

Outline

3.1 Allowed and Forbidden Energy Bands

3.2 Electrical Conduction in Solids

3.3 Extension to Three Dimensions

3.4 Density of States Function

3.5 Statistical Mechanics

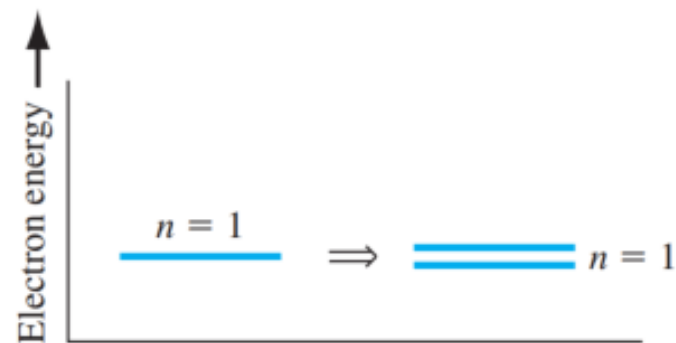
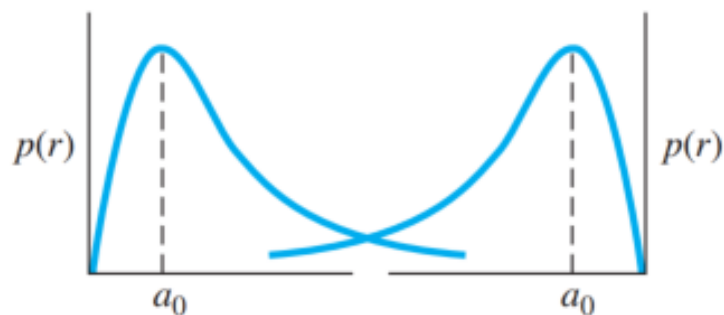
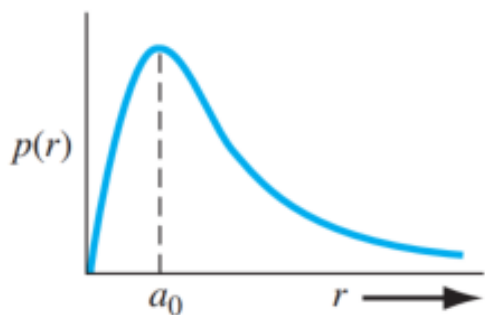
Pauli



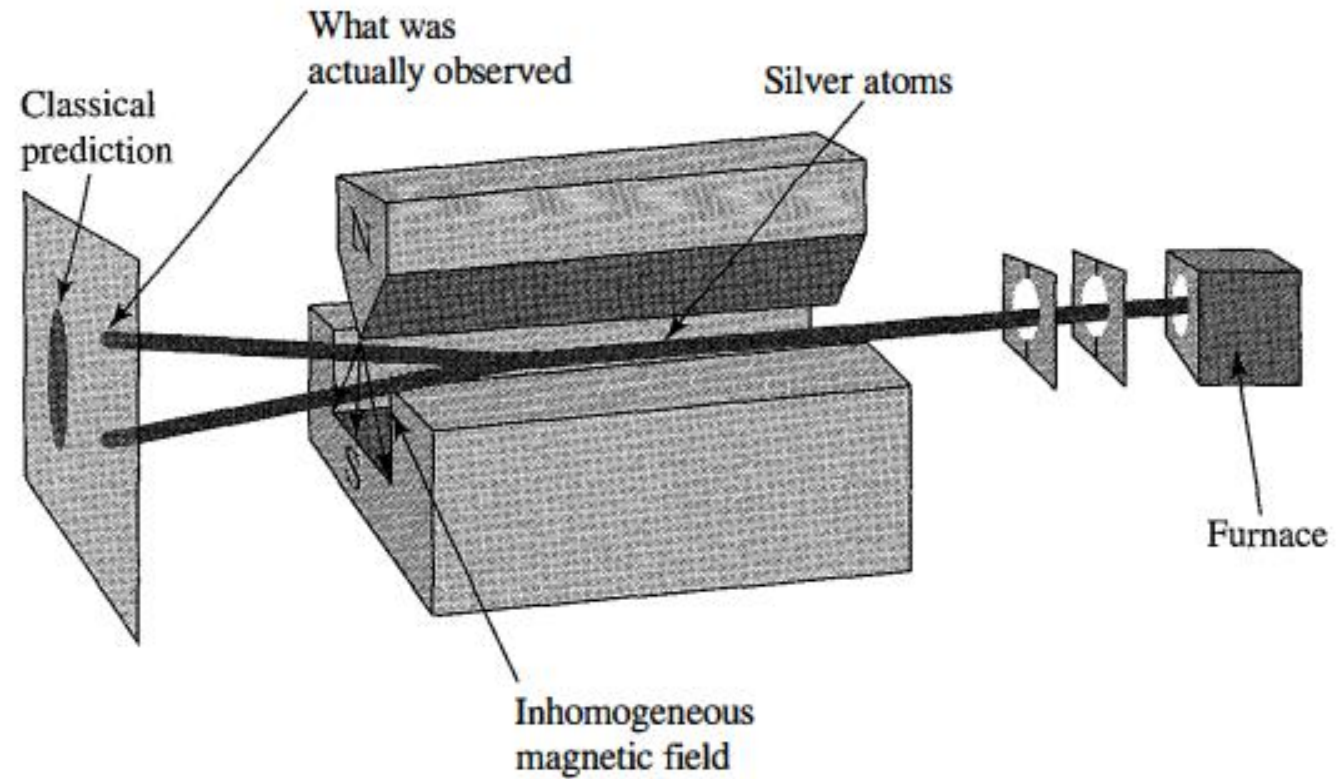
具有相同量子數的兩個電子是不可能同時存在的，也就是說，同一原子中的任一個電子，它在原子軌域中的4個量子數（主量子數 n 、副量子數 l 、磁量子數 m_l 和自旋量子數 m_s ）不可能完全相同。

能階分裂

- 無限位能井或氫原子模型的結果顯示電子的能量被量子化。
- 機率密度函數意謂著在某個位置找到電子的機率是多少。
- 我們將把這樣的單原子概念延伸到晶體並定性得到能帶的觀念。
- 根據**包利不相容原理**，兩個電子不能佔有相同的量子態(互相討厭)。
- 若兩個電子產生交互作用將導致能階分裂。

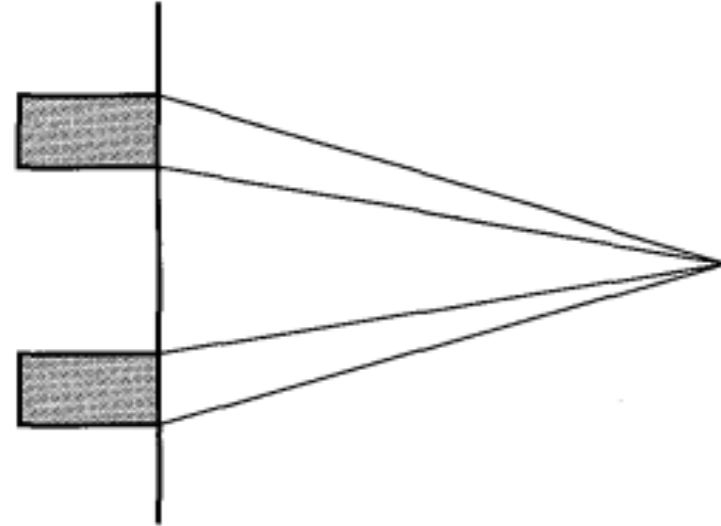
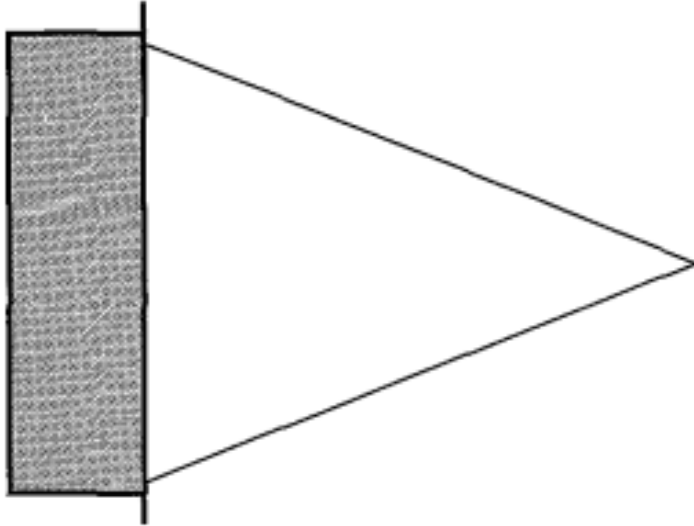


Stern-Gerlach experimental setup



Stern-Gerlach experimental setup

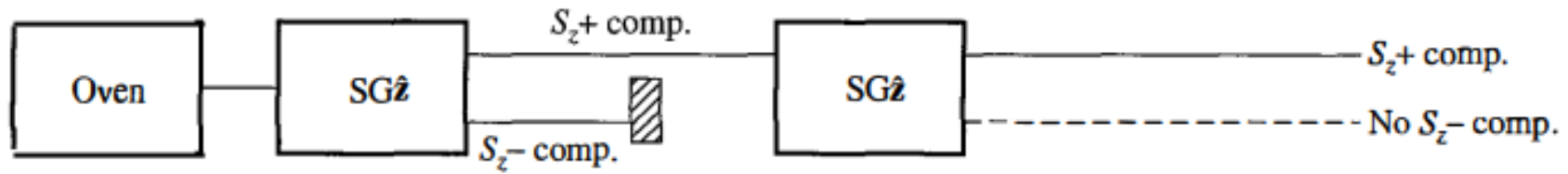
Electrons distribution



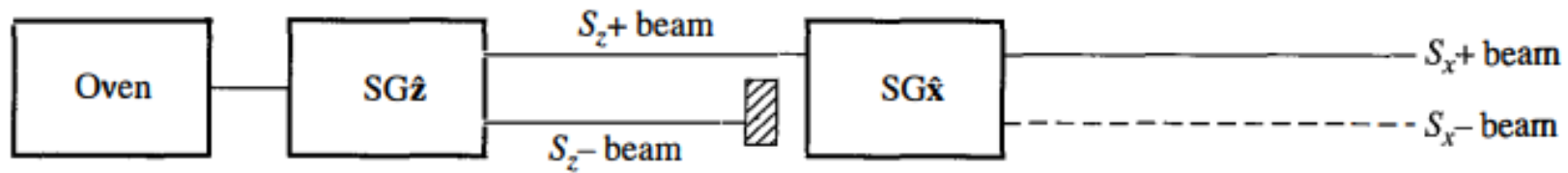
Classical physics prediction for results from the Stern-Gerlach experiment

These two orientations did not span the entire expected range

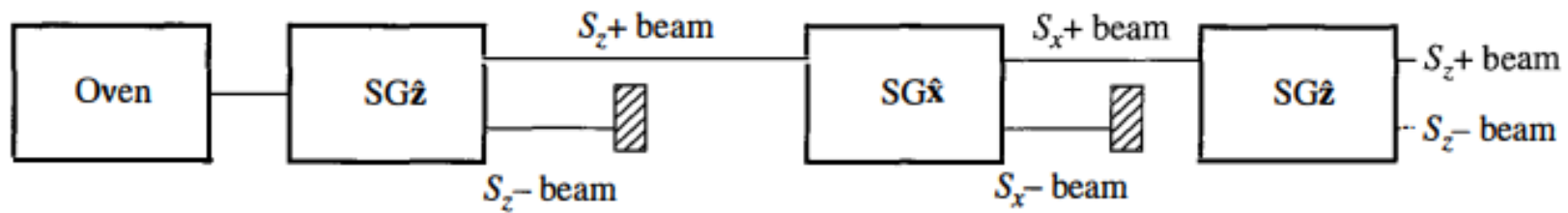
Sequential Stern-Gerlach



(a)



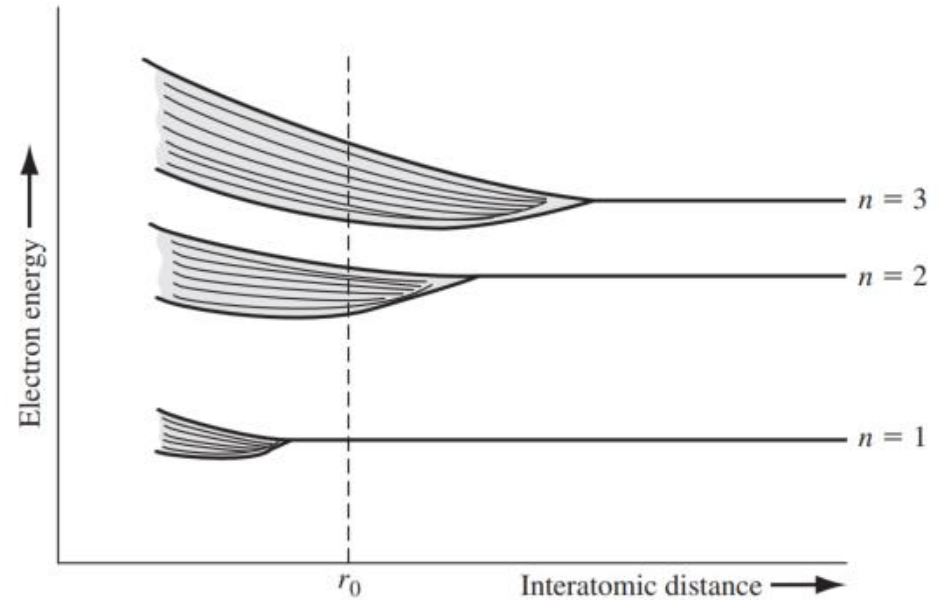
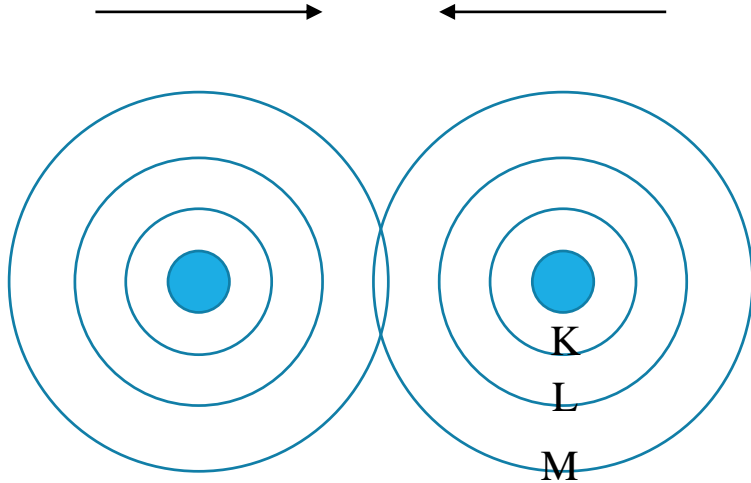
(b)



(c)

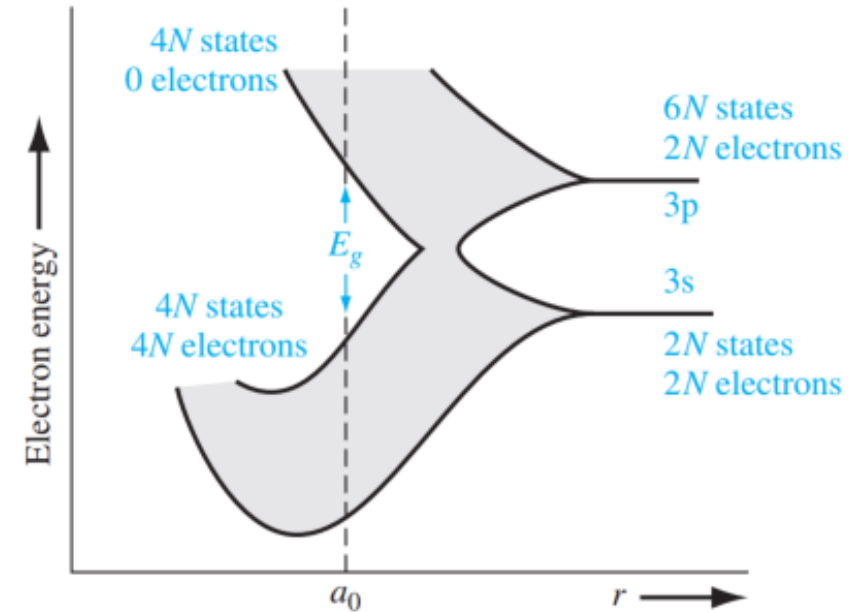
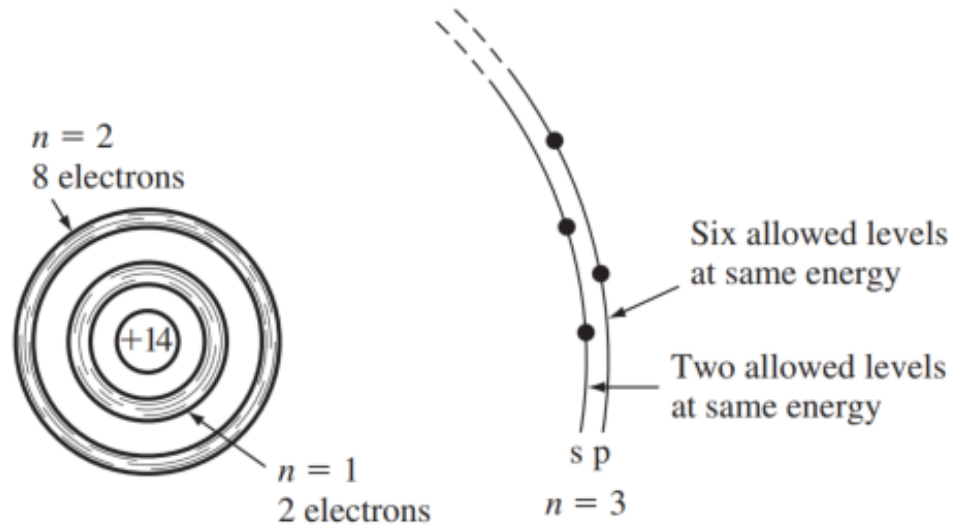
能帶形成

當原子間距愈來愈近時，M層的能量殼層開始互相作用，接著是L層和K層。



價帶與傳導帶

- 3s軌域和3p軌域逐漸合併成為能帶。達到平衡間距時：
 - 3s軌域總共有 $2N$ 個狀態， $2N$ 個電子。
 - 3p軌域總共有 $6N$ 個狀態， $2N$ 個電子。
- 上層帶被稱為傳導帶conduction band，下層帶被稱為價帶valence band。



Example 3.1

Objective: Calculate the change in kinetic energy of an electron when the velocity changes by a small amount.

Consider an electron traveling at a velocity of 10^7 cm/s. Assume that the velocity increases by a value of 1 cm/s. The increase in kinetic energy is given by

$$\Delta E = \frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2 = \frac{1}{2}m(v_2^2 - v_1^2)$$

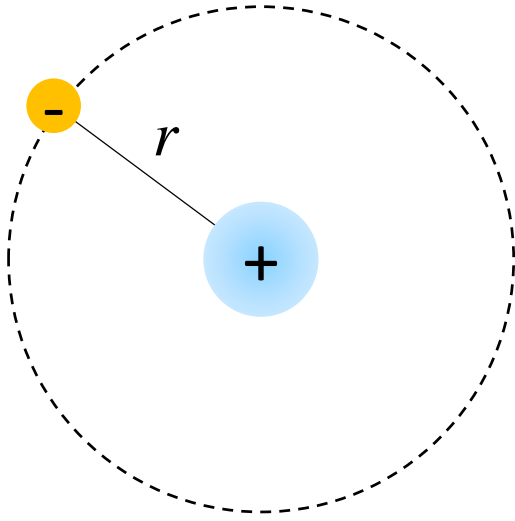
$$\Delta E \approx \frac{1}{2}m(2v_1\Delta v) = mv_1\Delta v$$

$$\Delta E = (9.11 \times 10^{-31})(10^5)(0.01) = 9.11 \times 10^{-28} \text{ J}$$

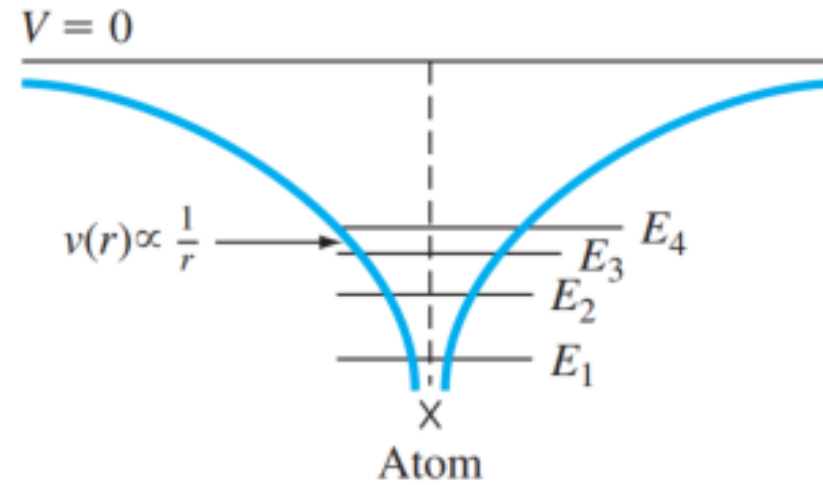
$$\Delta E = \frac{9.11 \times 10^{-28}}{1.6 \times 10^{-19}} = 5.7 \times 10^{-9} \text{ eV}$$

1. 每個電子能量差距非常小
2. 所以能量分布可以被近似為連續

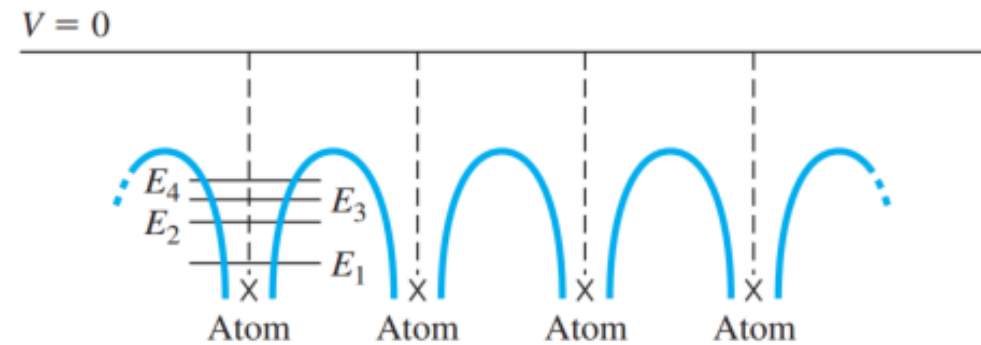
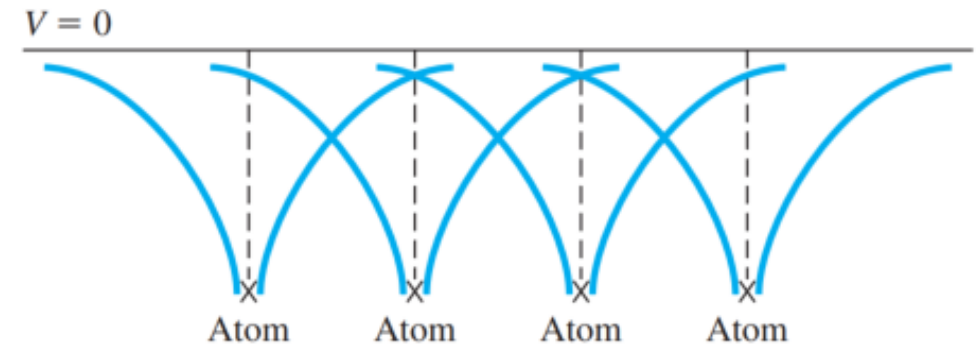
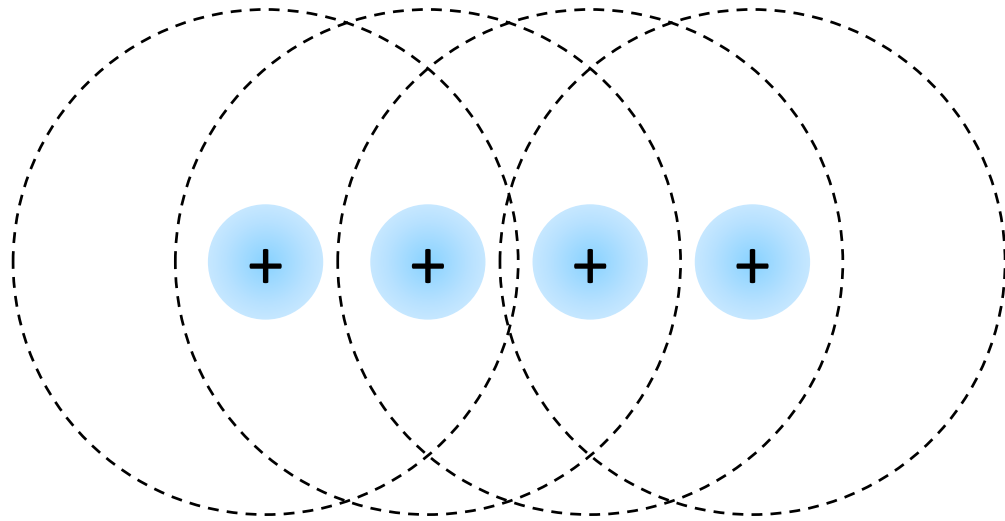
單原子系統的電位能



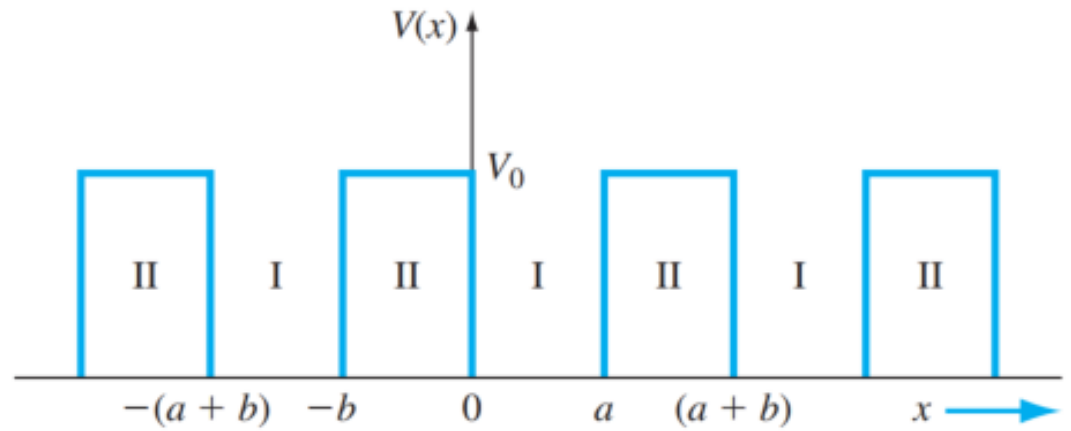
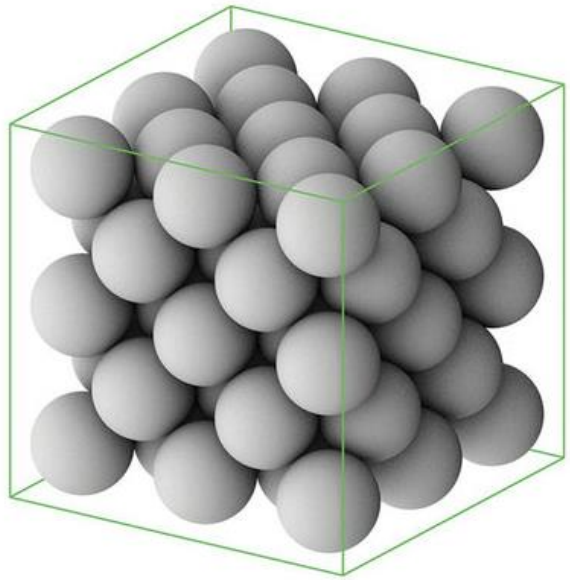
$$V = -\frac{e^2}{4\pi\epsilon_0 r}$$



固態系統的電位能

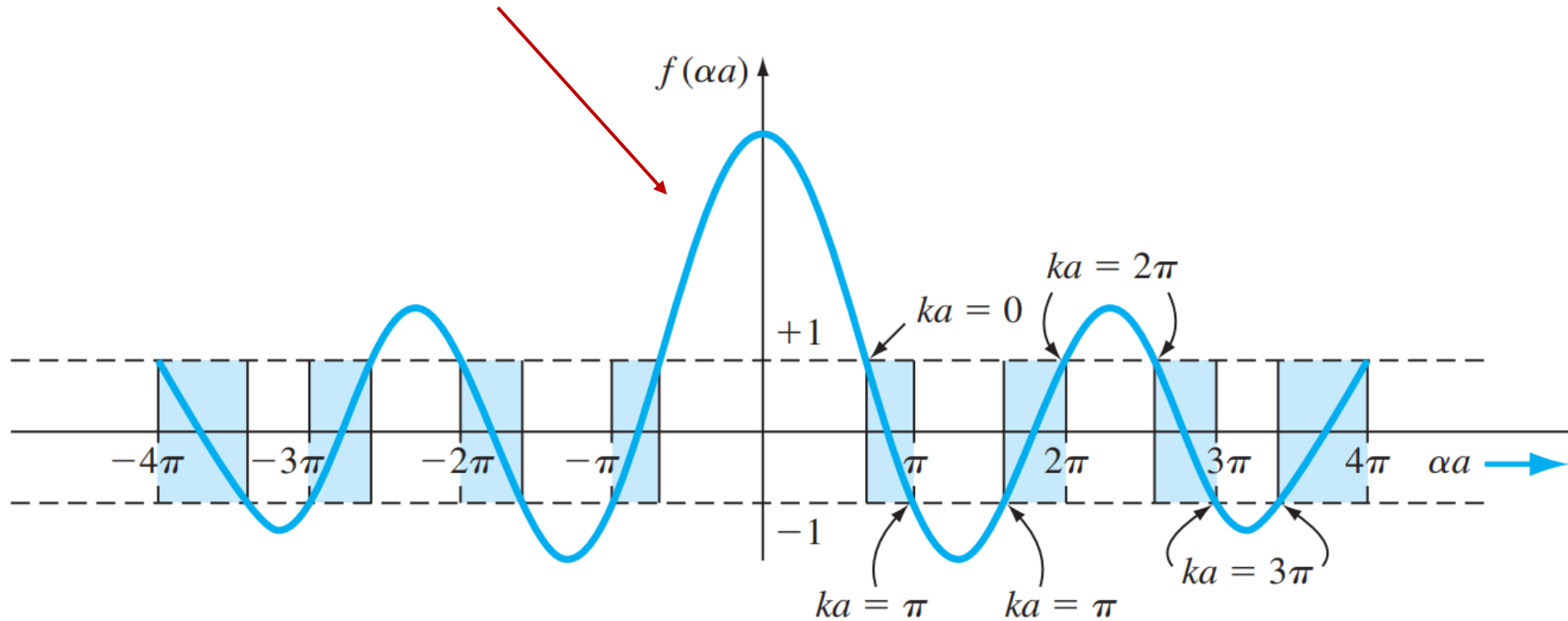


固態系統的電位能



The k-space Diagram(補)

$$P' \frac{\sin(\alpha a)}{\alpha a} + (\cos \alpha a) = \cos ka \quad , \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$



The E-k Diagram

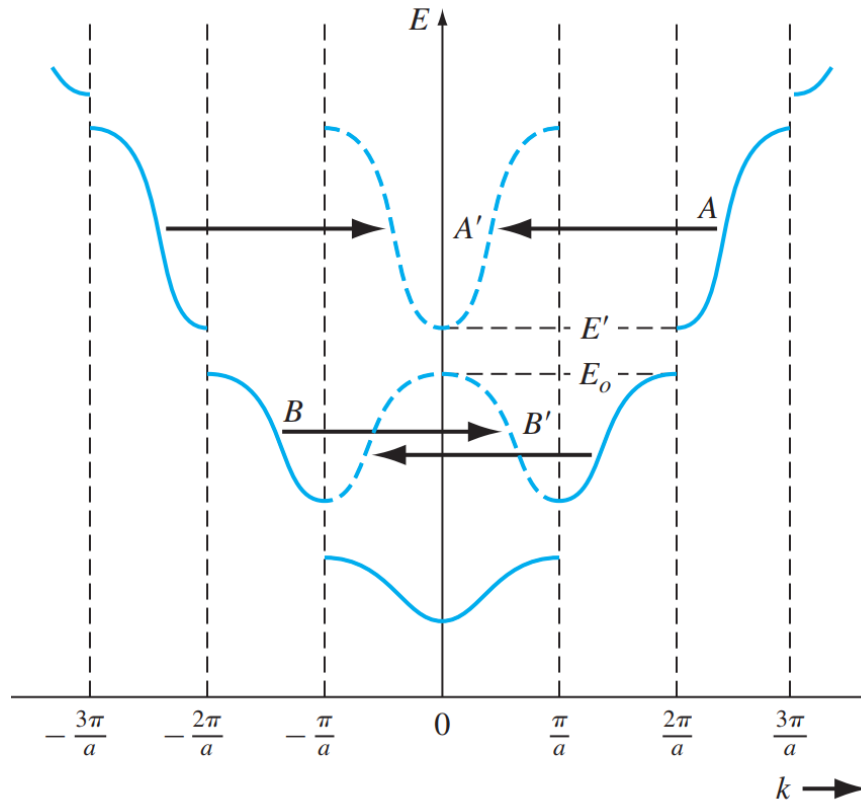


Figure 3.10 | The E versus k diagram showing 2π displacements of several sections of allowed energy bands.

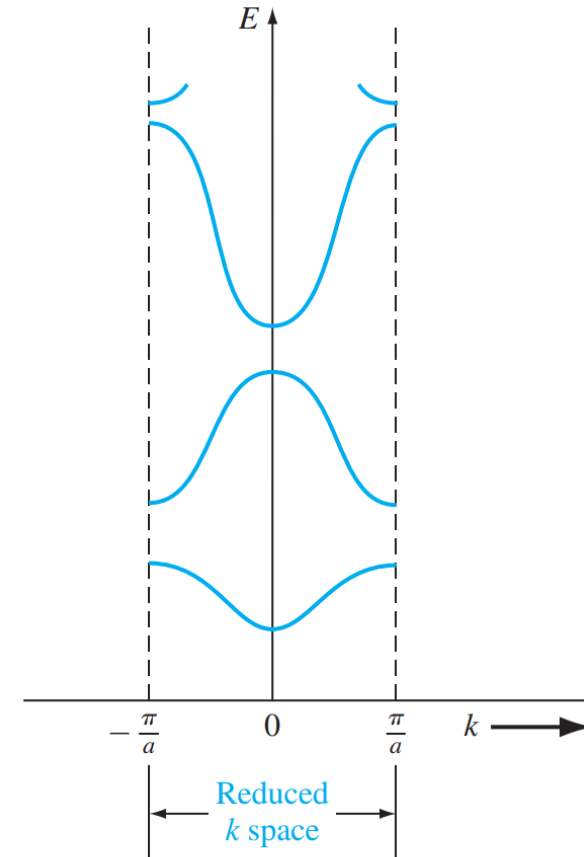
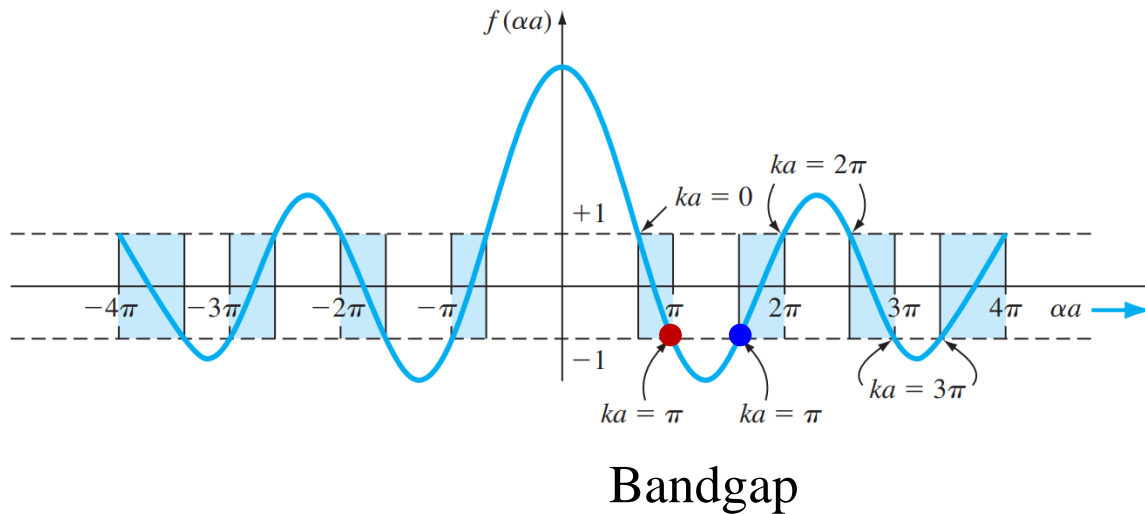


Figure 3.11 | The E versus k diagram in the reduced-zone representation.

Example 3.2

Objective: Determine the width (in eV) of a forbidden energy band.

Determine the width of the forbidden bandgap that exists at $ka = \pi$ (see Figure 3.9). Assume that the coefficient $P' = 8$ and the potential width is $a = 4.5 \text{ \AA}$.



$$P' \frac{\sin \alpha a}{\alpha a} + (\cos \alpha a) = \cos ka$$

$$8 \frac{\sin \alpha a}{\alpha a} + (\cos \alpha a) = -1$$

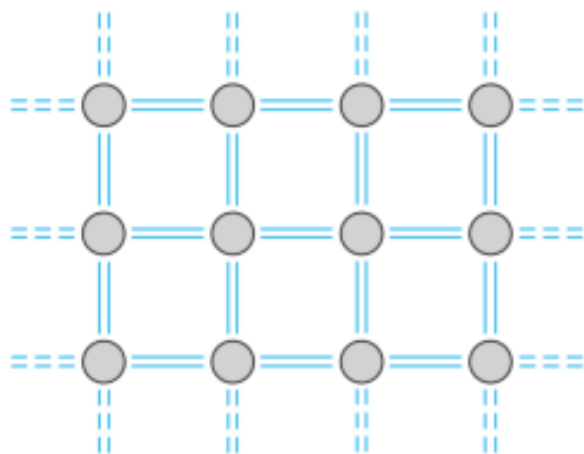
- $\alpha_1 a = \sqrt{\frac{2mE_1}{\hbar^2}} a = \pi \Rightarrow E_1 = 2.972 \times 10^{-19} \text{ J}$
- $\alpha_2 a = \sqrt{\frac{2mE_2}{\hbar^2}} a = 5.141 \Rightarrow E_2 = 7.958 \times 10^{-19} \text{ J}$

$$\frac{E_2 - E_1}{1.6 \times 10^{-19}} = 3.12 \text{ eV}$$

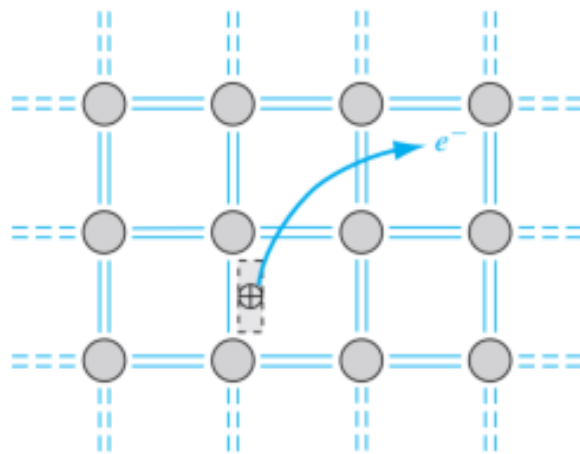
傳導帶中的電子

當絕對溫度 $T > 0\text{ K}$ 時：

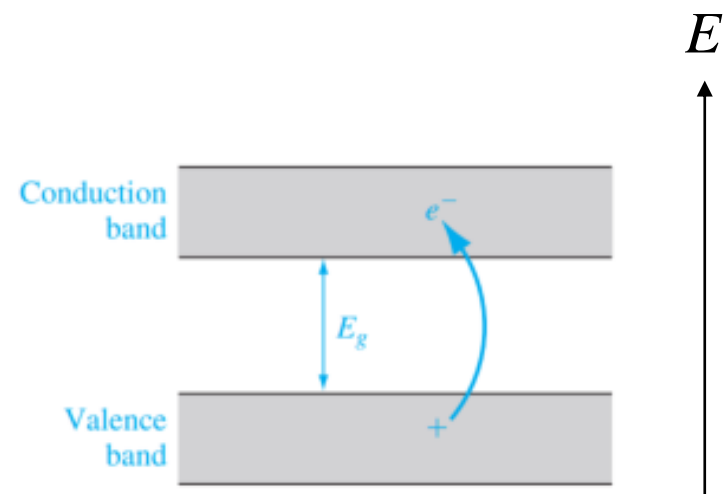
極少數的價帶電子會因熱能得到足夠能量突破能量間隙而進入傳導帶。



$T = 0\text{ K}$



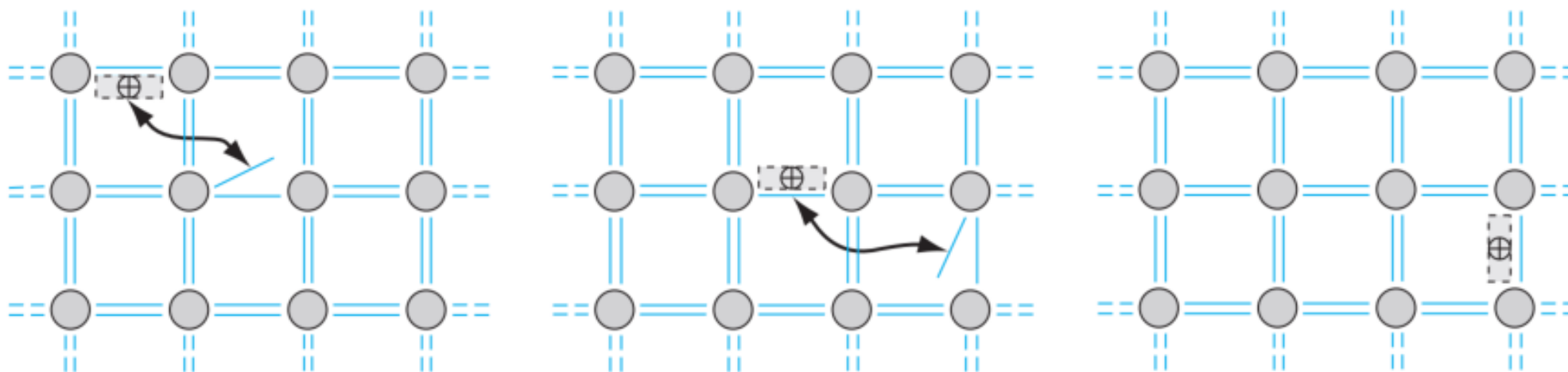
$T > 0\text{ K}$



價帶中的電洞

當絕對溫度 $T > 0\text{ K}$ 時：

當一個電子從價帶進入傳導帶，原本共價的位置就會空出一個位置，稱為電洞，相當於帶一個**正電**。



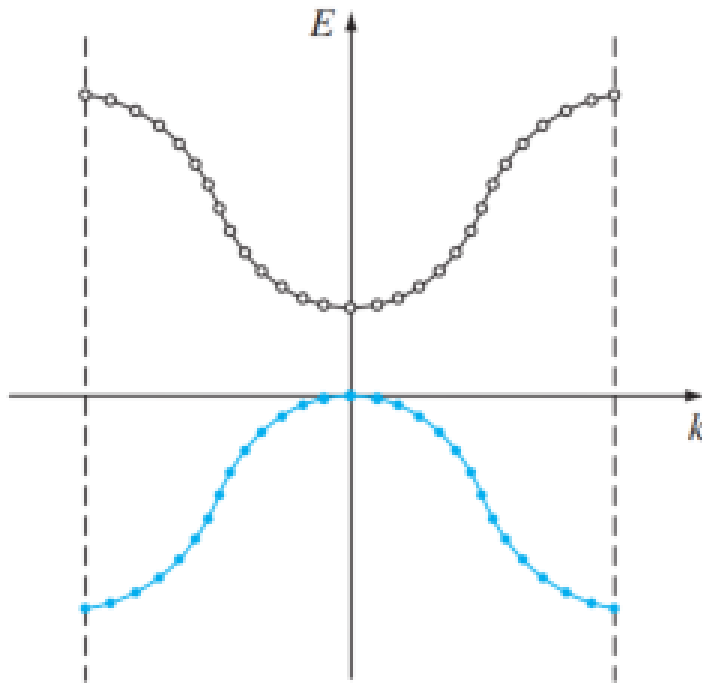
The Energy Band and the Bond Model

T = 0K

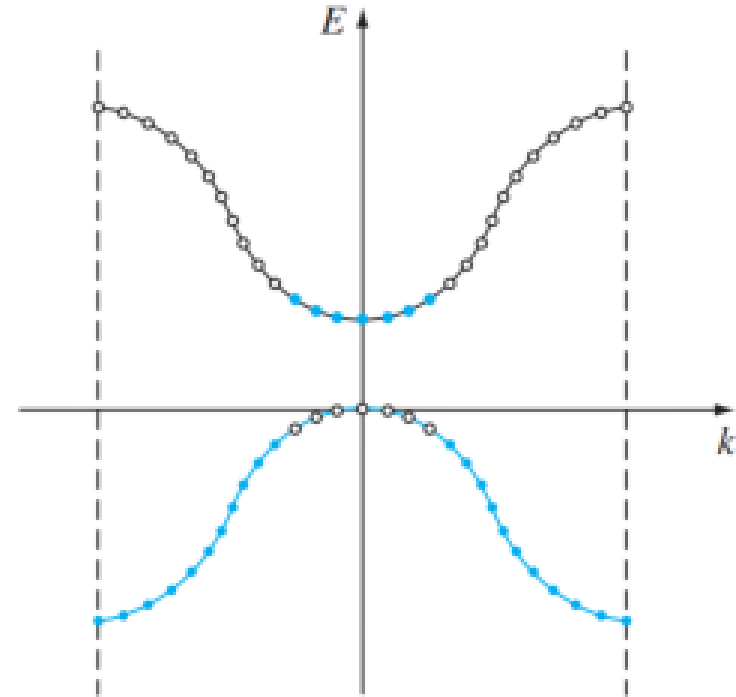
T > 0K

傳導帶

價帶



(a)

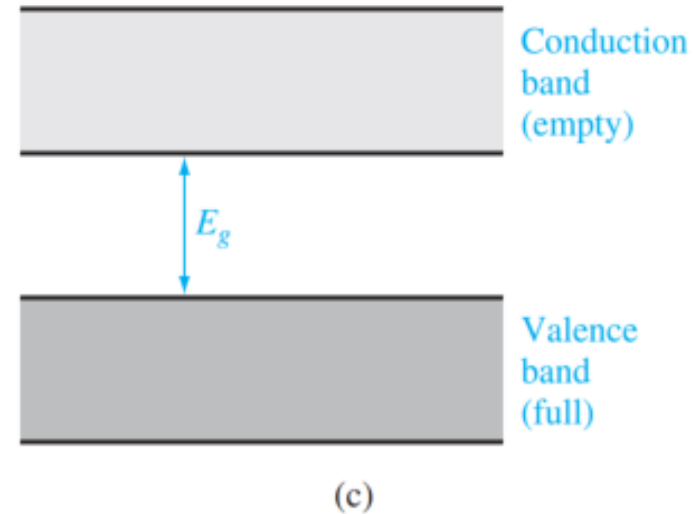
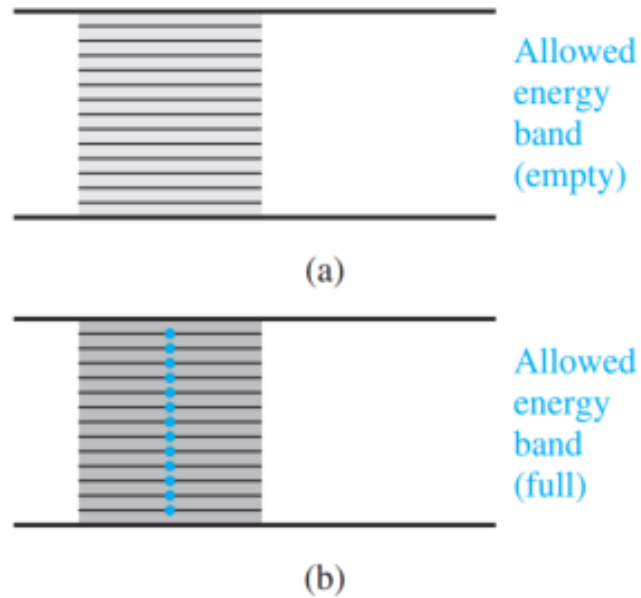


(b)

絕緣體能帶

Insulator 絕緣體

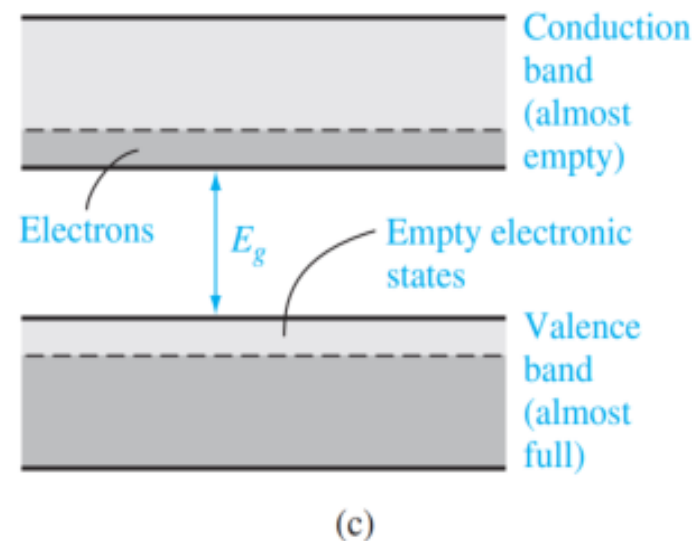
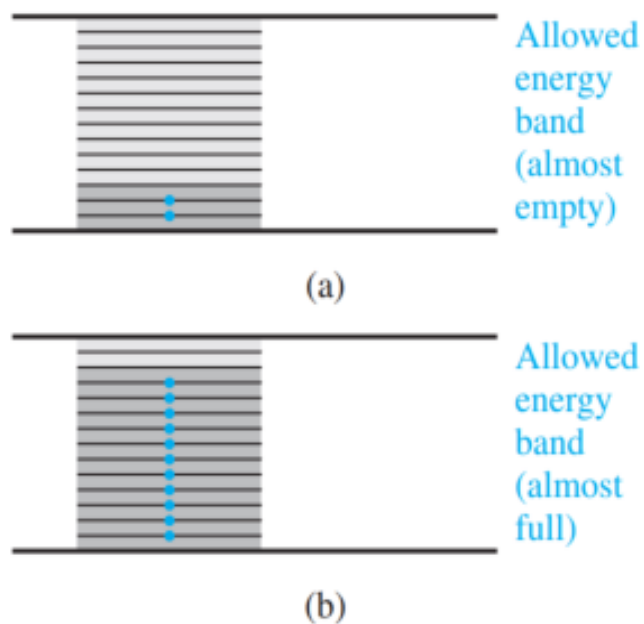
- 價帶完全填滿，傳導帶**完全**為空。此時兩個能帶無載子可傳遞能量
- 絕緣體能帶間隙約在 3.5 ~ 6 (eV) 或更大



半導體能帶

Semiconductor 半導體

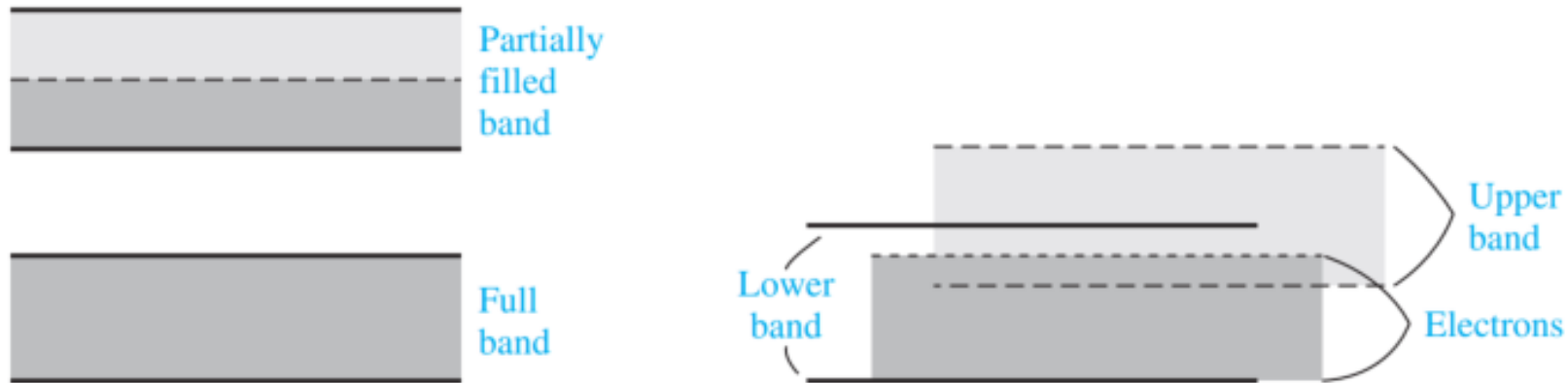
- 價帶幾乎填滿，傳導帶幾乎為空。此時兩個能帶有極少載子可傳遞能量
- 半導體能帶間隙約在 1 eV。1.12 eV (Si)
- 半導體的電阻率是可以透過摻雜加以控制。



金屬能帶

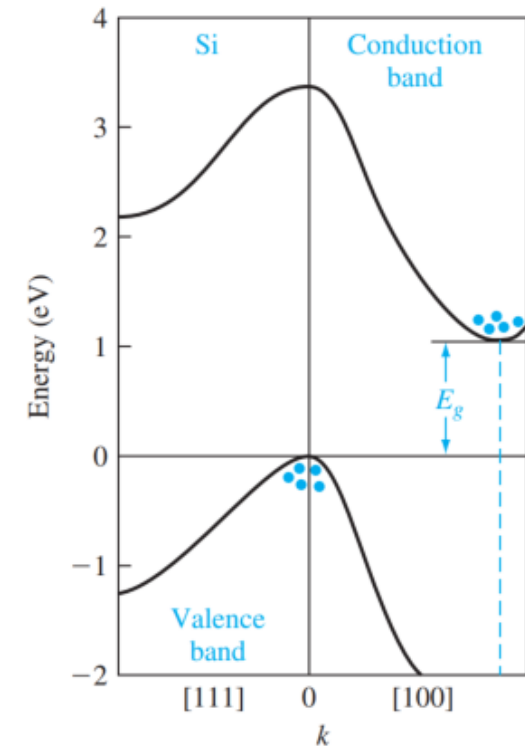
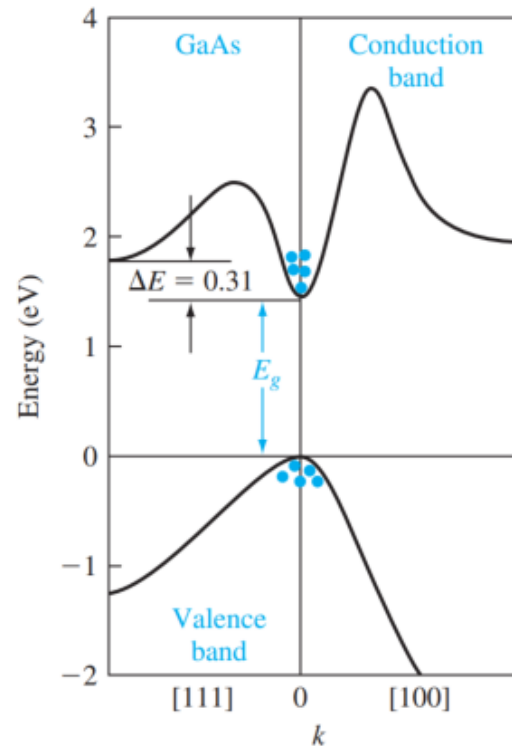
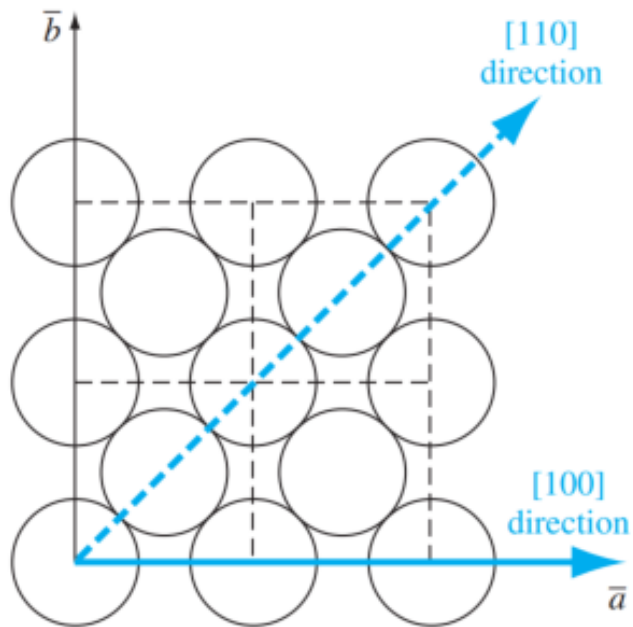
Metal 金屬

- 價帶完全填滿，傳導帶部分填滿。傳導帶中有大量電子可傳遞能量
- 價帶與傳導帶部分重疊，使得價帶電子不需能量就可以進入傳導帶。



Direct and Indirect Bandgap

- 對三維的晶體而言，原子間的週期和位能變化會隨著方向而變，因此也會有不同的E-K關係圖。
- 價帶的最大值和傳導帶的最小值對應到相同的k值，此種能帶稱為direct bandgap (GaAs)，否則稱為 indirect bandgap (Si, Ge)。



自由電子的狀態密度 (DoS)(補)

單電子三維無限位能井能量：

$$E = \frac{\hbar^2 \pi^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2)$$

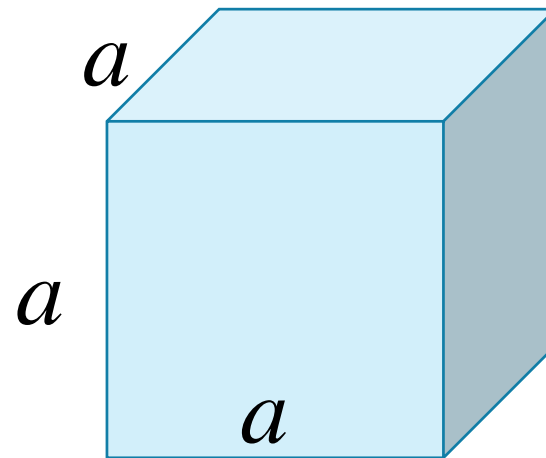
導出能態密度(DoS)：

$$g(E) = \frac{4\pi(2m)^{3/2}}{h^3} \sqrt{E} \quad \frac{\text{states}}{\text{cm}^3 \cdot \text{eV}}$$

理解方式：單位體積單位能量內有多少狀態數(房間數)

單位體積內某個能量區間內有多少狀態：

$$n_s = \int_{E_1}^{E_2} g(E) dE$$



Example

Objective: Calculate the density of states per unit volume over a particular energy range.

Consider the density of states for a free electron given by Equation (3.69). Calculate the density of states per unit volume with energies between 0 and 1 eV.

$$N = \int_0^{1 \text{ eV}} g(E) dE = \frac{4\pi(2m)^{3/2}}{h^3} \cdot \int_0^{1 \text{ eV}} \sqrt{E} dE$$

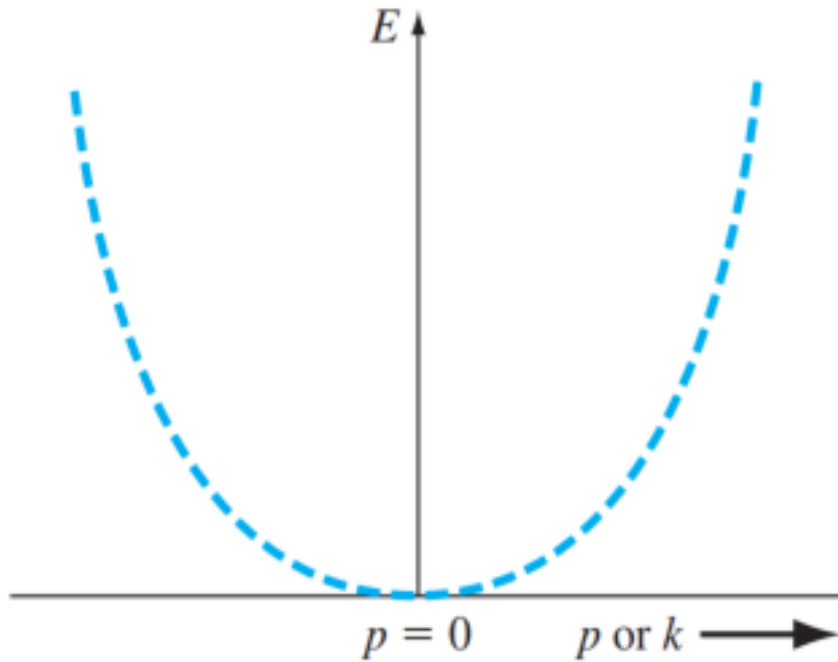
$$N = \frac{4\pi(2m)^{3/2}}{h^3} \cdot \frac{2}{3} \cdot E^{3/2}$$

$$N = \frac{4\pi[2(9.11 \times 10^{-31})]^{3/2}}{(6.625 \times 10^{-34})^3} \cdot \frac{2}{3} \cdot (1.6 \times 10^{-19})^{3/2} = 4.5 \times 10^{27} \text{ m}^{-3}$$

$$N = 4.5 \times 10^{21} \text{ states/cm}^3$$

自由電子的 E-K diagram

拋物線

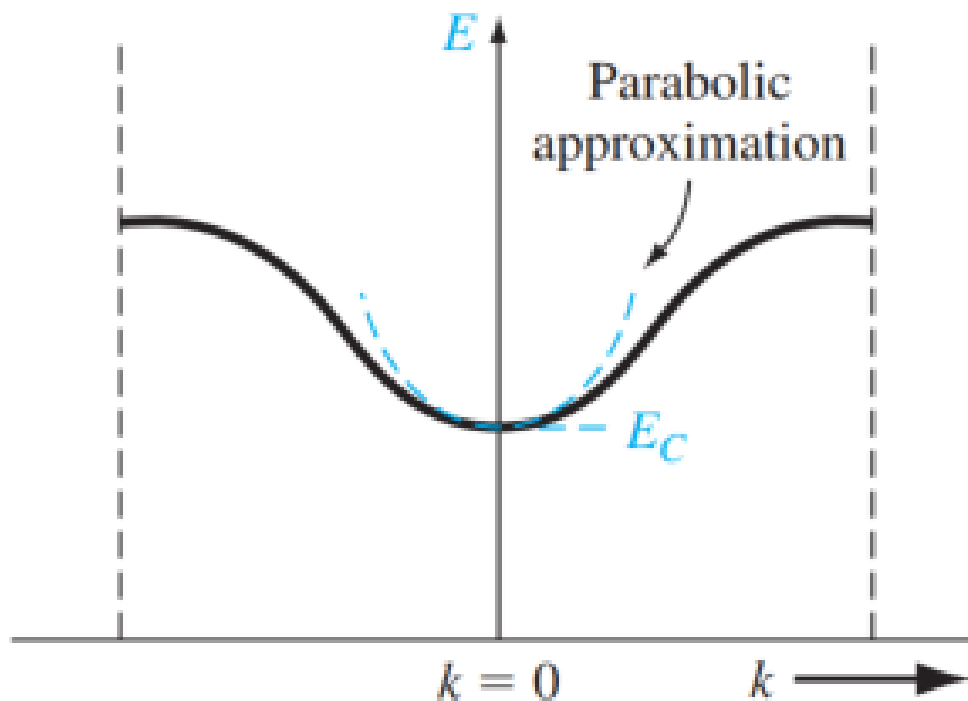


$$E = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2} (n_x^2 + n_y^2 + n_z^2)$$

$$E = \frac{\hbar^2 k^2}{2m_0}$$

傳導帶中電子的 E-K diagram

在 $k=0$ 的位置附近，可以近似成一個拋物線，也就是可以視為自由電子

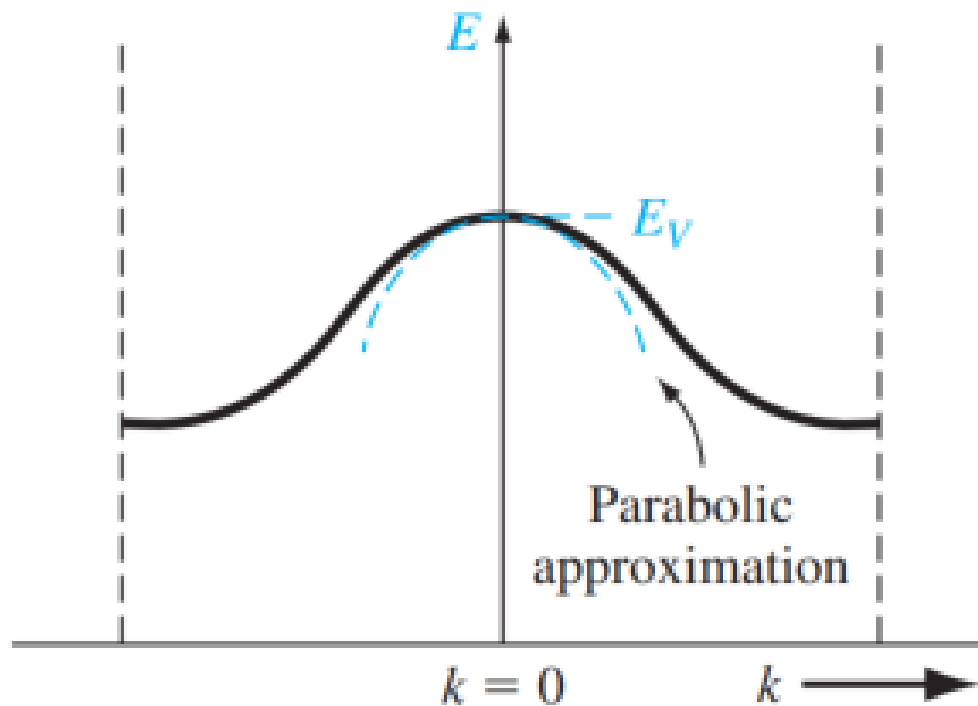


$$E - E_c = \frac{\hbar^2 k^2}{2m_n^*}$$

自由電子等效質量

價帶中電子的 E-K diagram

在 $k=0$ 的位置附近，可以近似成一個拋物線，也就是可以視為自由電子

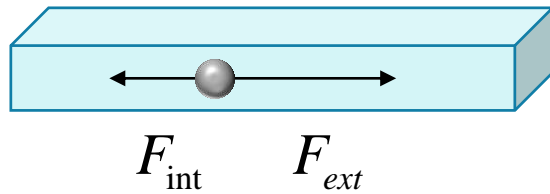


$$E_v - E = \frac{\hbar^2 k^2}{2m_p^*}$$

↓
電洞等效質量

等效質量 Effective Mass

- 在晶體中運動的電子和自由電子不一樣，受到晶體內部的阻力。
- 實際上很難估算內部阻力，於是定義當電子受到外力時，電子的等效質量即為施加外力與加速度的比值。
- 等效質量是由實驗測量得到。



$$F_{\text{total}} = F_{\text{ext}} + F_{\text{int}} = ma \quad \text{真實質量}$$

$$F_{\text{ext}} = m^* a \quad \text{等效質量}$$

	$N_c \text{ (cm}^{-3}\text{)}$	$N_v \text{ (cm}^{-3}\text{)}$	m_n^*/m_0	m_p^*/m_0
Silicon	2.8×10^{19}	1.04×10^{19}	1.08	0.56
Gallium arsenide	4.7×10^{17}	7.0×10^{18}	0.067	0.48
Germanium	1.04×10^{19}	6.0×10^{18}	0.55	0.37

晶體中電子的狀態密度 (DoS)

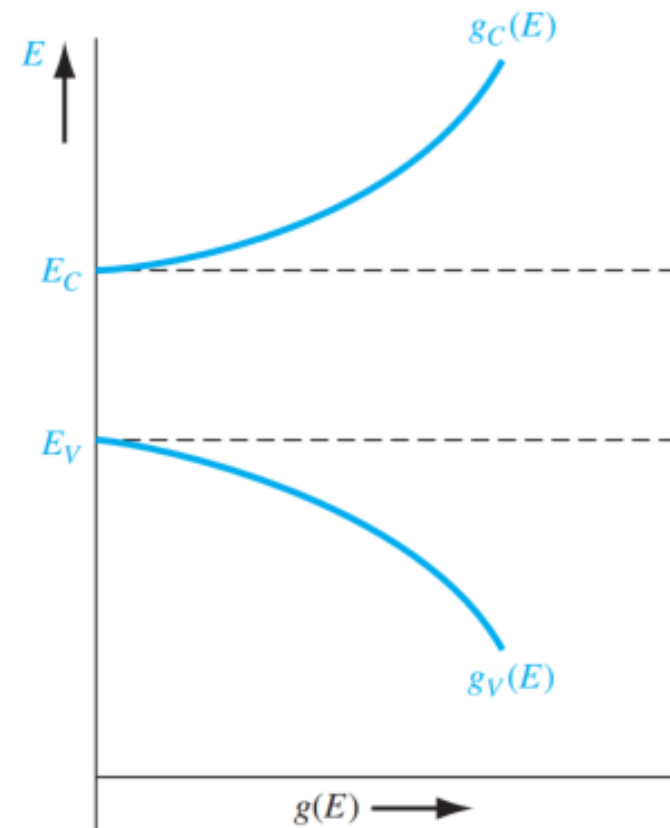
自由電子(無限位能井)

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow g(E) = \frac{4\pi(2m)^{3/2}}{h^3} \sqrt{E}$$

近似自由電子

$$E - E_c = \frac{\hbar^2 k^2}{2m_n^*} \Rightarrow g(E) = \frac{4\pi(2m_n^*)^{3/2}}{h^3} \sqrt{E - E_c}$$

$$E_v - E = \frac{\hbar^2 k^2}{2m_p^*} \Rightarrow g(E) = \frac{4\pi(2m_p^*)^{3/2}}{h^3} \sqrt{E_v - E}$$



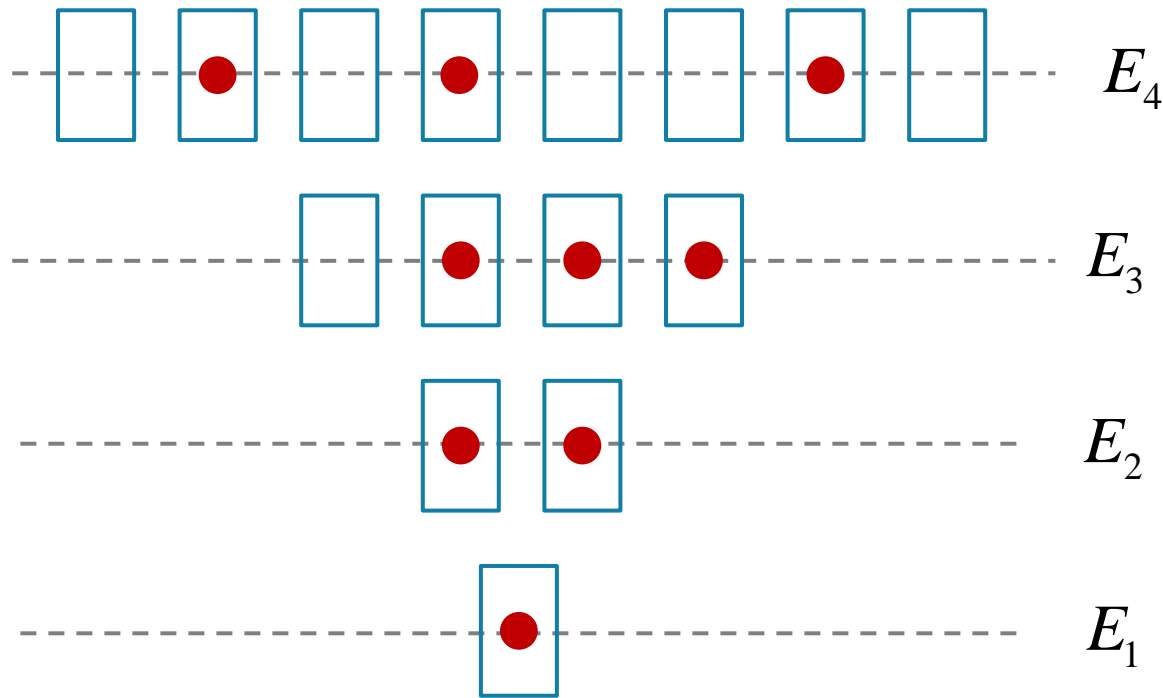
統計分佈函數

三種統計分佈，用以決定某個狀態被佔據的機率

Maxwell-Boltzmann	Fermi-Dirac	Bose-Einstein
允許多個粒子 擁有相同狀態	不允許多個粒子 擁有相同狀態	允許多個粒子 擁有相同狀態
古典粒子 Ex: 理想氣體	費米子 Ex: 電子	波色子 Ex: 光子
$f(E) = \exp\left(-\frac{E}{kT}\right)$	$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{kT}\right) + 1}$	$f(E) = \frac{1}{\exp\left(\frac{E}{kT}\right) - 1}$

費米－狄拉克機率分布函數

在能量 E 和溫度 T 時，有多少比例的量子態被填滿



$$f_F(E) = \frac{N}{g}$$

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

N: 幾個盒子被填滿

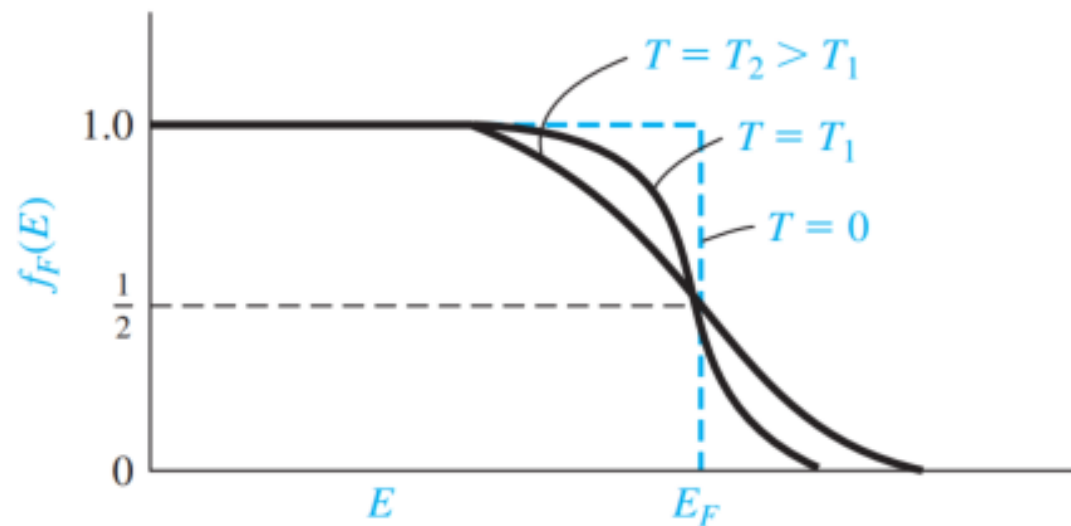
g: 總共幾個盒子

費米能量 Fermi Energy

當 $T > 0 \text{ K}$ 時，費米能階上的量子態恰好有一半被填滿。(k 波茲曼常數)

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

$$f_F(E = E_F) = \frac{1}{2}$$

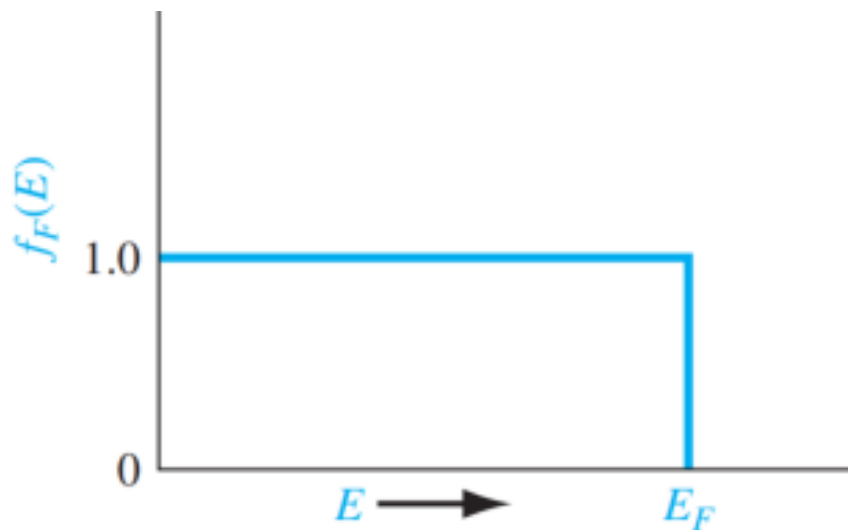


費米能量 Fermi Energy

當 $T = 0 \text{ K}$ 時，小於費米能階的每一層量子態均被填滿。(k 波茲曼常數)

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

$$\begin{cases} E < E_F & f_F(E) = \frac{1}{1 + \exp(-\infty)} = 1 \\ E > E_F & f_F(E) = \frac{1}{1 + \exp(\infty)} = 0 \end{cases}$$



Example 3.6

Objective: Calculate the probability that an energy state above E_F is occupied by an electron.

Let $T = 300$ K. Determine the probability that an energy level $3kT$ above the Fermi energy is occupied by an electron.

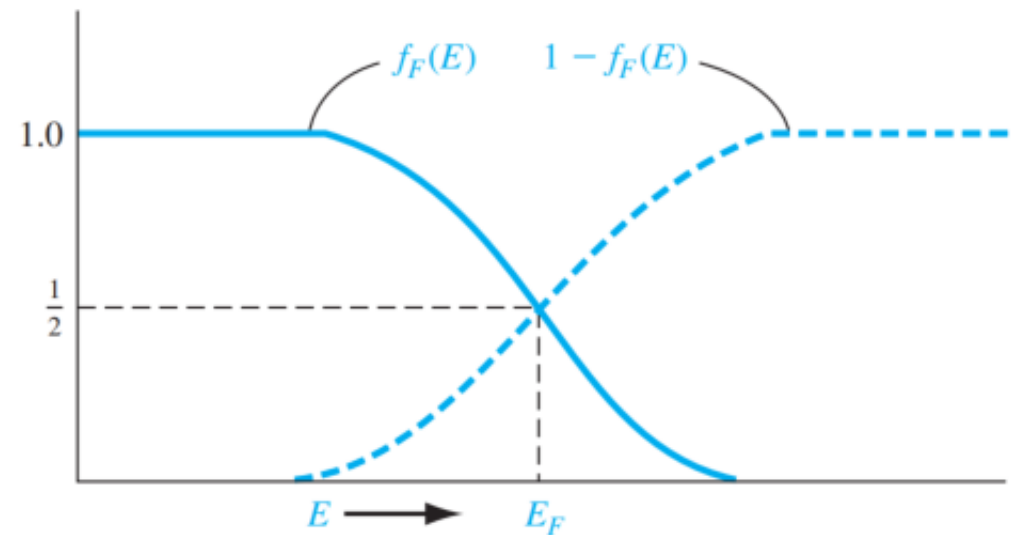
$$f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} = \frac{1}{1 + \exp\left(\frac{3kT}{kT}\right)} = \frac{1}{1 + 20.09} = 4.74\%$$

Example 3.7

Objective: Determine the temperature at which there is 1 percent probability that an energy state is empty.

Assume that the Fermi energy level for a particular material is 6.25 eV and that the electrons in this material follow the Fermi–Dirac distribution function. Calculate the temperature at which there is a 1 percent probability that a state 0.30 eV below the Fermi energy level will not contain an electron.

$$\begin{aligned} 0.01 &= 1 - \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} \\ \Rightarrow 0.99 &= \frac{1}{1 + \exp\left[\frac{-0.3}{0.0259(T / 300)}\right]} \\ \Rightarrow T &= 756K \end{aligned}$$



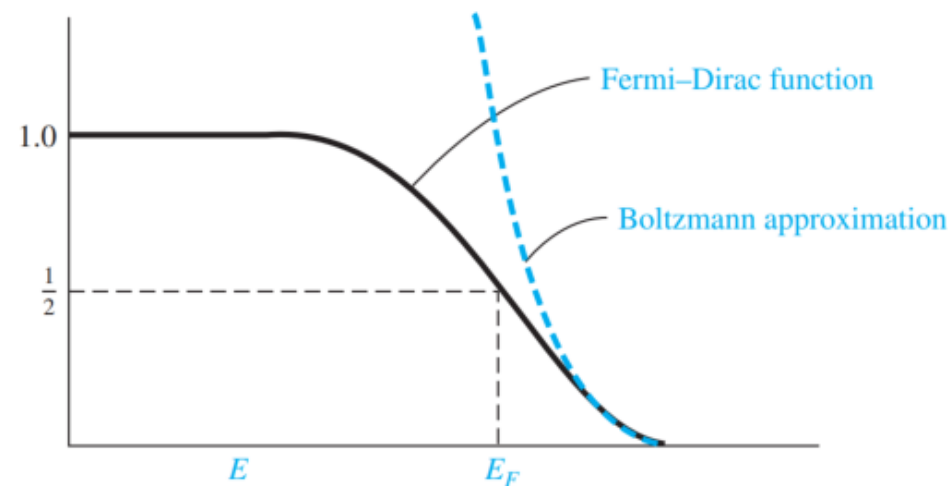
3kT 原則

- 當 $E - E_f > 3kT$ 時，費米狄拉克分佈可以被簡化為波茲曼分佈
- 誤差值小於 5 %。實際上，能量差值愈大，誤差愈小。
- 此近似是為了後續方便做積分運算

$$E - E_F = 3kT$$

$$f_F = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} = \frac{1}{1 + \exp(3)} = 0.04742$$

$$f_B = \exp\left(-\frac{E - E_F}{kT}\right) = \exp(-3) = 0.04978$$



$kT = \text{能量}$

$T = 300 \text{ K}$ 時 (常溫) :

$$1 \text{ eV (電子伏特)} = 1.6 \times 10^{-19} \text{ J (焦耳)}$$

$$kT = (1.38 \times 10^{-23})(300) \text{ J}$$

$$kT = \frac{(1.38 \times 10^{-23})(300)}{1.6 \times 10^{-19}} = 0.0259 \text{ eV}$$

$$T = 400 \text{ K 時} : 0.0259 \cdot \frac{400}{300} = 0.03453 \text{ eV}$$

Conclusion

- The concept of allowed and forbidden energy.
- Conduction band, valence band and bandgap.
- The concept of negatively charged electrons and positively charged holes.
- E-k curves in a single-crystal material
- The concept of direct and indirect bandgap semiconductor materials.
- The concept of effective mass of an electron and a hole.
- The density of quantum states in the allowed energy bands.
- The Fermi-Dirac probability function.
- The Fermi energy level.