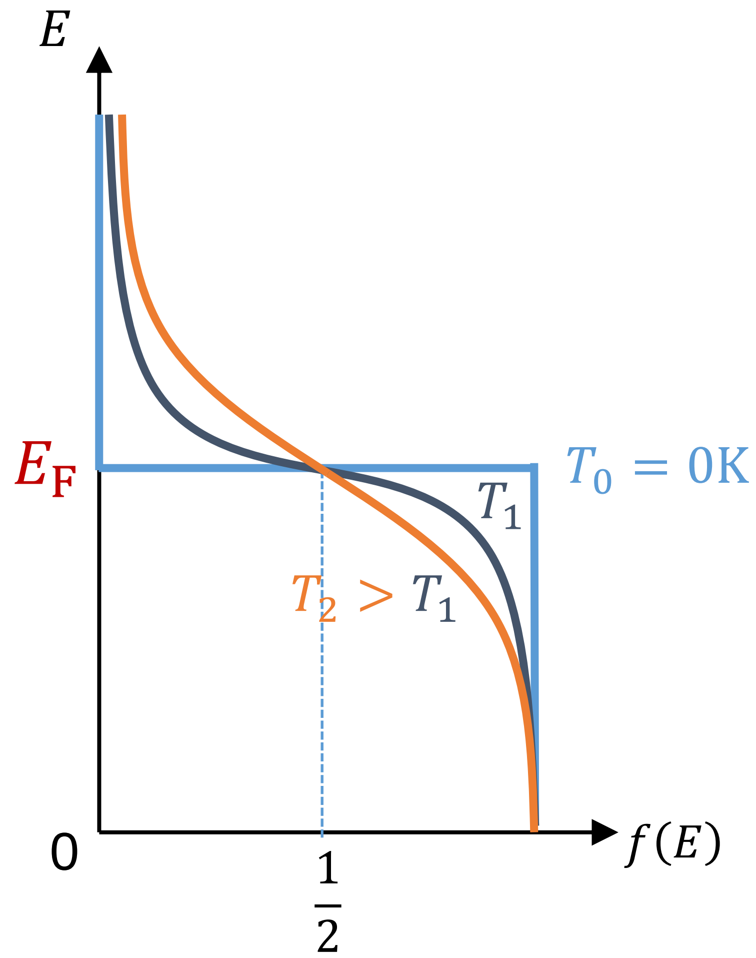
$$f(E_1)f(E_2)[1 - f(E_3)][1 - f(E_4)]$$
$$= f(E_3)f(E_4)[1 - f(E_1)][1 - f(E_2)]$$

By an “intelligent guess”, the solution is:

$$f(E) = \frac{1}{1 + A\exp\left(\frac{E}{kT}\right)}$$

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

Fermi-Dirac function

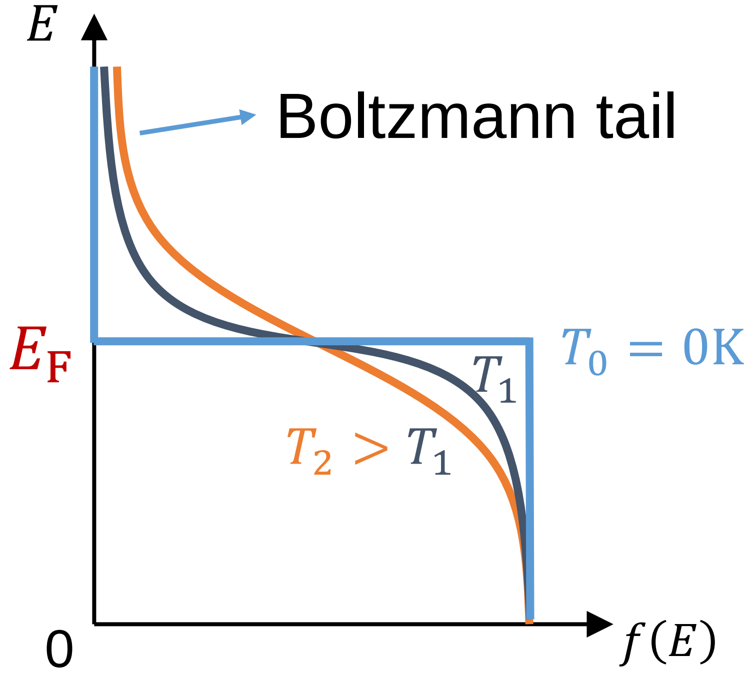


Particles follow Fermi-Dirac function are called Fermion费米子: electron.

When $E - E_F \gg kT$,

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} \Rightarrow f(E) = \exp\left(-\frac{E - E_F}{kT}\right)$$

Fermi-Dirac function **Boltzmann function**

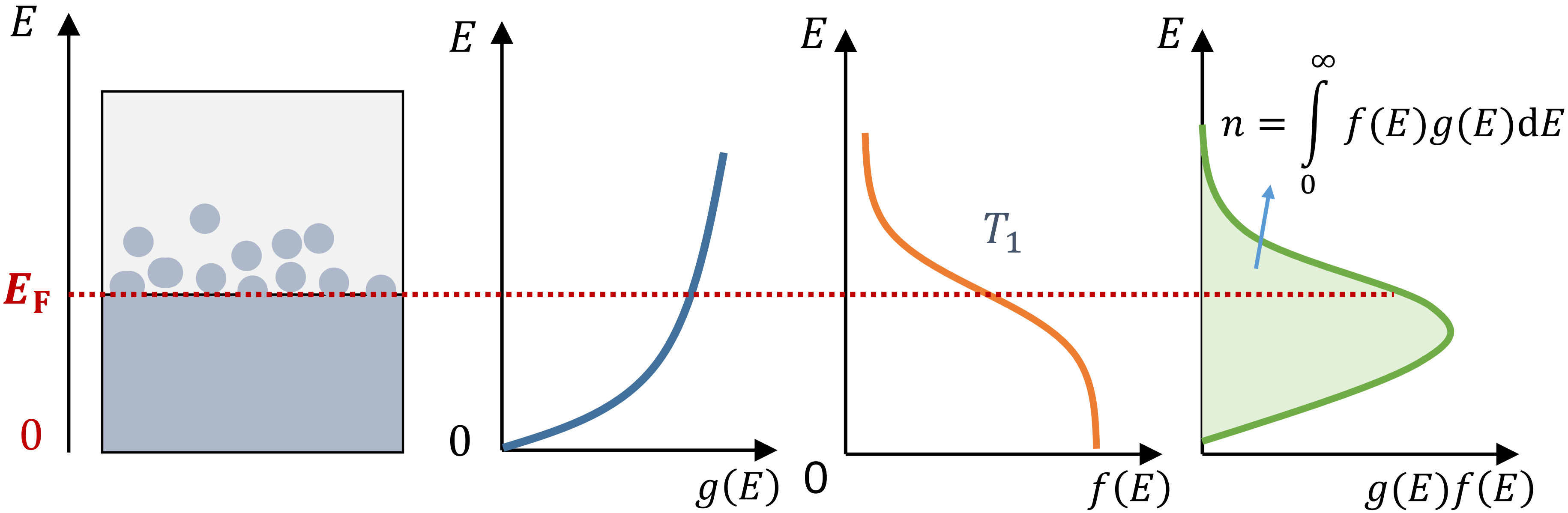


The carrier density n in metals

$$n = \int_0^\infty f(E)g(E)\mathrm{d}E$$

$$g(E) = 8\pi\sqrt{2E}\left(\frac{m_\mathrm{e}}{h^2}\right)^{3/2}$$

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_\mathrm{F}}{kT}\right)}$$



Relationship between *n* and E_F

When T=0K:

$$E_{\mathrm{F0}} = \left(\frac{h^2}{8m_{\mathrm{e}}}\right)\left(\frac{3n}{\pi}\right)^{2/3}$$

When T>0K:

$$E_{\mathrm{F}} = E_{\mathrm{F0}}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{\mathrm{F0}}}\right)^2\right]$$

Fermi energy slightly depends on temperature.

Average energy of an electron in metal:

$$E_{\mathrm{av}} = \frac{\int E g(E) f(E) dE}{\int g(E) f(E) dE}$$

$$\Downarrow$$

$$E_{\mathrm{av}} \approx \frac{3}{5} E_{\mathrm{F0}} \left[1 + \frac{5\pi^2}{12} \left(\frac{kT}{E_{\mathrm{F0}}} \right)^2 \right]$$

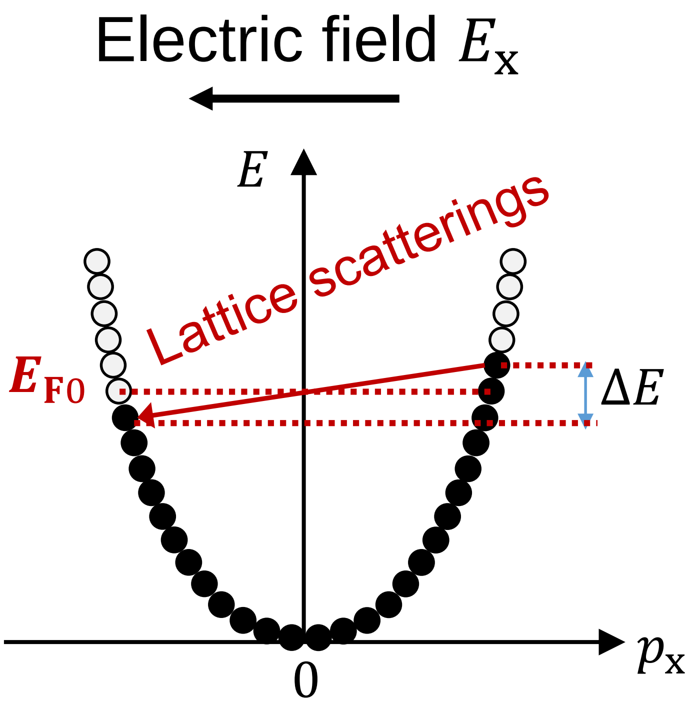
$$\Downarrow$$

$$E_{\mathrm{av}} \approx \frac{3}{5} E_{\mathrm{F0}}$$

Average Kinetic energy (KE) of electron: $\frac{3}{5} E_{\mathrm{F0}}$

Average speed of electron: $\frac{1}{2} m_{\mathrm{e}} v_{\mathrm{e}}^2 = \frac{3}{5} E_{\mathrm{F0}}$

Reexamine the conduction in metals using quantum theory (1-dimension model)



Electrical conduction is contributed by electrons in a small range ΔE near E_F.

Electrons are accelerated by electric field

Electrons are scattered by lattice.

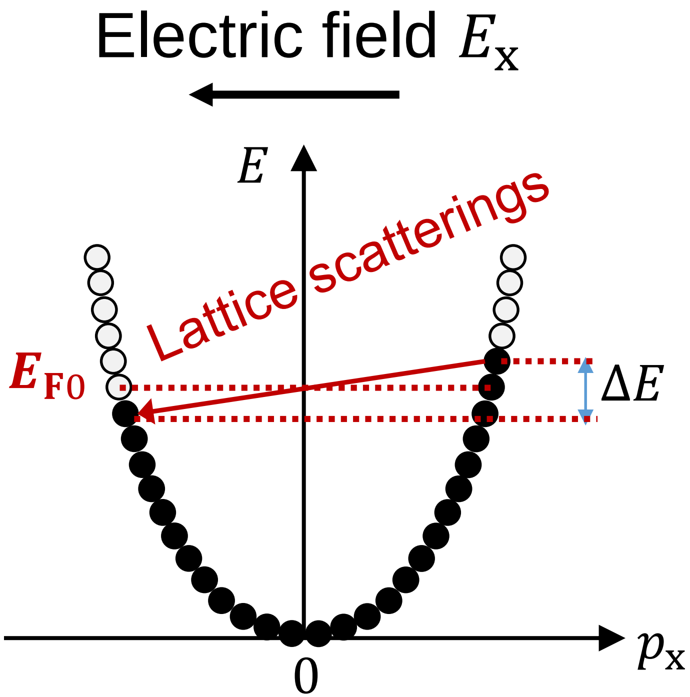
In equilibrium, p_x gain=p_x loss

$$\Delta p_x = eE_x\tau$$

$$\Delta E = \frac{p_x}{m_e^*}\Delta p_x = \frac{m_e^* v_F}{m_e^*}(eE_x\tau)$$

$$= eE_x\tau v_F$$

Electrical conduction is contributed by electrons in a small range ΔE near E_F.



$$
\begin{aligned}
J_x &= e n_F v_F \\
&= e[g(E_F)\Delta E]v_F \\
&= e[g(E_F)eE_x\tau v_F]v_F \\
&= e^2 v_F^2 \tau g(E_F)\, E_x
\end{aligned}
$$

1-dimensional conductivity:

$$\sigma = e^2 v_F^2 \tau g(E_F)$$

3-dimensional conductivity:

$$\sigma = \frac{1}{3} e^2 v_F^2 \tau g(E_F)$$

Electrical conductivity in quantum model

$$\sigma = \frac{1}{3} e^2 v_{\mathrm{F}}^2 \tau g(E_{\mathrm{F}})$$

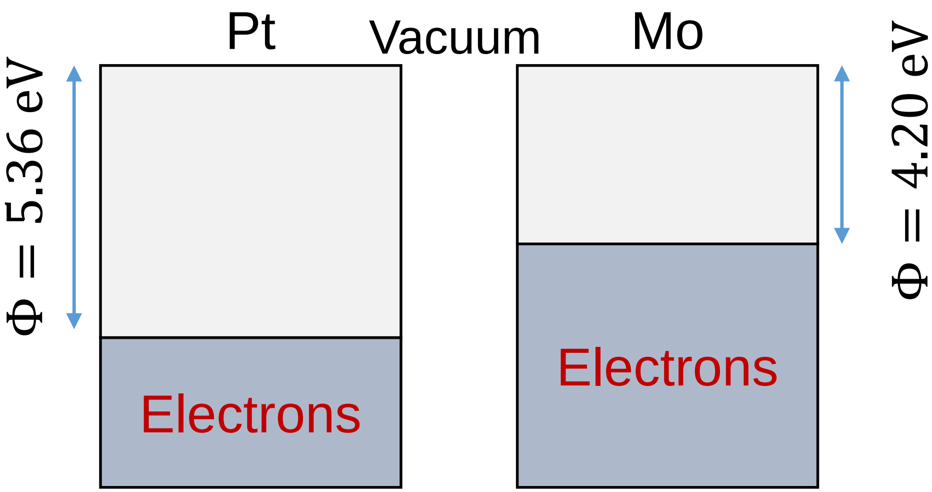
Electrical conductivity in classic Drude model

$$\sigma = \frac{e^2 n \tau}{m_{\mathrm{e}}^*}$$

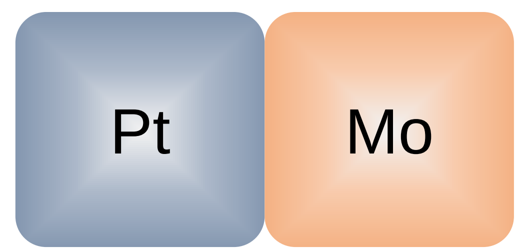
Homework 3-2: Prove that above two equations are identical. (6th)

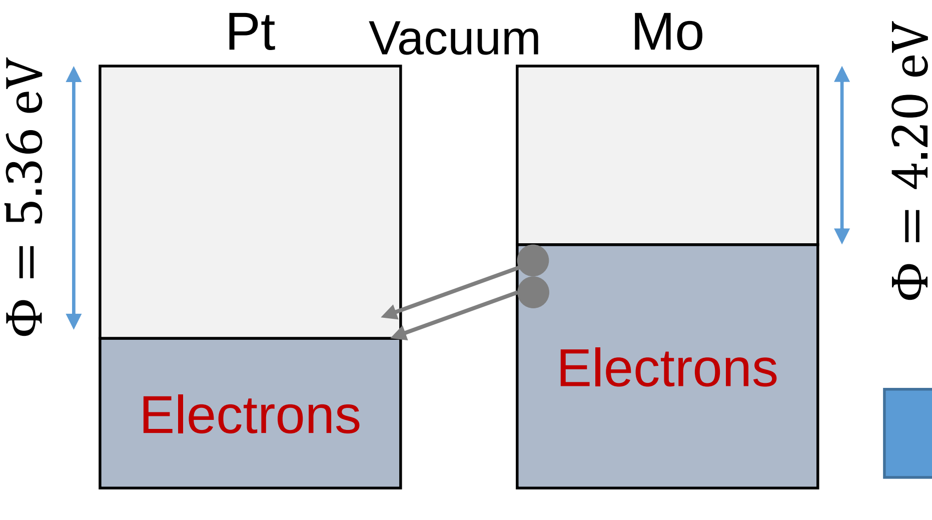
3.12 Fermi energy significance and device applications

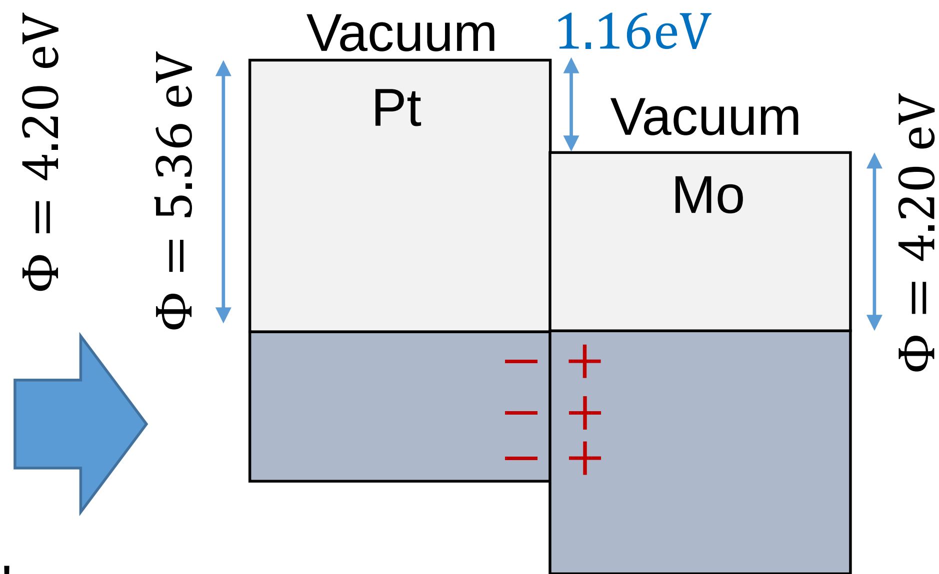
Metal-metal contacts: contact potential 接触势



Q: Pt and Mo has different work function. What will happen when Pt and Mo contact?

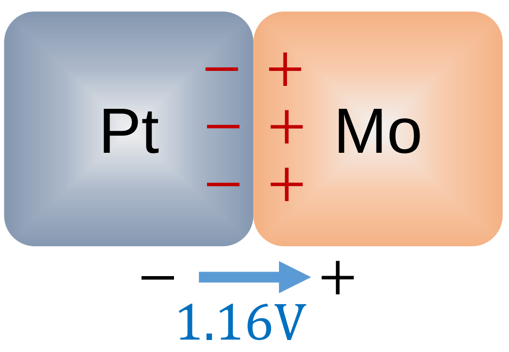


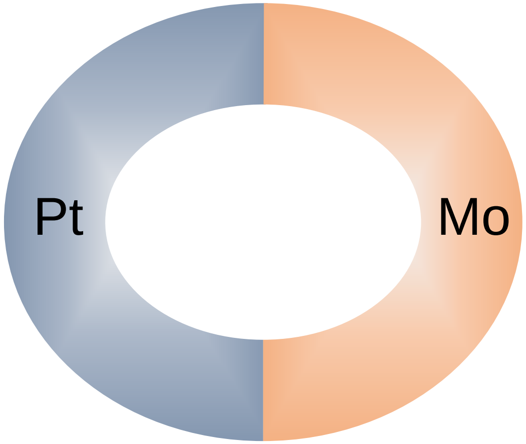




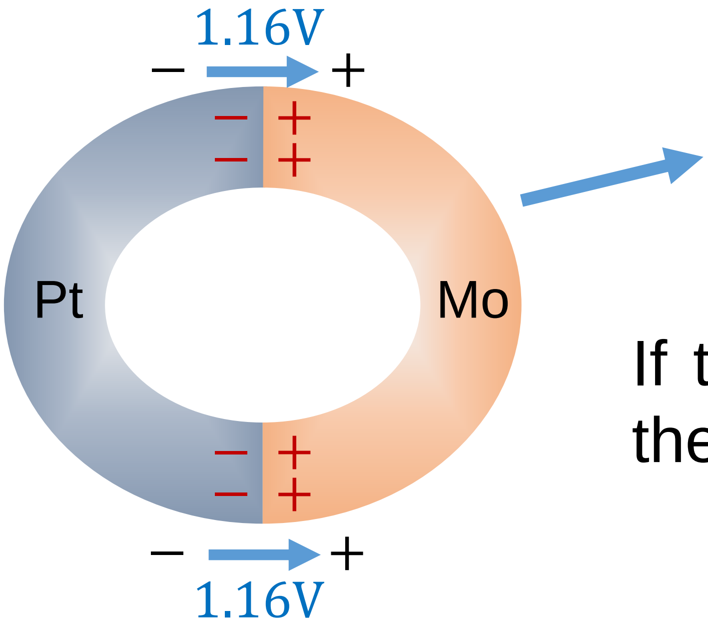
Electrons in Mo are more energetic!

Electrons in Mo will flow into Pt.





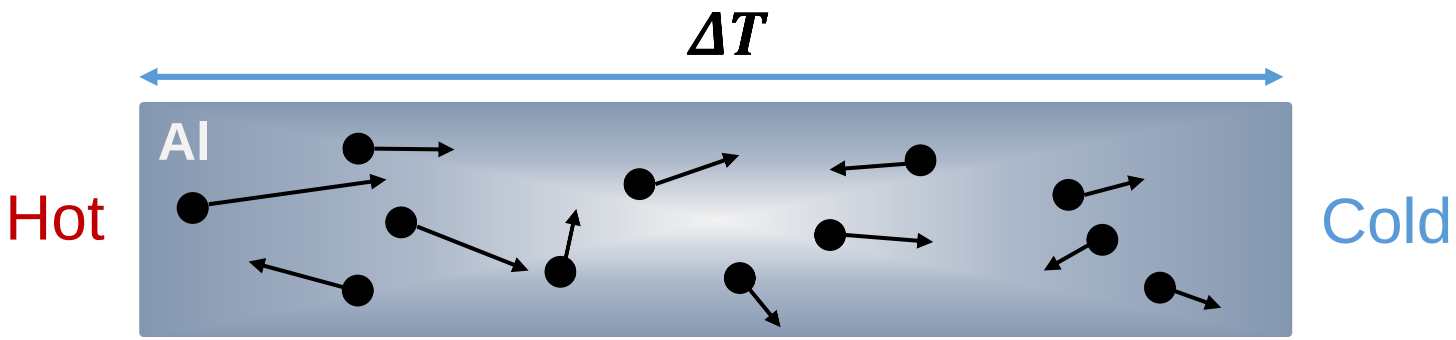
Q: In this configuration, will there be net current?



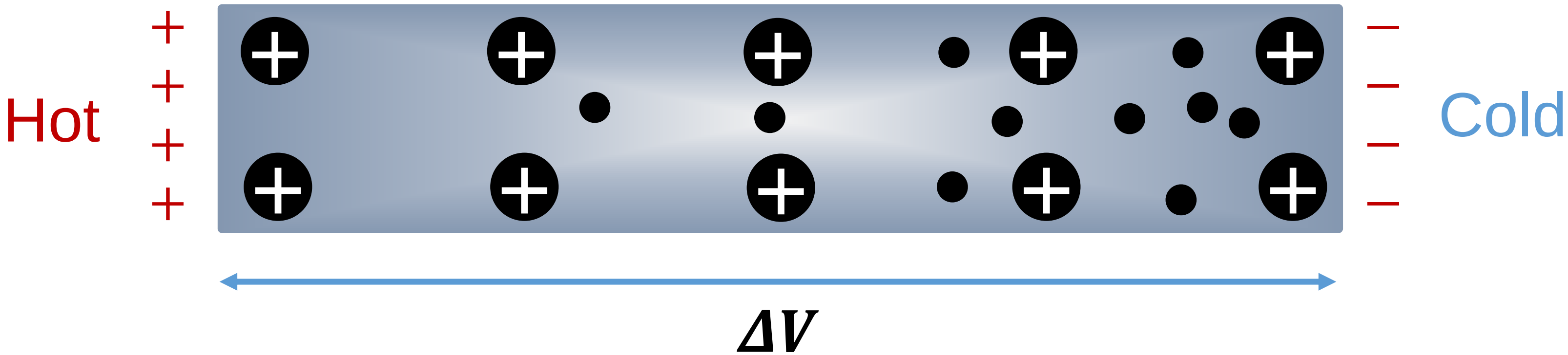
Two contacts are identical, no net current.

If two contacts are not identical, there will be net current.

Seebeck effect 塞贝克效应



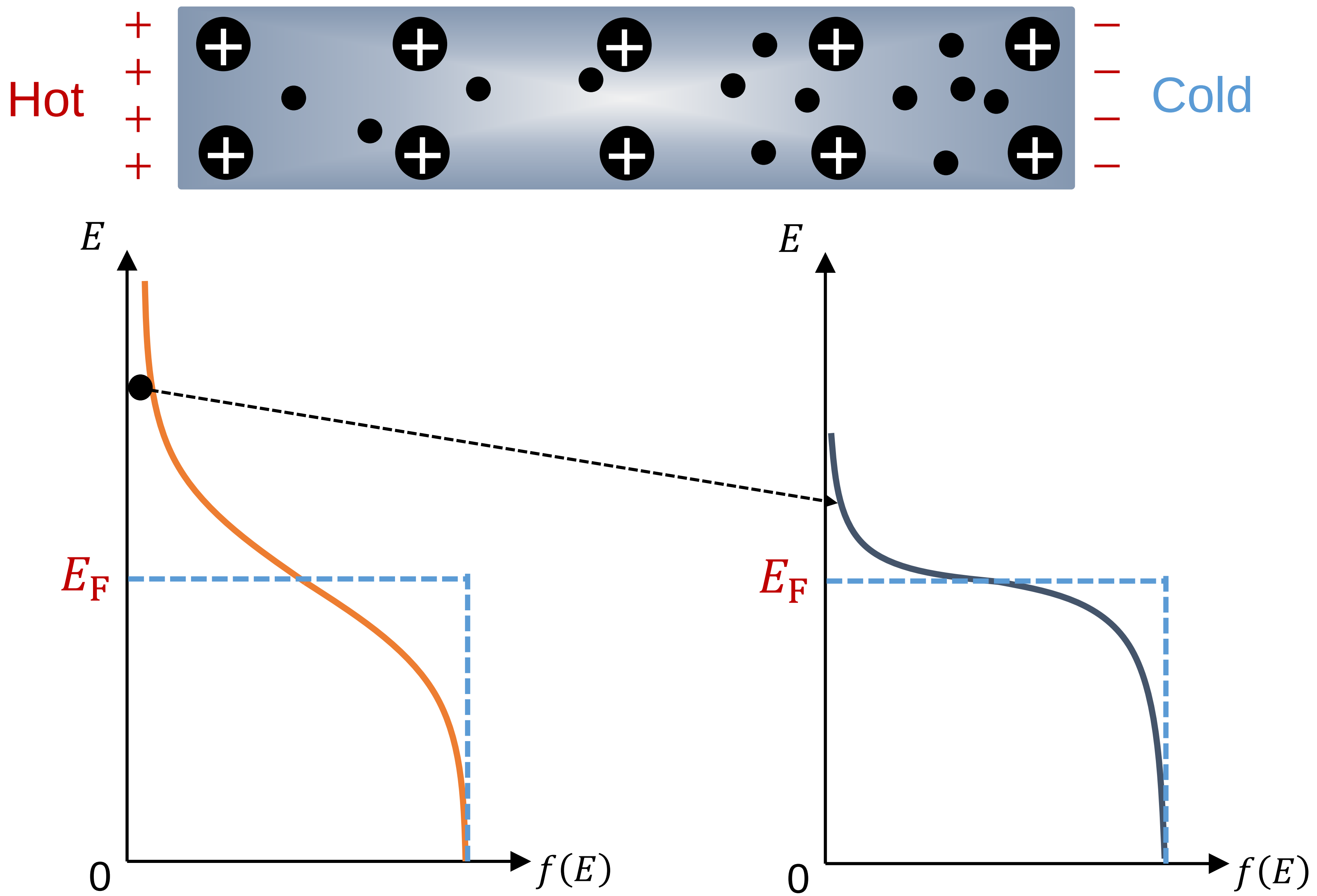
Electrons are more energetic in hot terminal.



Seebeck coefficient: $S = \dfrac{\mathrm{d}V}{\mathrm{d}T}$

The potential of cold side respect to the hot side.

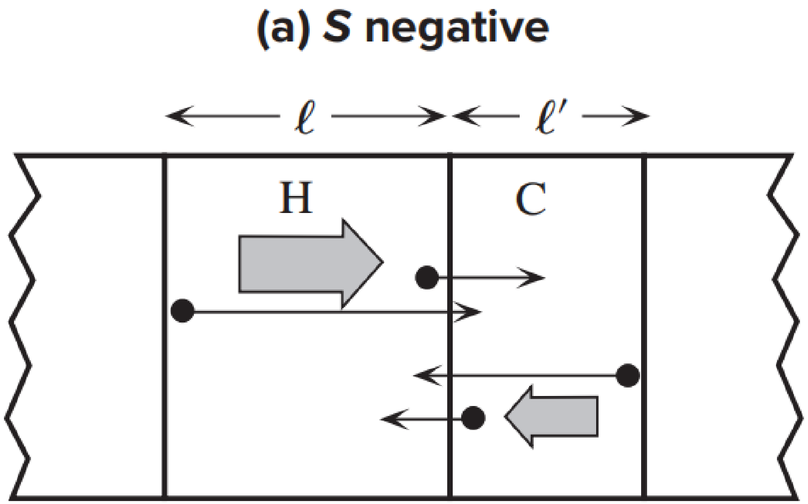
Q: How to explain Seebeck effect using band diagram?



Metal	*S* at 27 °C (μV/K)	E_F (eV)
Al	-1.7	11.7
Au	+2.08	5.53
Cu	+1.94	7.00
K	-13.7	2.12
Li	+11.4	4.74
Na	-6.3	3.24
Mg	-1.46	7.08
Ni	-19.5	~7.4
Pt	-4.92	~6.0

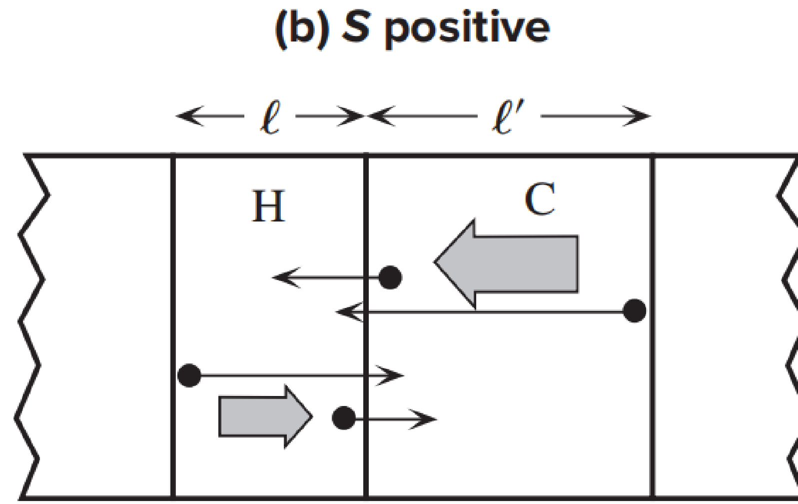
$S < 0$: cold side is negative.

$S > 0$: hot side is negative, electrons diffusive from cold to hot end.



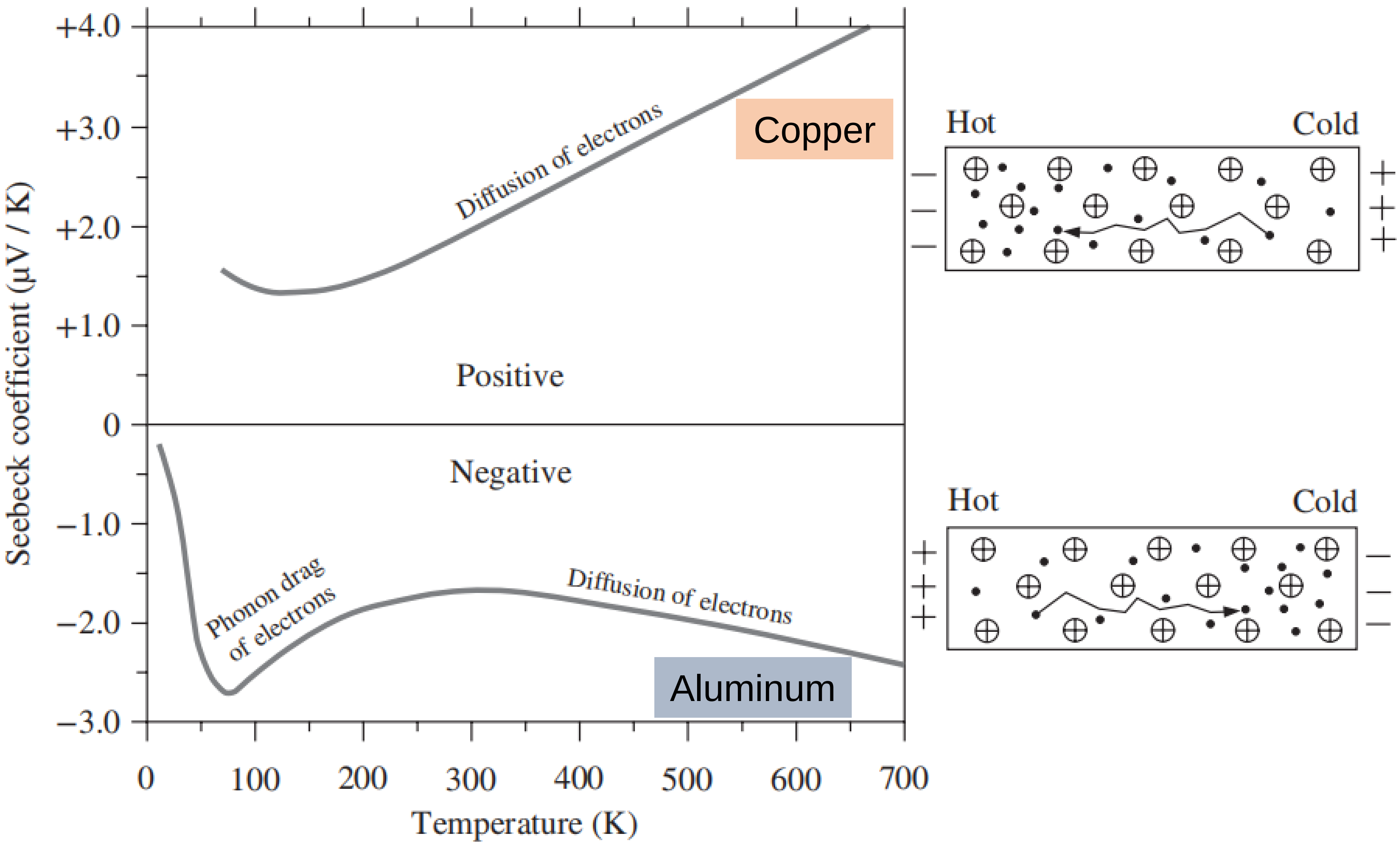
Energy (hot) > Energy (cold)

Mean free path (hot) >
Mean free path (cold)



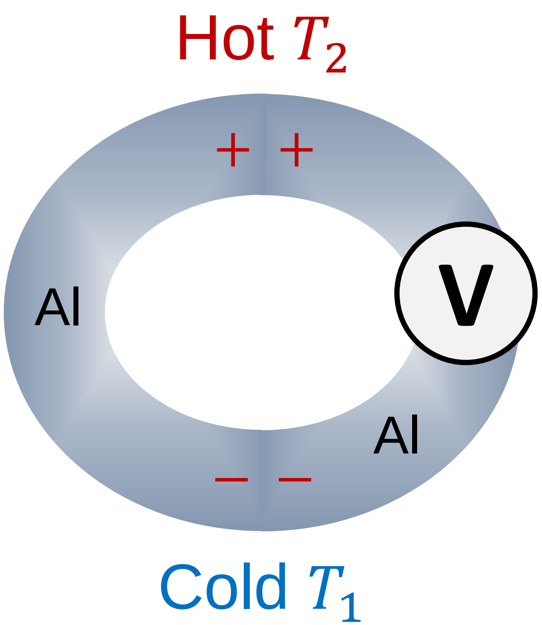
Energy (hot) > Energy (cold)

Mean free path (hot) <
Mean free path (cold)


+4.0
+3.0
+2.0
+1.0
0
−1.0
−2.0
−3.0
Seebeck coefficient (μV / K)
0
100
200
300
400
500
600
700
Temperature (K)
Diffusion of electrons
Copper
Positive
Negative
Phonon drag of electrons
Diffusion of electrons
Aluminum
Hot
Cold
Hot
Cold

Thermocouple 热电偶

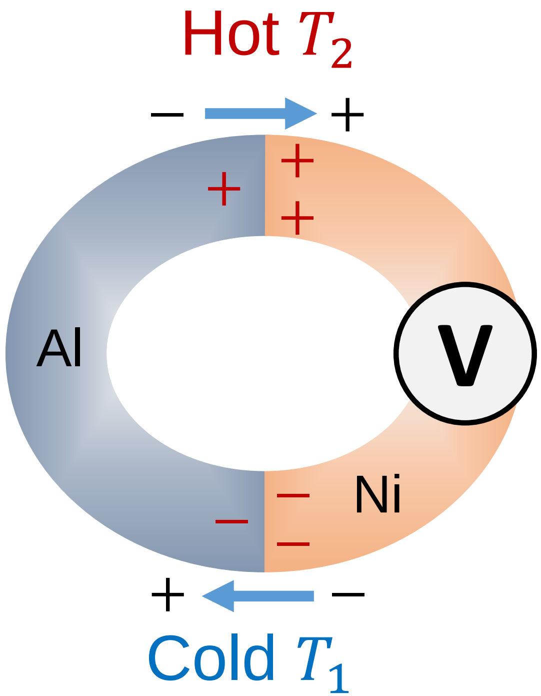
Metal	*S* at 27 ºC (μV/K)
Al	-1.7
Ni	-19.5



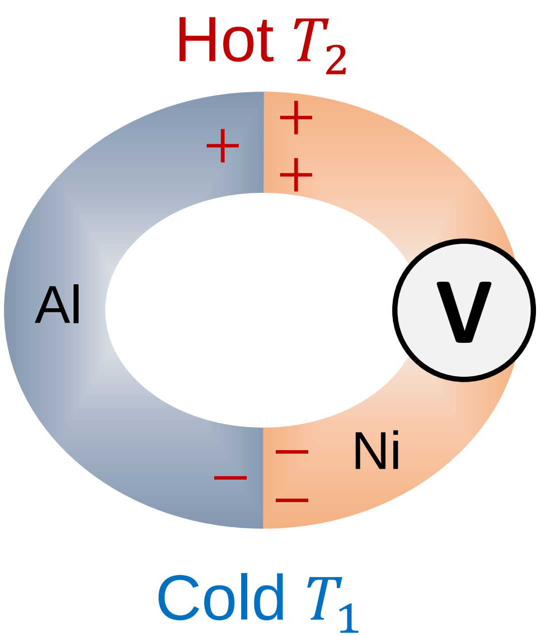
Voltage meter: 0 V

Thermocouple 热电偶

Metal	*S* at 27 °C (μV/K)
Al	-1.7
Ni	-19.5



Thermocouple 热电偶



Metal	*S* at 27 ºC (μV/K)
Al	-1.7
Ni	-19.5

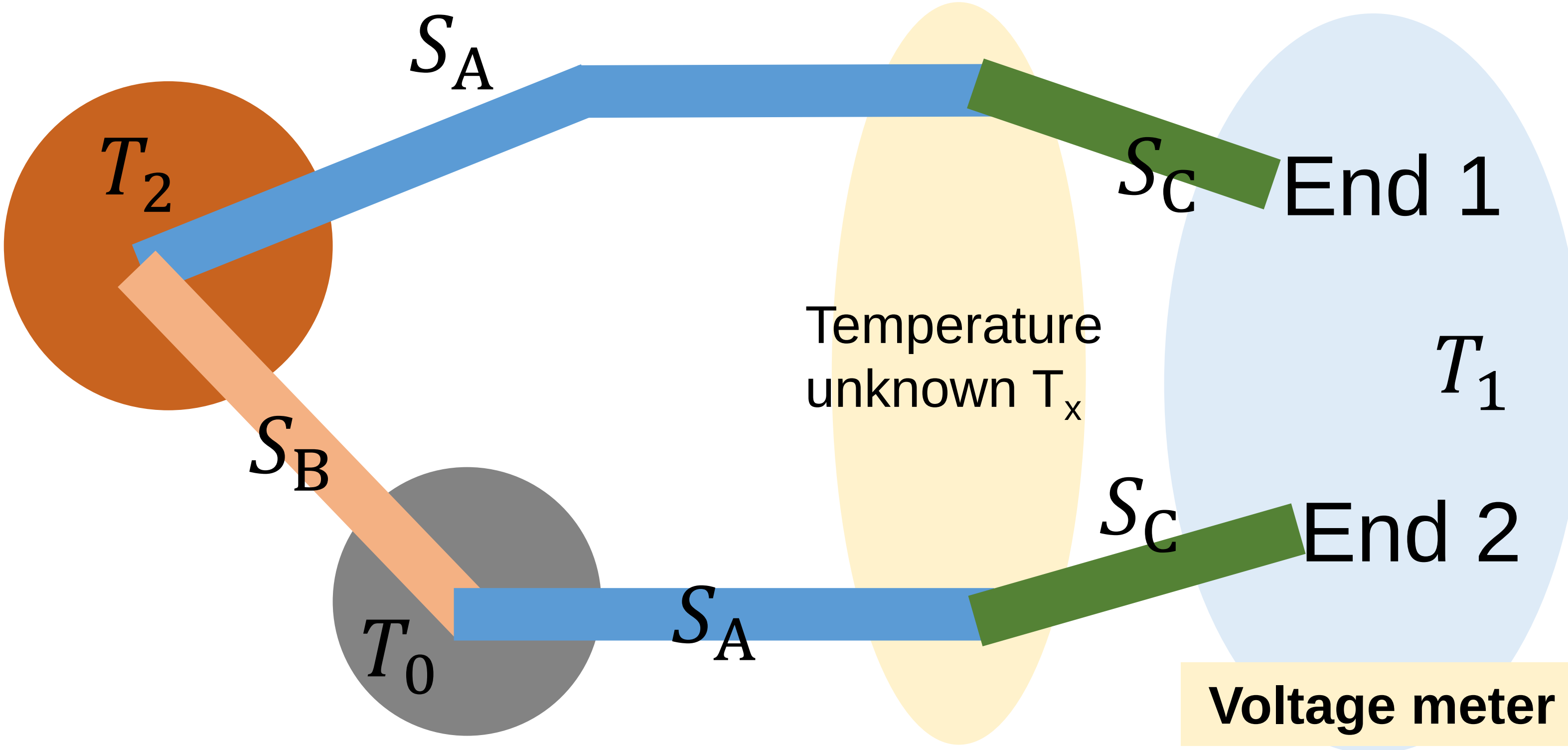
The electromotive force 电动势 between two metal wires A and B:

$$V_{\mathrm{AB}} = \int_{T_1}^{T_2} (S_{\mathrm{A}} - S_{\mathrm{B}})\mathrm{d}T$$

Thermoelectric power 热电功 for the thermocouple pair:

$$S_{\mathrm{AB}} = S_{\mathrm{A}} - S_{\mathrm{B}}$$

Homework 3-3: The electromotive force between End 1 and End 2: $V_{12} = V_1 - V_2$. **(7th)**

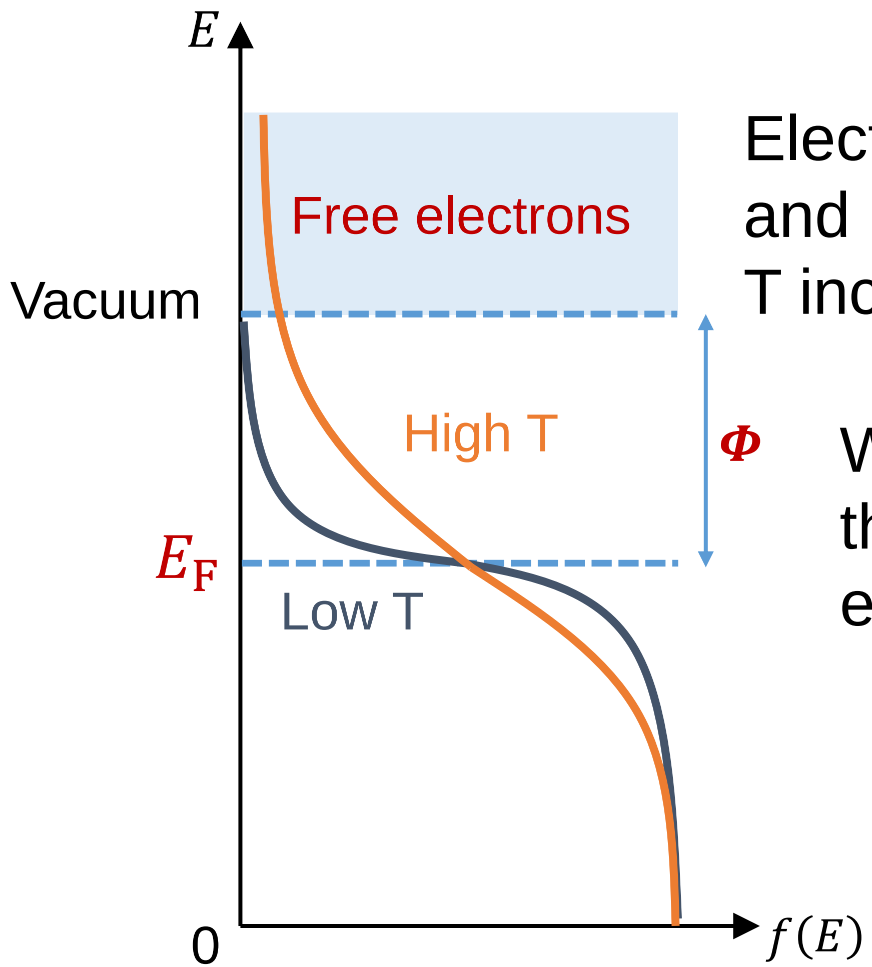


3 types of metals: A, B, C

Assume Seebeck coefficient is independent of temperature.

3.13 Thermionic emission and vacuum tube devices

What happens when temperature of a metal is too high?



Electron concentration extends more and more to higher temperatures as T increases.

When electron energy is higher than vacuum level, they are free: emitted from metals.

Vacuum tube

1st generation electronic device 第一代电子器件

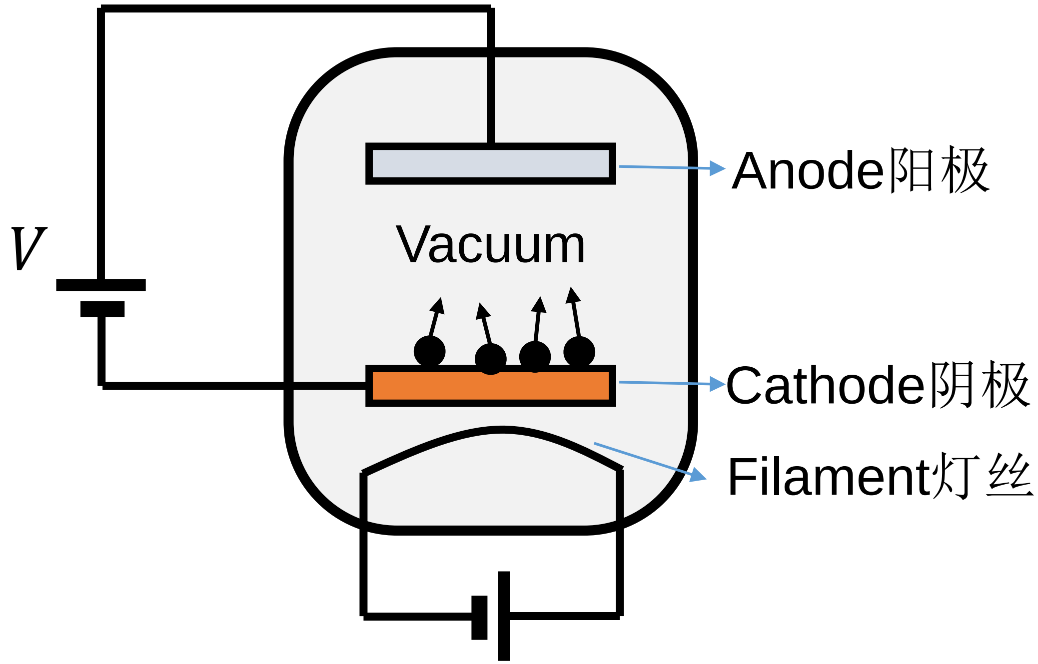
Electronic (vacuum) tube 电子管（真空管）

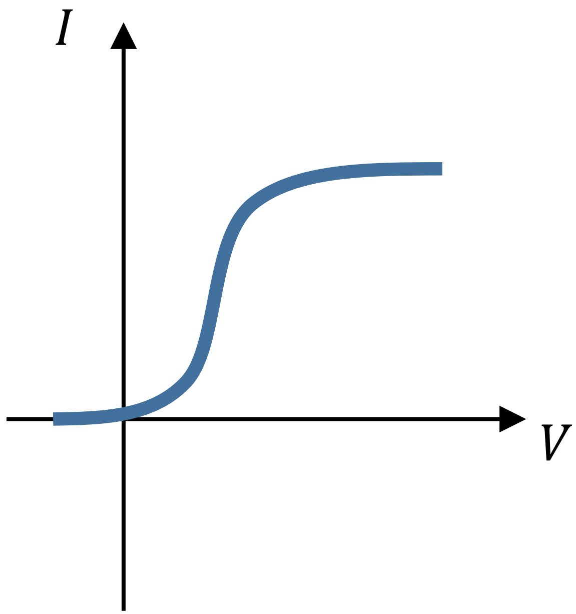
a. Vacuum shield

b. Cathode 阴极

c. Heated cathode will emit electrons阴极可由灯丝加热，使温度升高，发射出电子

d. Current: Electrons motion under the electric field and magnetic field电子受外加电场和磁场的作用下，在真空中运动就形成了电子管中的电流





Thermionic emission current density:

$$J = B_0 T^2 \exp\left(-\frac{\Phi}{kT}\right), B_{\mathrm{o}} = \frac{4\pi e m_{\mathrm{e}} k^2}{h^3}$$

Richardson-Dushman equation

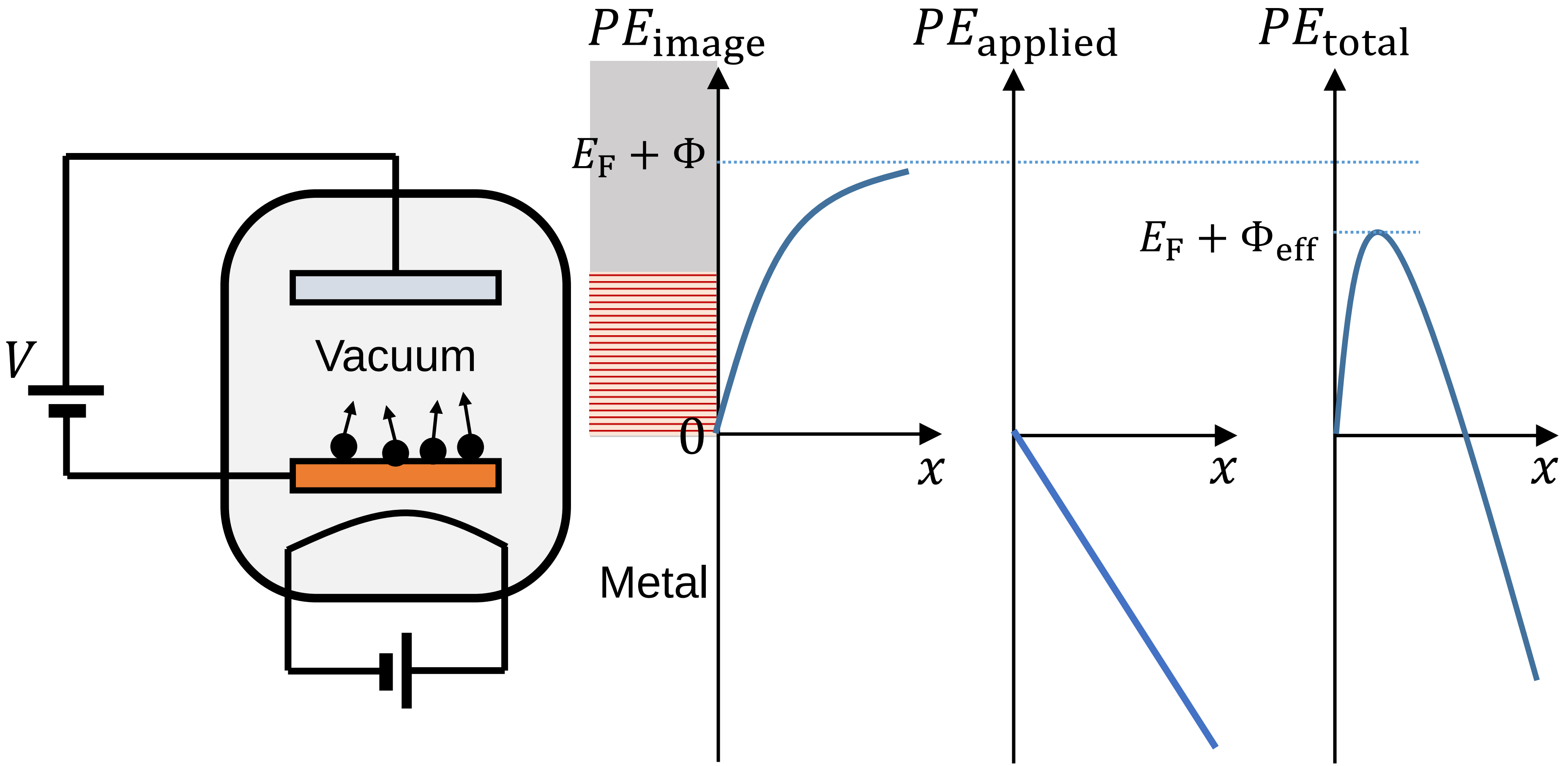
Richardson-Dushman equation

$$J = B_0 T^2 \exp\left(-\frac{\Phi}{kT}\right), B_\mathrm{o} = \frac{4\pi e m_\mathrm{e} k^2}{h^3} \approx 1.2 \times 10^6 \mathrm{Am}^{-2}\mathrm{K}^{-2}$$

In real case, electrons will have chance to be reflected back.

$$J = B_\mathrm{e} T^2 \exp\left(-\frac{\Phi}{kT}\right), B_\mathrm{e} = (1 - R) B_0$$

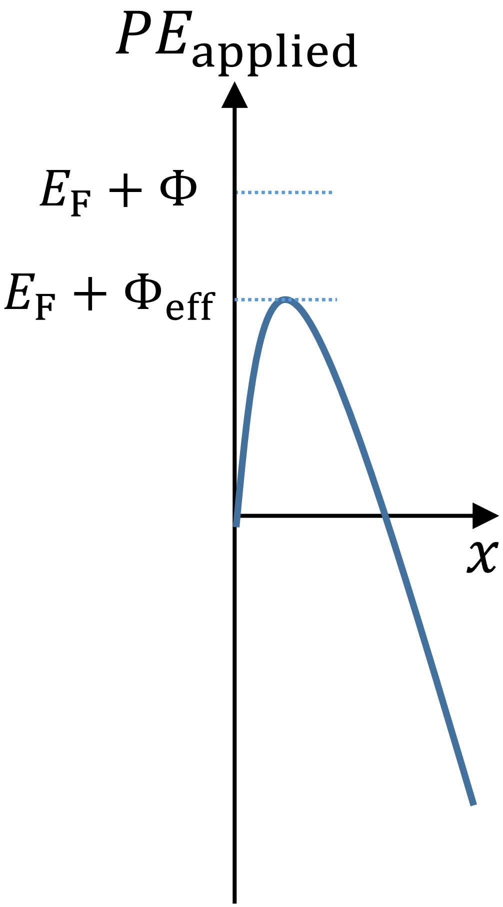
Effect of applied voltage



Metal surface: x=0

$$PE_{\mathrm{image}} = E_{\mathrm{F}} + \Phi - \frac{e^2}{16\pi\varepsilon_0 x} \quad PE_{\mathrm{applied}} = -exE$$

Schottky effect 肖特基效应



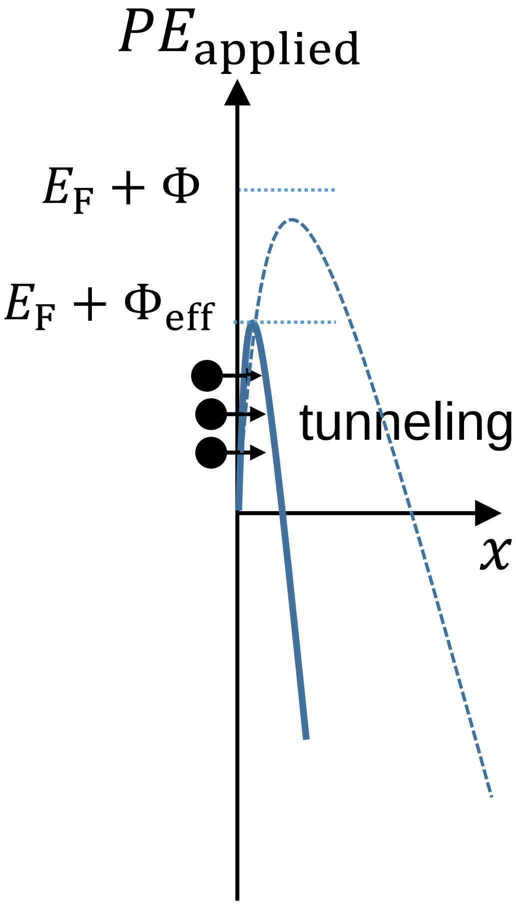
Schottky effect: using electric field to lower the potential barrier (PE).

$$\Phi_{\mathrm{eff}} = \Phi - \left(\frac{e^3 E}{4\pi\varepsilon_0}\right)^{\frac{1}{2}} = \Phi - \beta_{\mathrm{s}}\sqrt{E}$$

$$J = B_{\mathrm{e}} T^2 \exp\left(-\frac{\Phi - \beta_{\mathrm{s}}\sqrt{E}}{kT}\right), B_{\mathrm{e}} = (1-R)B_0$$

β_{s}: Schottky coefficient

Field emission 场发射



When electric field is very large:

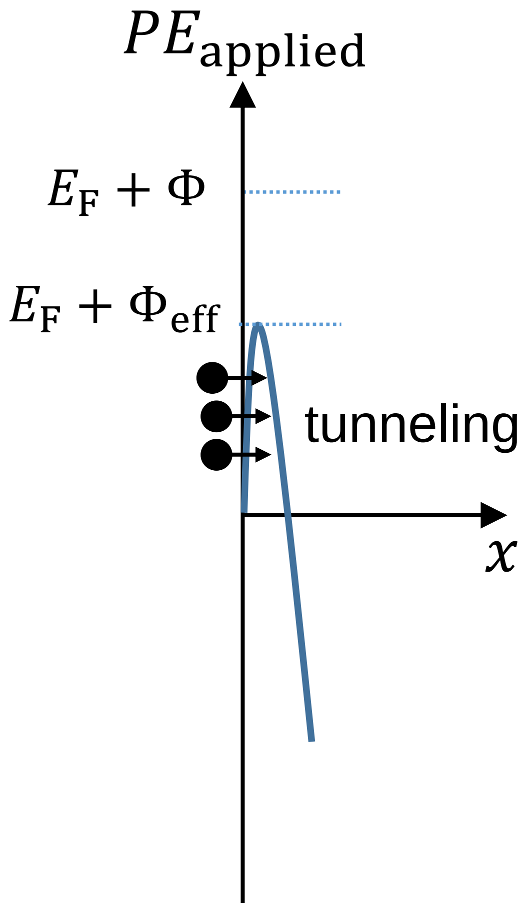
$E > 10^7 \text{V/cm}$

Barrier is very narrow.

Electrons can directly tunnel into vacuum.

Since tunneling is temperature independent, the emission process is called field emission.

Field emission 场发射

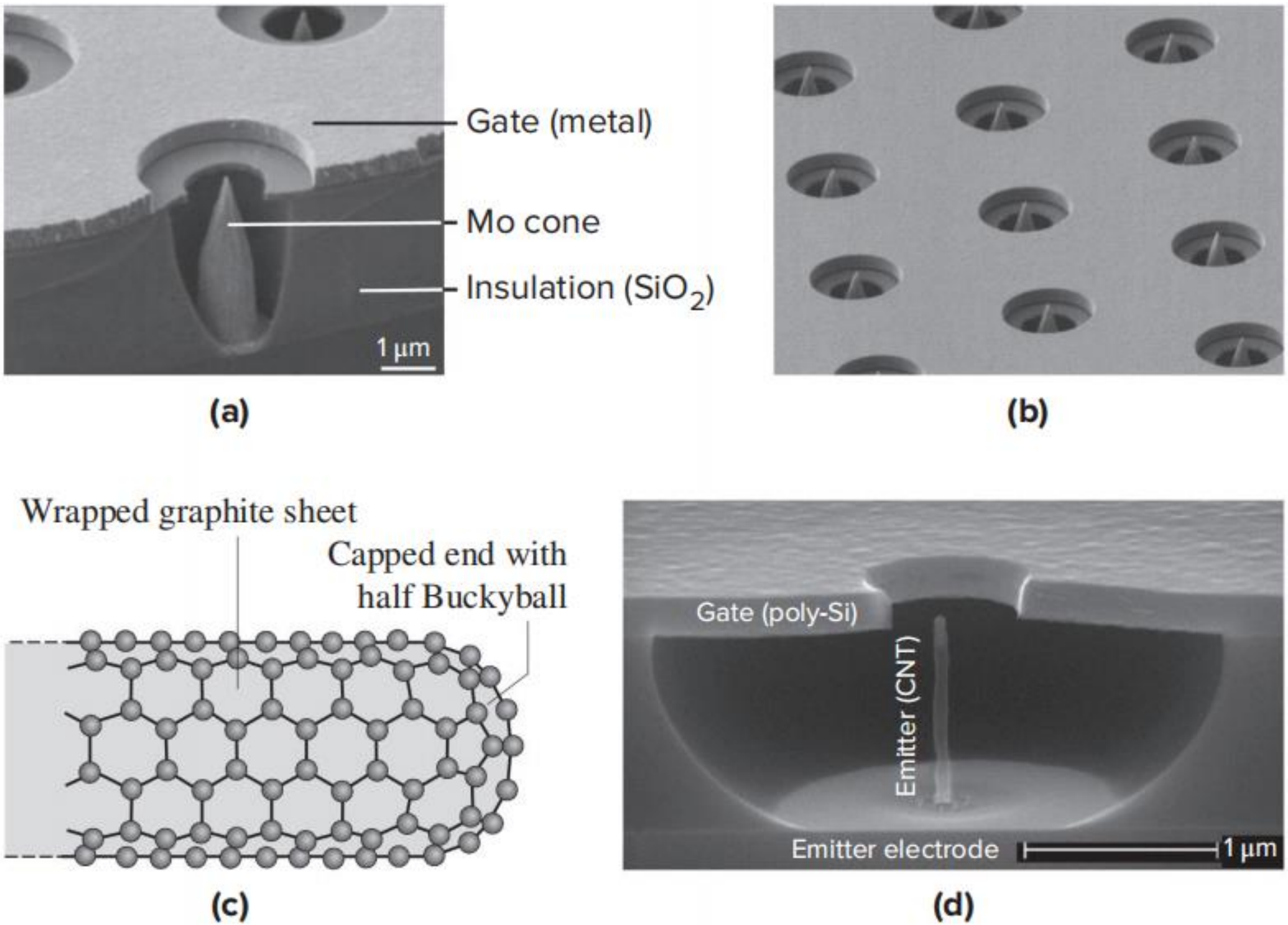


$$J_{\mathrm{field}} = CE^2 \exp\left(-\frac{E_{\mathrm{c}}}{E}\right),$$

$$C = \frac{e^3}{8\pi h\Phi}, E_{\mathrm{c}} = \frac{8\pi\left(2m_{\mathrm{e}}\Phi^3\right)^{1/2}}{3eh}$$

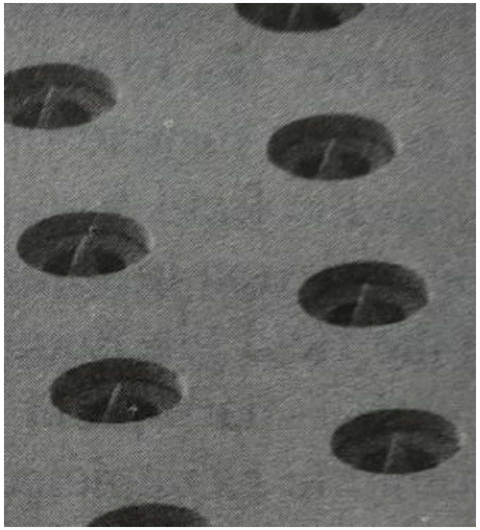
Q: the advantages of field emission compared with thermionic emission?

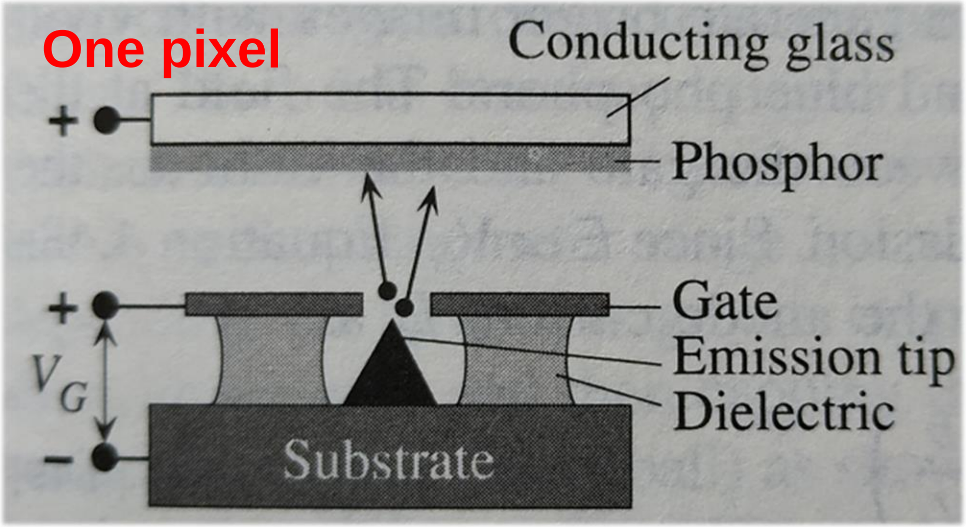
Applications of field emission effect



Applications of field emission effect

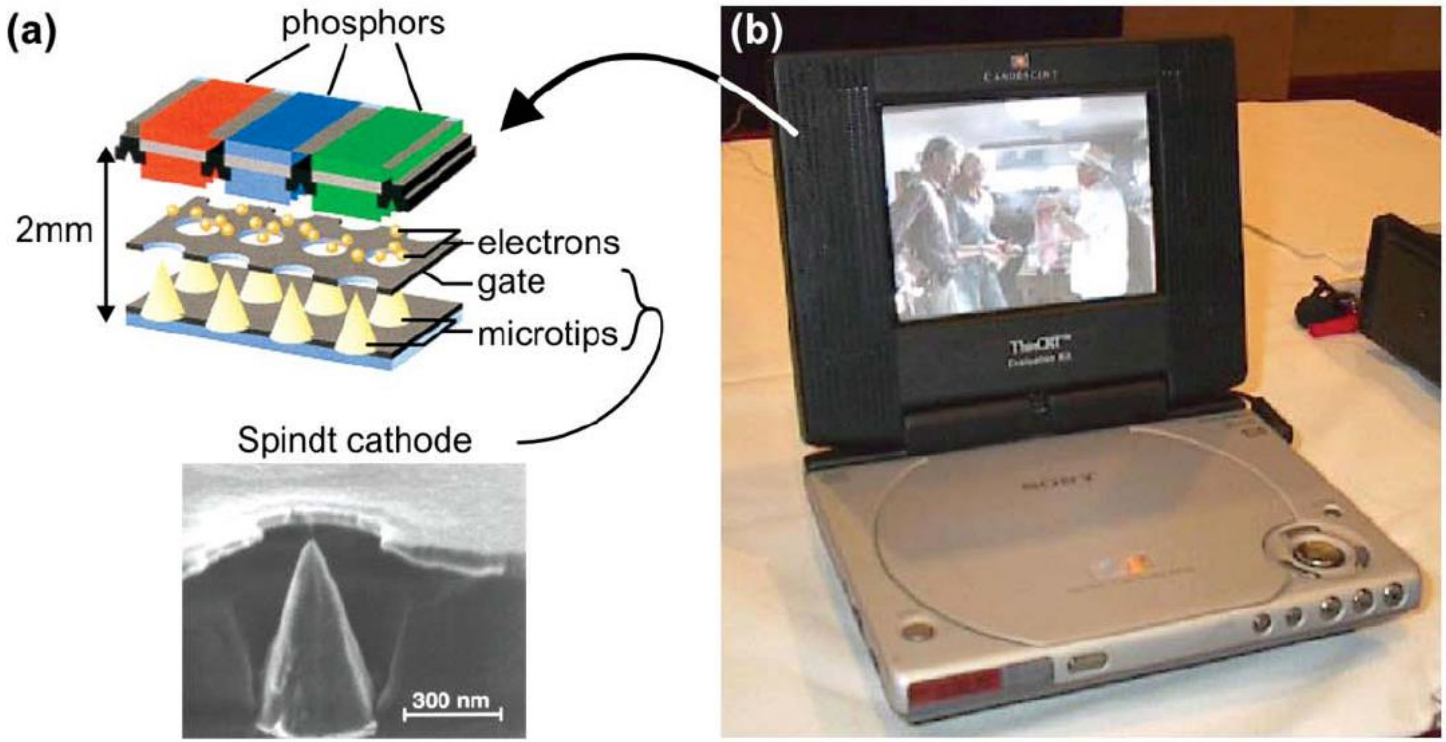
Field emission displays (FED)



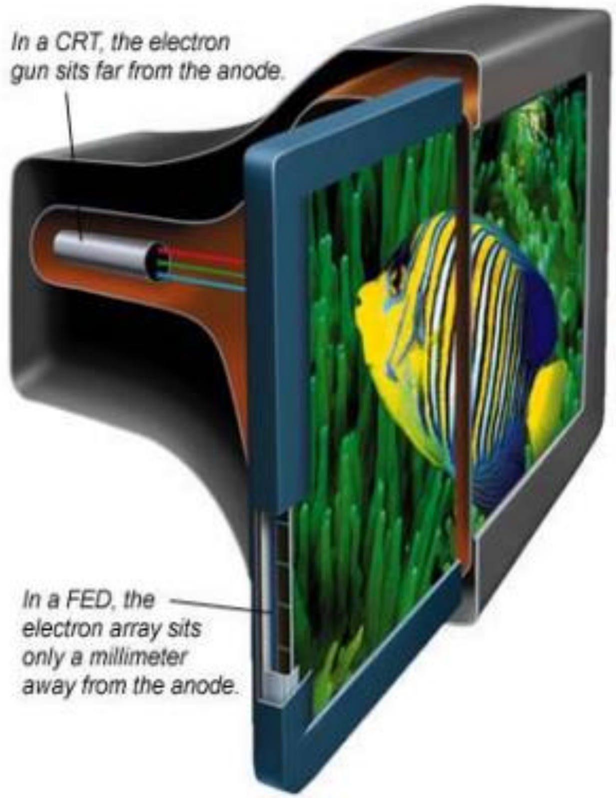


FED can be very thin <6 mm, low weight, low power consumption.

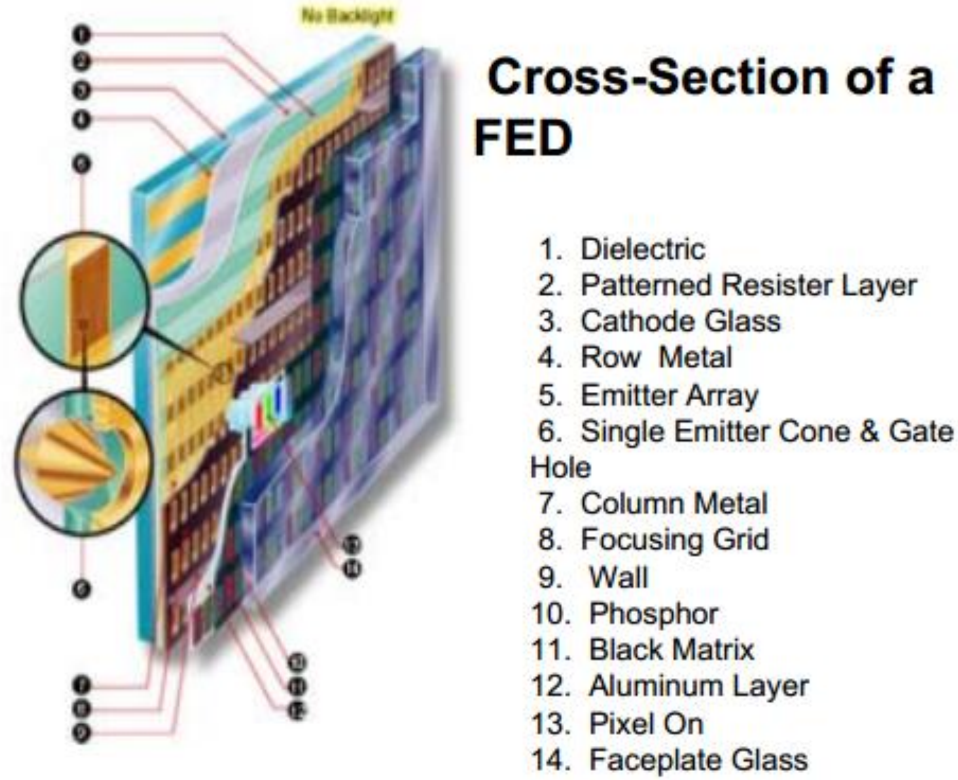
Sony was leading the investigation of FED since 2000, but it was not successful as LCD (liquid crystal displays).



(a) Cross-section of a field emission display showing a Spindt tip cathode;
(b) Sony portable DVD player using a field emission display.



Hot cathode



Cold cathode

Advantages: Thinner, lighter, vivid color, fast response, wide viewing angle etc.

Applications of field emission effect

Electronic gan 电子枪

Scanning electron microscope (SEM)

TEM