

Stationary State in 1Dimension Periodic Potential

一維固態物理初步



發現

節目

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課程

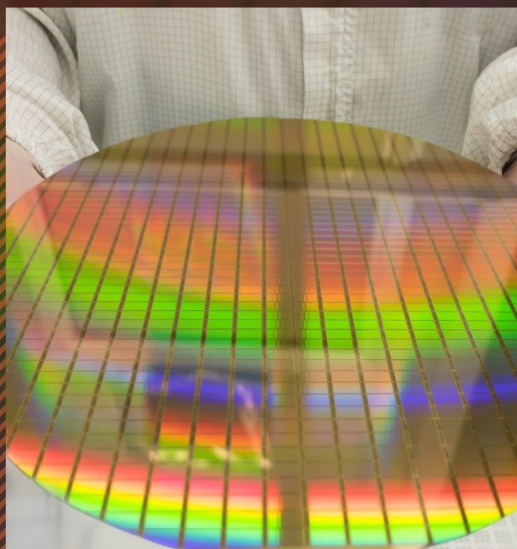
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節目 知識好好玩

EP08 | 台灣這美麗的矽島——聊 一聊半導體物理

主持人 | 張嘉泓

單曲長度 | 00:25:46 發布時間 | 2021-08-03

#科學

#張嘉泓

#物理好好玩

#晶圓

#半導體

#矽島

#台積電

#電洞

#自動計算機



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開始播放

固體是原子組成的晶格 Lattice

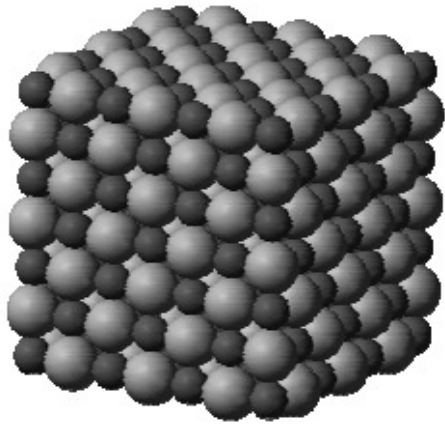
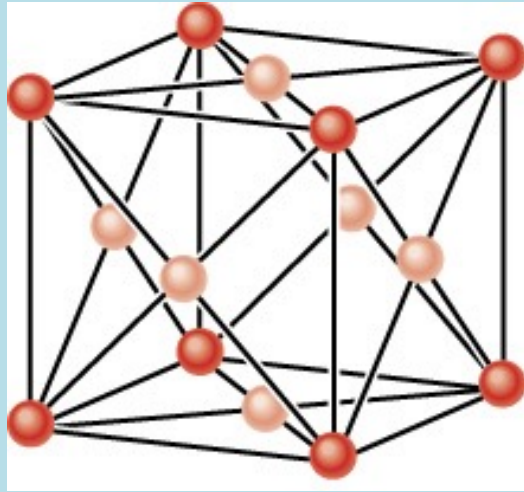
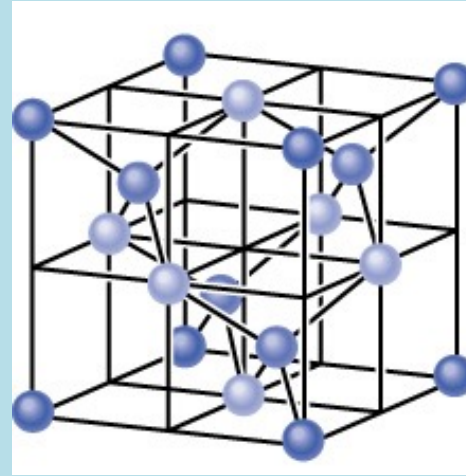


Fig. 7.1: **Left:** Small units reproduced periodically to form a crystal. This particular figure depicts NaCl (table salt), with the larger spheres being Cl^- ions and the smaller spheres being Na^+ ions. **Right:** The macroscopic morphology of a crystal often will reflect the underlying microscopic structure. These are large crystals of salt (also known as halite). Photograph by Piotr Włodarczyk, used by kind permission.

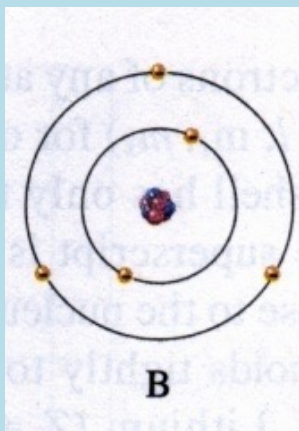
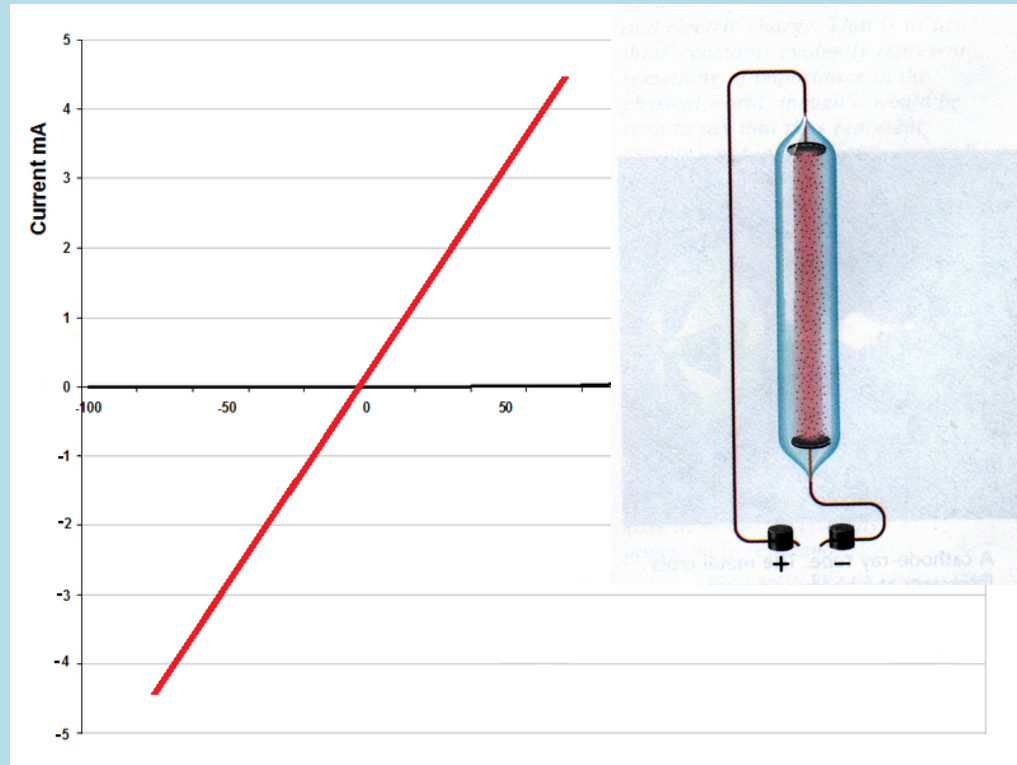
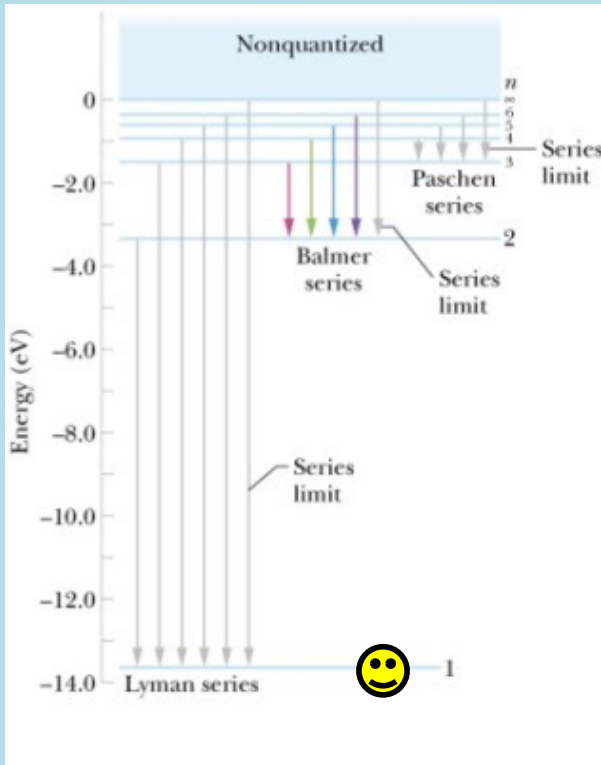
三維的晶體比較複雜，因此先從一維出發！



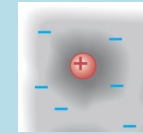
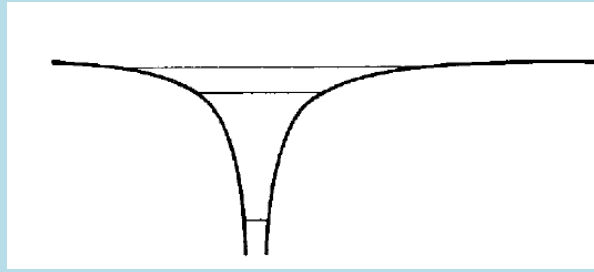
Copper fcc



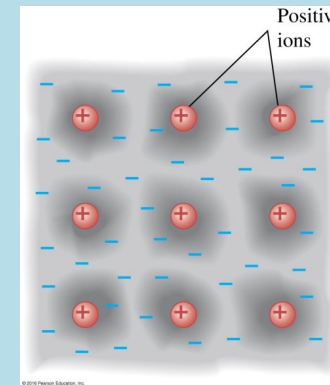
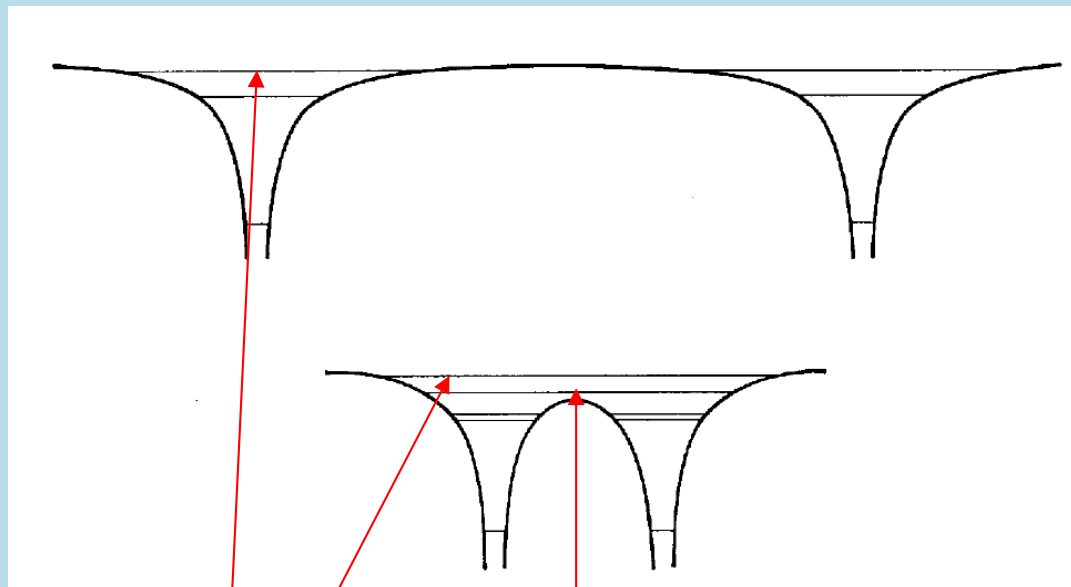
Silicon and Carbon



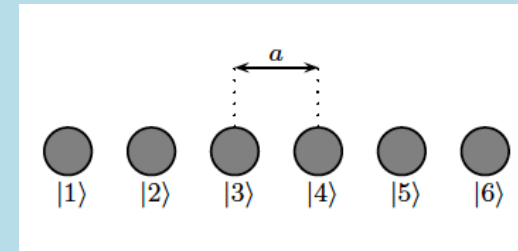
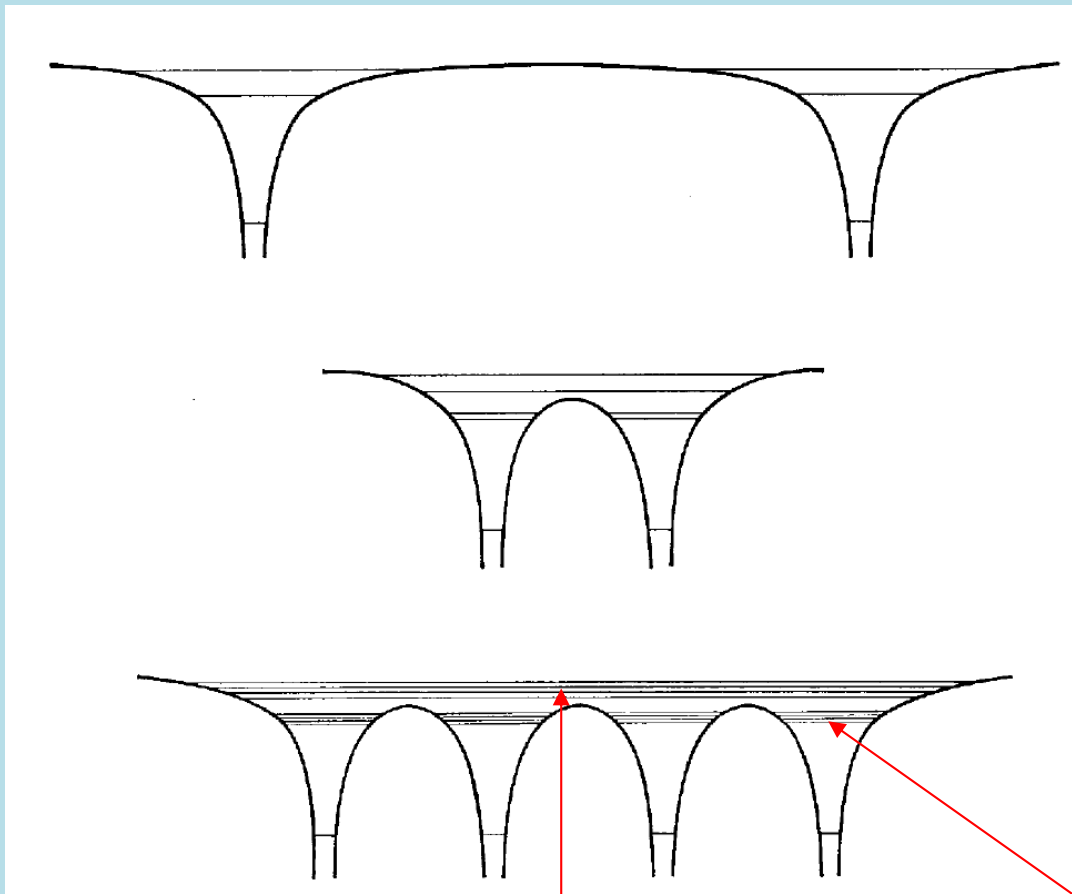
在原子中，電子被束縛在原子核旁邊。能量呈現能階的形式。要讓原來處於基態的電子離開原子核，至少需要13伏特的電壓。這對氣態的原子的確是對的！稱為氣體放電。但在固態導體中，顯然很小的電壓就能產生電流。歐姆定律。導體內為何有機動的mobile電荷可以自由流動？絕緣體內為何又沒有電荷可以流動呢？



在獨立的原子中，位能為庫倫位能，電子處於分離的態。
 當原子彼此靠近時，鄰近原子核的庫倫位能也必須考慮，
 也就是，電子會同時感覺多個原子核的電力。



原子間的庫倫電位能疊加後會下降，
 能量比較高的態，就可能跨越原子間的位能。



這些原來屬於私人的電子現在是**公共財產**！其餘電子還是束縛在單一原子內。

電子多多少少分成 **Localized**與**Globalized**兩種！

Globalized的電子會受到所有原子影響！波函數會分布於所有原子間整個固體內。

感受到的位能應該會是如晶格般、週期性的。這件事竟完全改變了電子的樣貌！

週期性晶格位能是電子機動性的關鍵原因。

Supplement 4-C

Periodic Potentials

Metals generally have a crystalline structure; that is, the ions are arranged in a way that exhibits a spatial periodicity. In our one-dimensional discussion of this topic, we will see that this periodicity has two effects on the motion of the free electrons in the metal. One is that for a perfect *lattice*—that is, for ions spaced equally—the *electron propagates without reflection*; the other is that there are restrictions on the energies allowed for the electrons; that is, *there are allowed and forbidden energy “bands.”*

We begin with a discussion of the consequences of perfect periodicity.

The periodicity will be built into the potential, for which we require that

$$V(x + a) = V(x) \quad (4C-1)$$

若是完美的晶格，這樣的電子不會被反彈，而且自由自在。

晶格些許的不完美，可以視為雜質。

這樣的全球化電子的容許能量落在一道道連續的能帶 band。

真實可解的Dirac梳週期性位能

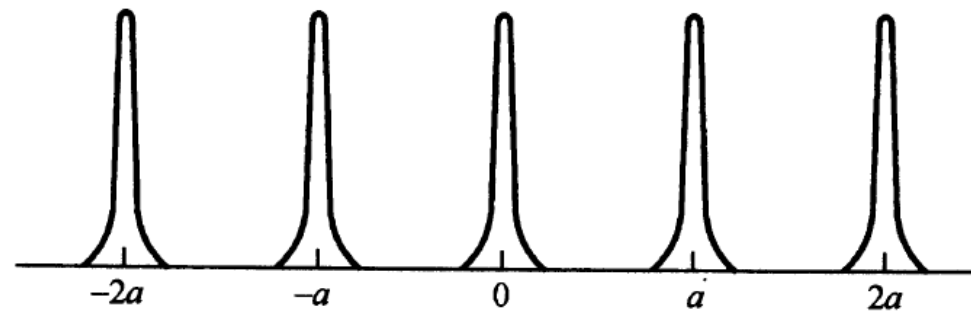
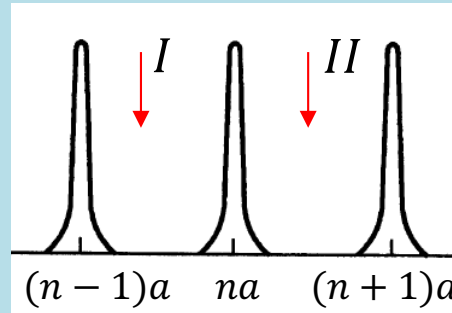


图 3.33 Dirac 梳

Dirac Comb



這個模型可解的關鍵：在delta函數間，位能為零，其解就是自由電子平面波。

Away from the points $x = na$, the solution will be that of the free-particle equation—that is, some linear combination of $\sin kx$ and $\cos kx$ (we deal with real functions for simplicity). Let us assume that in the region R_n defined by $(n - 1) a \leq x \leq na$, we have

$$\psi(x) = A_n \sin k(x - na) + B_n \cos k(x - na) \quad I$$

$$k = \frac{\sqrt{2mE}}{\hbar}$$

and in the region R_{n+1} defined by $na \leq x \leq (n + 1) a$ we have

$$\psi(x) = A_{n+1} \sin k[x - (n + 1) a] + B_{n+1} \cos k[x - (n + 1) a] \quad II$$

只要仔細納入連續條件即可。

請注意這些定態解除了Delta函數的位置之外，都是自由電子平面波。

換言之，都是Globalized的電子，波函數會分布於所有原子間整個固體內。

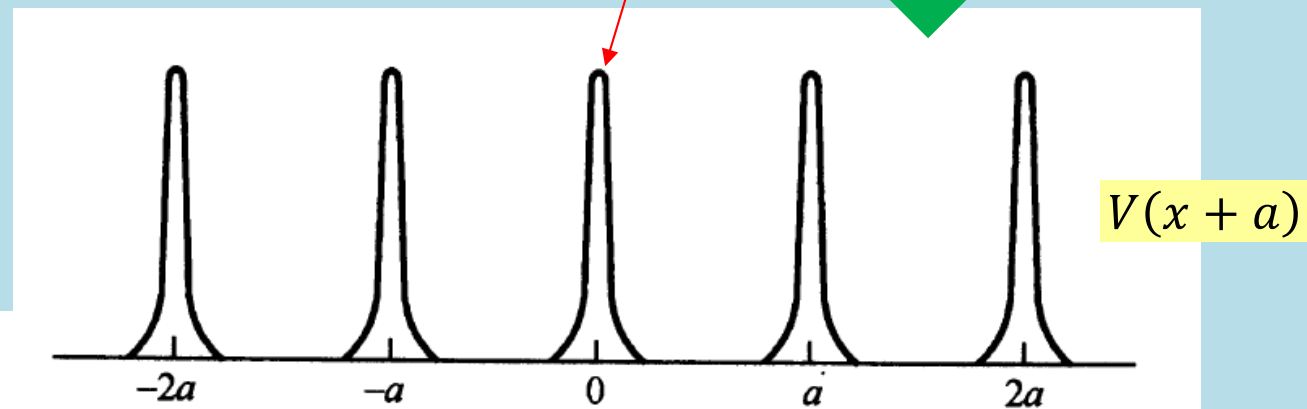
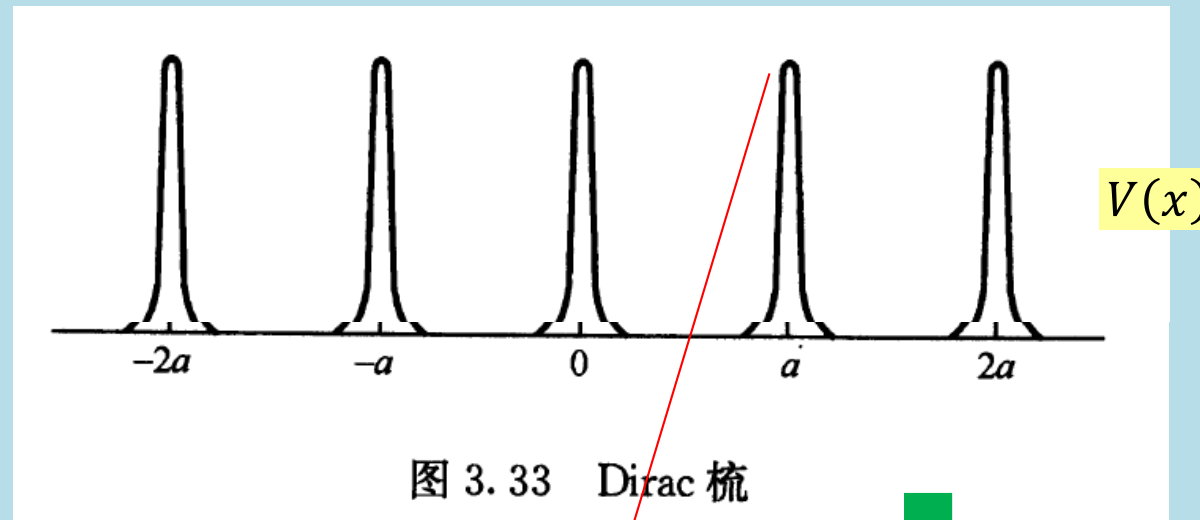
週期位能： $V(x + a) = V(x)$

將 $x + a$ 代入函數的 x ，等於把函數圖形向左移 a ，這稱為平移。

看移動後的原點，函數值來自之前的 $x = a$ 。

補充教材

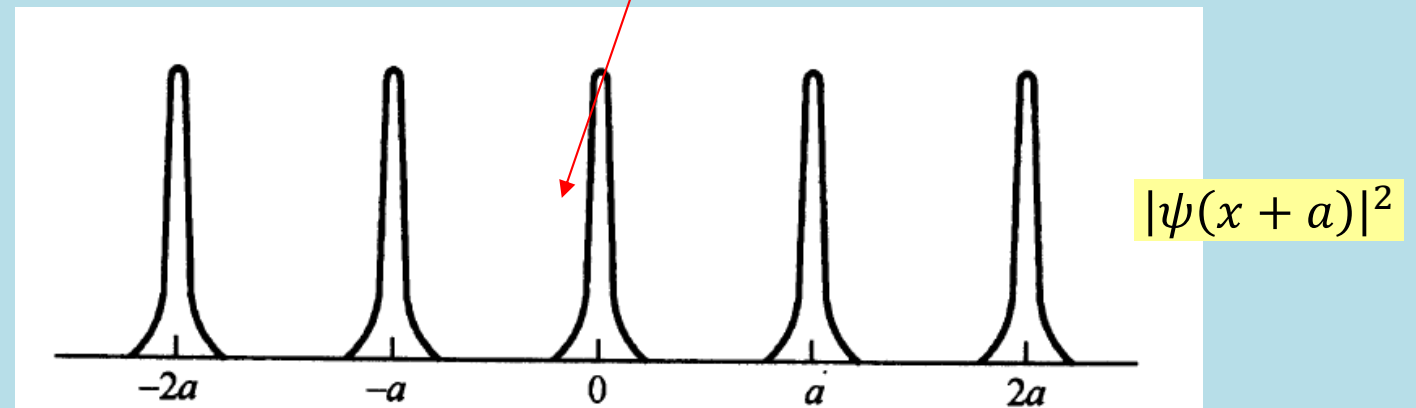
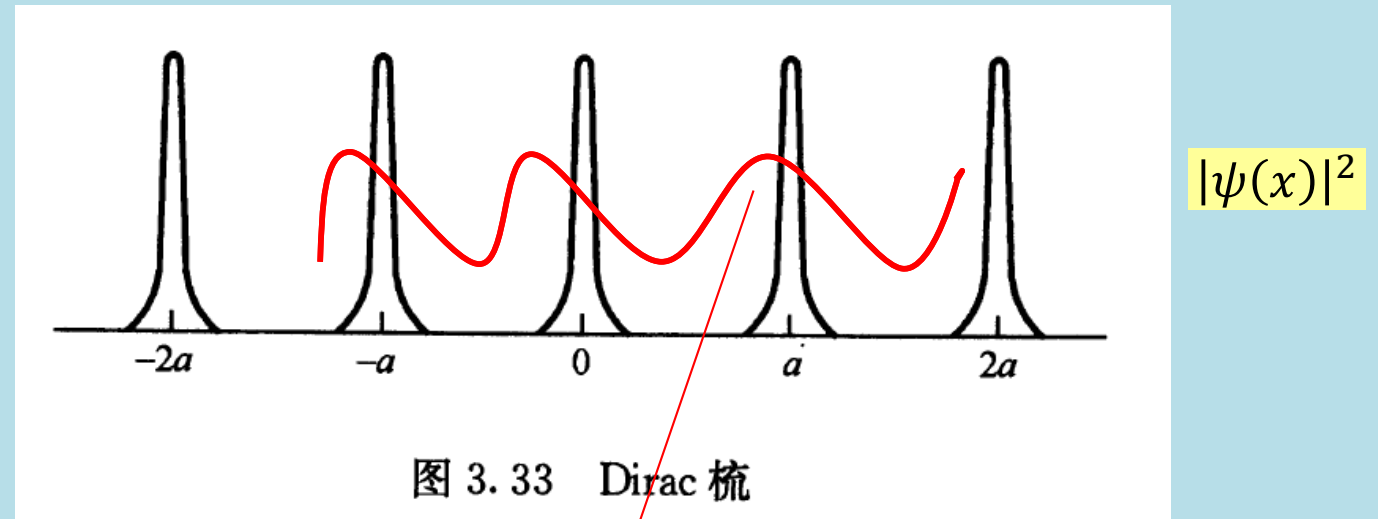
週期位能平移前與平移後完全沒有差別：

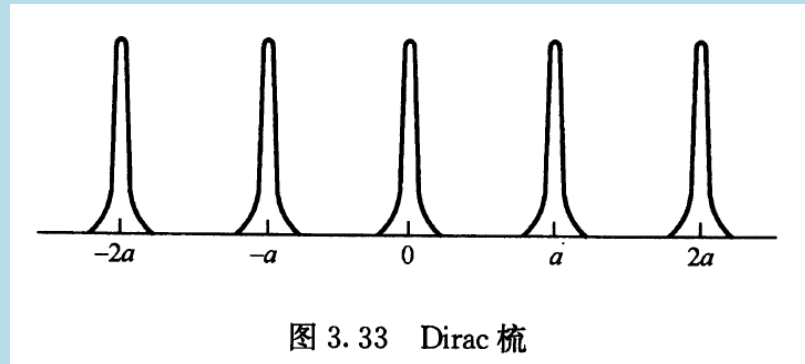


週期位能： $V(x + a) = V(x)$

在週期位能下，我們也期待它的定態滿足各處絕對值平移不變：

$$|\psi(x + a)|^2 = |\psi(x)|^2$$





在週期位能下，我們也期待它的定態滿足各處絕對值平移不變：

$$|\psi(x + a)|^2 = |\psi(x)|^2$$

波函數本身 $\psi(x + a)$ 與 $\psi(x)$ 不定要一樣，

但 $\psi(x)$ 是能量本徵態，平移後 $\psi(x + a)$ 物理測量不變，

平移後波函數 $\psi(x + a)$ 應該也是同樣本徵值的能量本徵態。

如果能量本徵態沒有簡併，一個本徵值只有一個本徵態。

如此 $\psi(x + a)$ 與 $\psi(x)$ 只能相差一個相角：

$$\psi(x + a) = e^{-iqa} \psi(x)$$

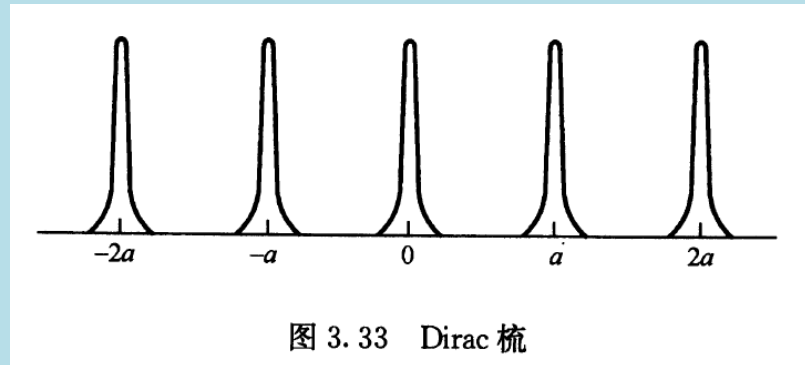


图 3.33 Dirac 梳

在週期位能下，我們也期待它的定態滿足各處絕對值平移不變：

$$|\psi(x + a)|^2 = |\psi(x)|^2$$

如此 $\psi(x + a)$ 與 $\psi(x)$ 絕對值在各處相等，那就只能相差一個相角：

$$\psi(x + a) = e^{-iqa} \psi(x)$$

Hamiltonian under a displacement $x \rightarrow x + a$ can be treated formally as follows. Let D_a be an operator whose rule of operation is that

$$D_a f(x) = f(x + a) \quad (4C-5)$$

The invariance implies that

$$[H, D_a] = 0 \quad (4C-6)$$

We can find the eigenvalues of this operator by noting that

$$D_a \psi(x) = \lambda_a \psi(x) \quad (4C-7)$$

together with

$$D_{-a} D_a f(x) = D_a D_{-a} f(x) = f(x) \quad (4C-8)$$

implies that $\lambda_a \lambda_{-a} = 1$. This then implies that λ_a must be of the form e^{iqa} . Here q must be

已知 $\psi(x + a)$ 與 $\psi(x)$ 只能相差一個相角：

$$\psi(x + a) = e^{iqa} \psi(x)$$

如此：我們可以引進一個函數 $u(x)$ ：

補充教材

$$u(x) = e^{-iqx} \psi(x)$$

則 $u(x)$ 在平移下是不變的，或稱空間的週期函數：

$$u(x + a) = e^{-iq(x+a)} \psi(x + a) = e^{-iqx} e^{-iqa} e^{iqa} \psi(x) = e^{-iqx} \psi(x) = u(x)$$

因此定態波函數一定可以寫成一個虛數指數函數乘一個平移不變函數！

$$\psi(x) = e^{iqx} u(x)$$

此虛數指數函數有一角波數 q 待解！但並不是整個波函數的角波數！

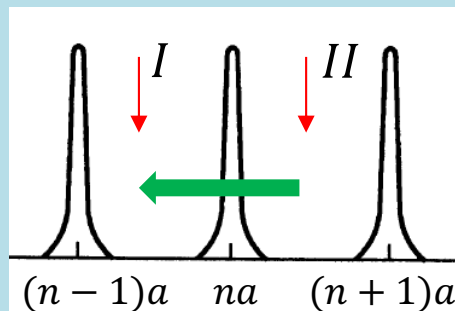
這樣的函數稱為 **Block Function**。自然滿足：

$$|\psi(x + a)|^2 = |\psi(x)|^2$$

固態物理之父 Bloch



Dirac Comb



$(n + 1)a$

補充教材

Away from the points $x = na$, the solution will be that of the free-particle equation—that is, some linear combination of $\sin kx$ and $\cos kx$ (we deal with real functions for simplicity). Let us assume that in the region R_n defined by $(n - 1) a \leq x \leq na$, we have

$$\psi(x) = A_n \sin k(x - na) + B_n \cos k(x - na) \quad I \quad (4C-22)$$

$$k = \frac{\sqrt{2mE}}{\hbar}$$

and in the region R_{n+1} defined by $na \leq x \leq (n + 1) a$ we have

$$\psi(x) = A_{n+1} \sin k[x - (n + 1) a] + B_{n+1} \cos k[x - (n + 1) a] \quad II \quad (4C-23)$$

4C-22式可以寫成，注意 a 可以消掉。

$$\psi(x) = A_n \sin[k(x + a) - (n + 1)a] + B_n \cos[k(x + a) - (n + 1)a] \quad x \text{在第一區}$$

根據Bloch定理： $\psi(x + a) = e^{-iqa}\psi(x)$

$$e^{-iqa}\psi(x) = e^{-iqa} A_n \sin[k(x + a) - (n + 1)a] + e^{-iqa} B_n \cos[k(x + a) - (n + 1)a]$$

此式，必須等於 $\psi(x + a)$ ，即4C-23以 $x + a$ 代入：

$$\psi(x + a) = A_{n+1} \sin[k(x + a) - (n + 1)a] + B_{n+1} \cos[k(x + a) - (n + 1)a]$$

比較兩式得到：

$$\begin{aligned} A_{n+1} &= e^{iqa} A_n \\ B_{n+1} &= e^{iqa} B_n \end{aligned}$$

$$\psi(x) = A_n \sin k(x - na) + B_n \cos k(x - na) \quad (4C-22)$$

and in the region R_{n+1} defined by $na \leq x \leq (n + 1) a$ we have

$$\psi(x) = A_{n+1} \sin k[x - (n + 1) a] + B_{n+1} \cos k[x - (n + 1) a] \quad (4C-23)$$

Continuity of the wave function implies that ($x = na$)

補充教材

$$-A_{n+1} \sin ka + B_{n+1} \cos ka = B_n \quad (4C-24)$$

$$\begin{aligned} \left(\frac{du}{dx}\right)_\varepsilon - \left(\frac{du}{dx}\right)_{-\varepsilon} &= \int_{-\varepsilon}^{\varepsilon} dx \frac{d}{dx} \frac{du}{dx} \\ &= \int_{-\varepsilon}^{\varepsilon} dx \frac{2m}{\hbar^2} [V(x) - E] u(x) = 0 \end{aligned} \quad (4-12)$$

We note, for future reference, that if the potential contains a term like $\lambda\delta(x - a)$, then integration of the equation from $a - \varepsilon$ to $a + \varepsilon$ gives

$$\begin{aligned} \left(\frac{du}{dx}\right)_{a+\varepsilon} - \left(\frac{du}{dx}\right)_{a-\varepsilon} &= \frac{2m}{\hbar^2} \int_{a-\varepsilon}^{a+\varepsilon} dx \lambda\delta(x - a) u(x) \\ &= \frac{2m}{\hbar^2} \lambda u(a) \end{aligned} \quad (4-13)$$

and the discontinuity condition (4-68) here reads

$$kA_{n+1} \cos ka + kB_{n+1} \sin ka - kA_n = \frac{\lambda}{a} B_n \quad (4C-25)$$

A little manipulation yields

$$\begin{aligned} A_{n+1} &= A_n \cos ka + (g \cos ka - \sin ka) B_n \\ B_{n+1} &= (g \sin ka + \cos ka) B_n + A_n \sin ka \end{aligned} \quad (4C-26)$$

where $g = \lambda/ka$.

Continuity of the wave function implies that ($x = na$)

$$-A_{n+1} \sin ka + B_{n+1} \cos ka = B_n \quad (4C-24)$$

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where $g = \lambda/ka$.

$$\begin{aligned} A_{n+1} &= e^{iqa} A_n \\ B_{n+1} &= e^{iqa} B_n \end{aligned} \quad (4C-28)$$

When this is inserted into the (4C-26), that is, into the conditions that the wave equation obeys the Schrödinger equation with the delta function potential, we get

$$\begin{aligned} A_n(e^{iqa} - \cos ka) &= B_n(g \cos ka - \sin ka) \\ B_n(e^{iqa} - (g \sin ka + \cos ka)) &= A_n \sin ka \end{aligned} \quad (4C-29)$$

This leads to the condition

$$(e^{iqa} - \cos ka)(e^{iqa} - (g \sin ka + \cos ka)) = \sin ka(g \cos ka - \sin ka) \quad (4C-30)$$

This may be rewritten in the form

$$e^{2iqa} - 2(\cos ka + \frac{g}{2} \sin ka)e^{iqa} + 1 = 0 \quad (4C-31)$$

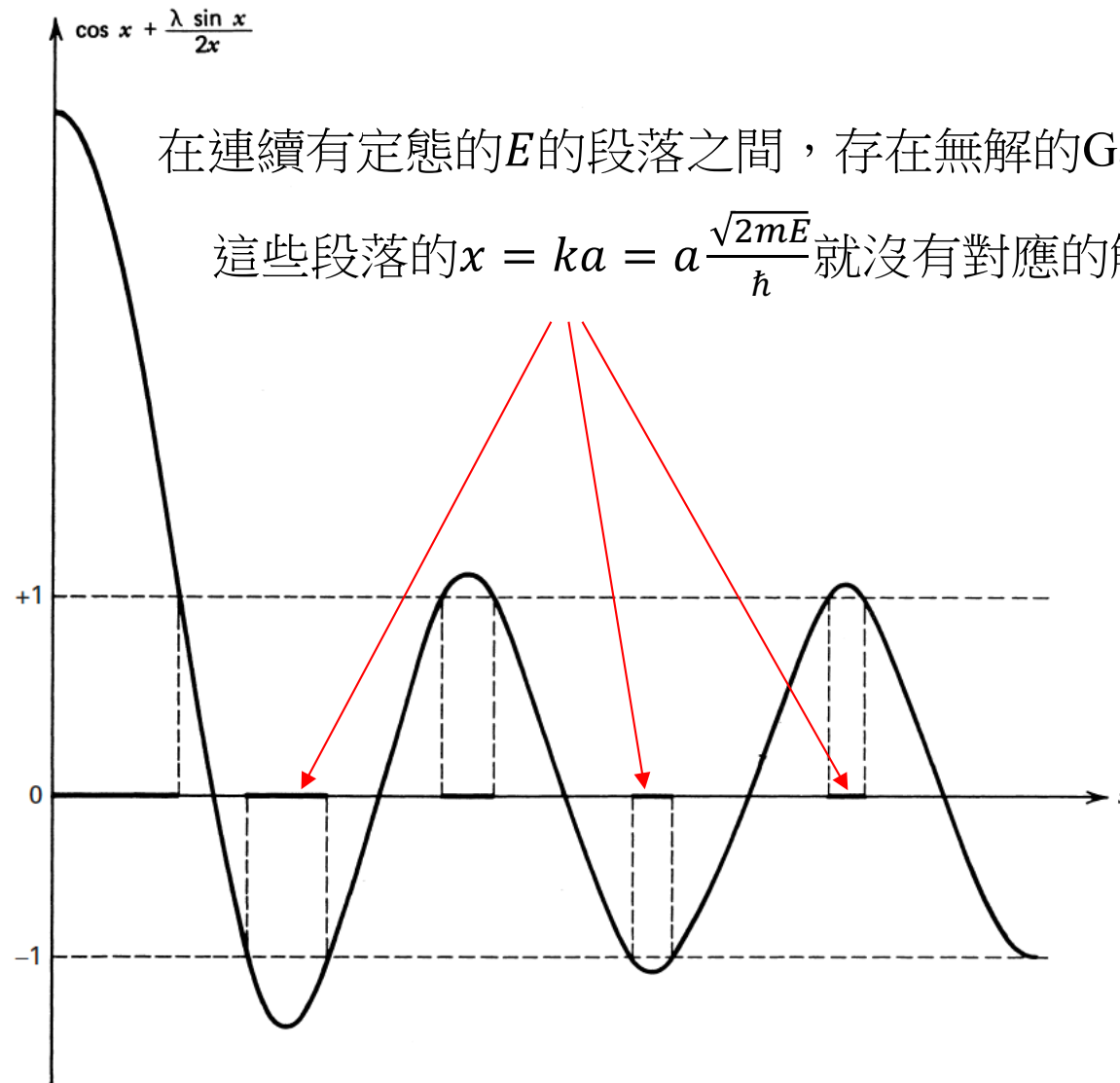
This quadratic equation can be solved, and both real and imaginary parts lead to the condition

$$\cos qa = \cos ka + \frac{\lambda}{2} \frac{\sin ka}{ka} \quad (4C-32)$$

補充教材

$$\cos qa = \cos ka + \frac{\lambda}{2} \frac{\sin ka}{ka}$$

此式有解的 $ka \sim \sqrt{E}$ 才對應有定態！
 左邊 $\cos qa$ 只能在 -1 與 1 之間！



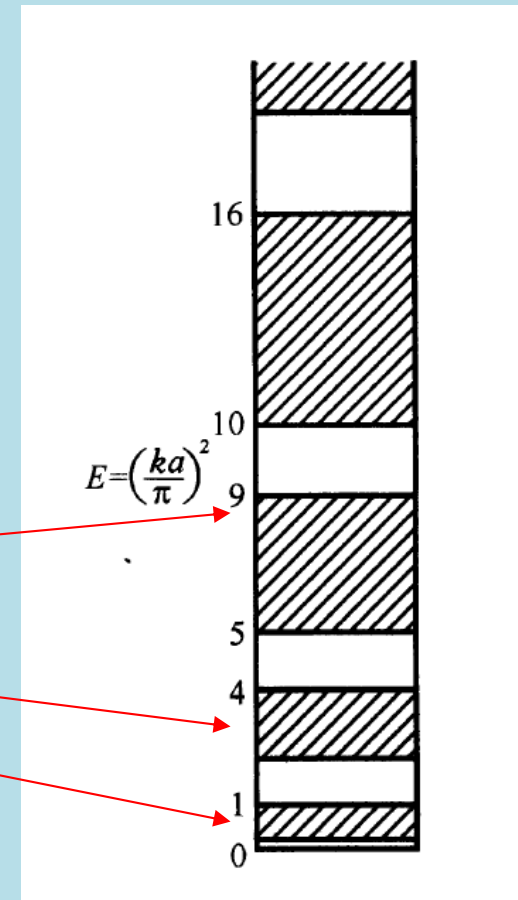
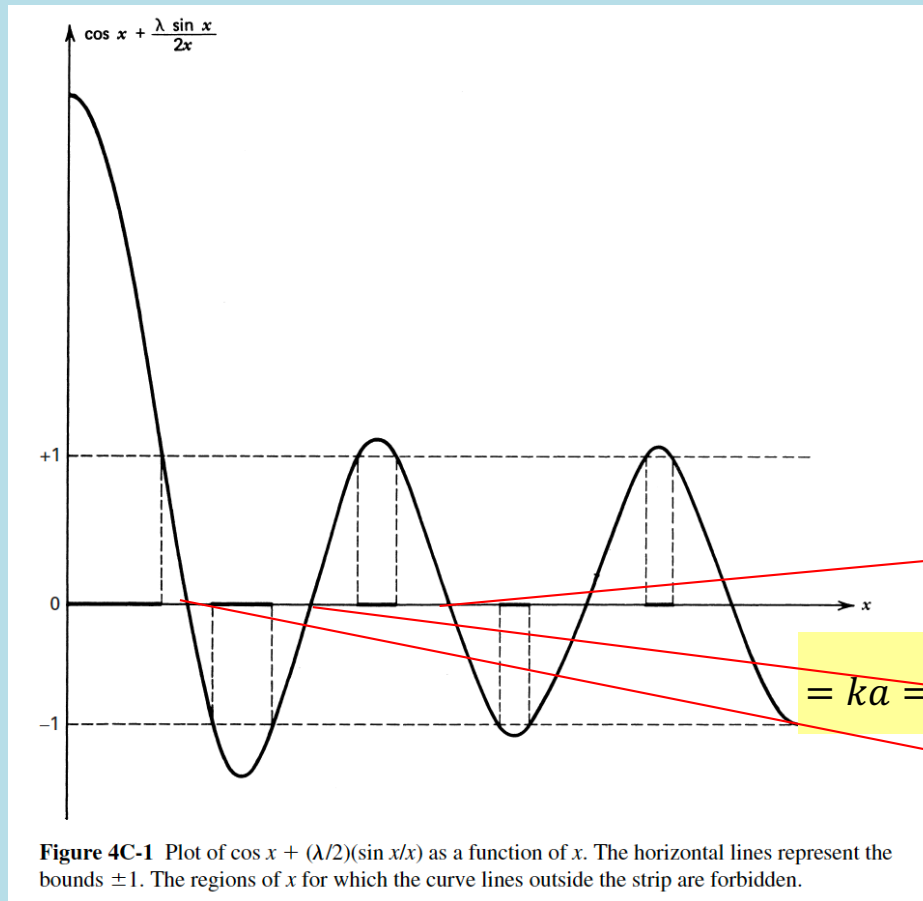
在連續有定態的 E 的段落之間，存在無解的 Gap!

這些段落的 $x = ka = a \frac{\sqrt{2mE}}{\hbar}$ 就沒有對應的解！

$$= ka = a \frac{\sqrt{2mE}}{\hbar}$$

Figure 4C-1 Plot of $\cos x + (\lambda/2)(\sin x/x)$ as a function of x . The horizontal lines represent the bounds ± 1 . The regions of x for which the curve lines outside the strip are forbidden.

把有解的 ka 對應的 E 收集起來，就得一系列有間隙Gap的能帶Band！



這是典型在週期性晶格位能下的電子能態分佈。

這樣的全球化電子的容許能量落在一道道連續的能帶 band。

這與真實可解的Dirac梳週期性位能非常類似！

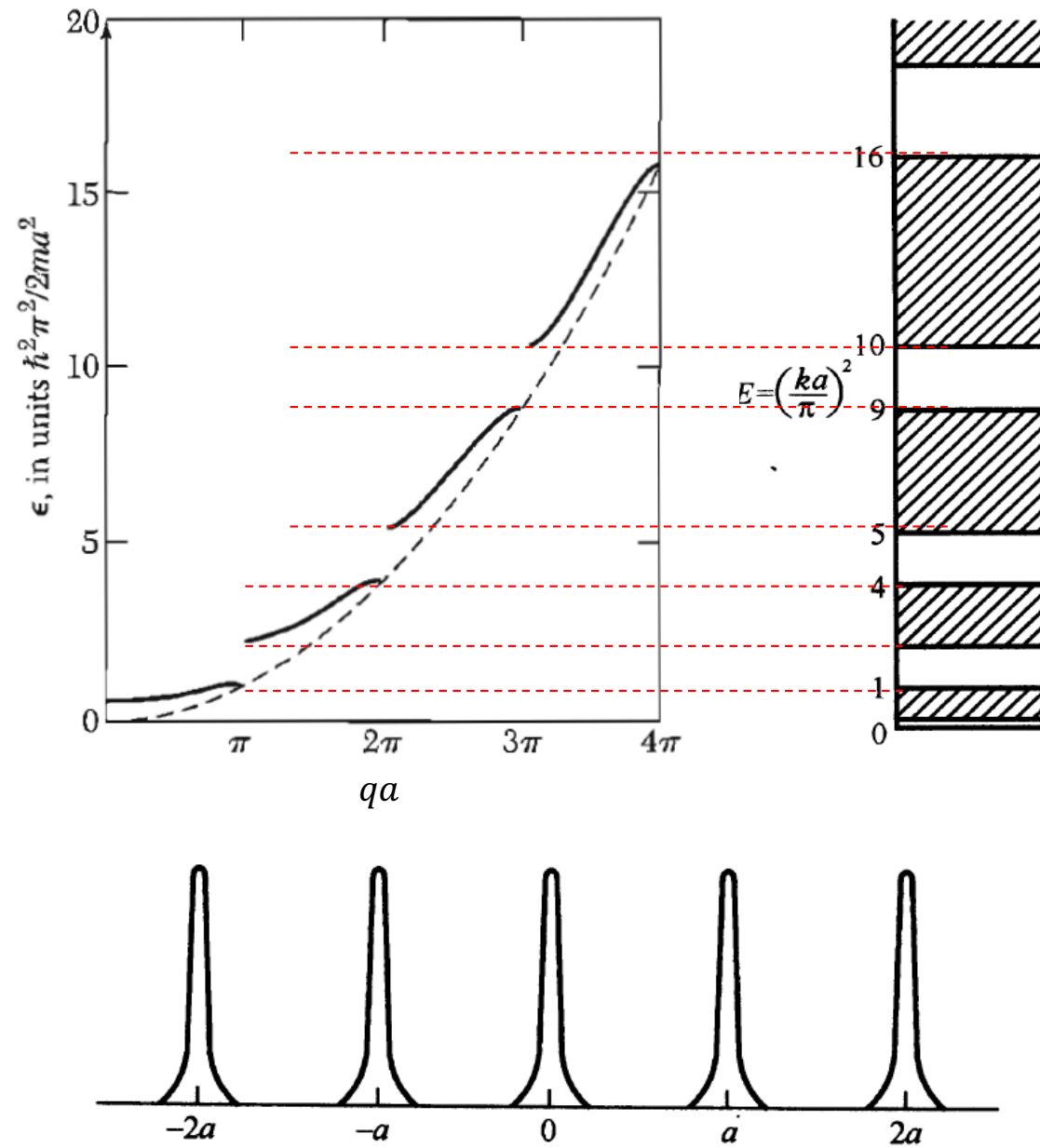
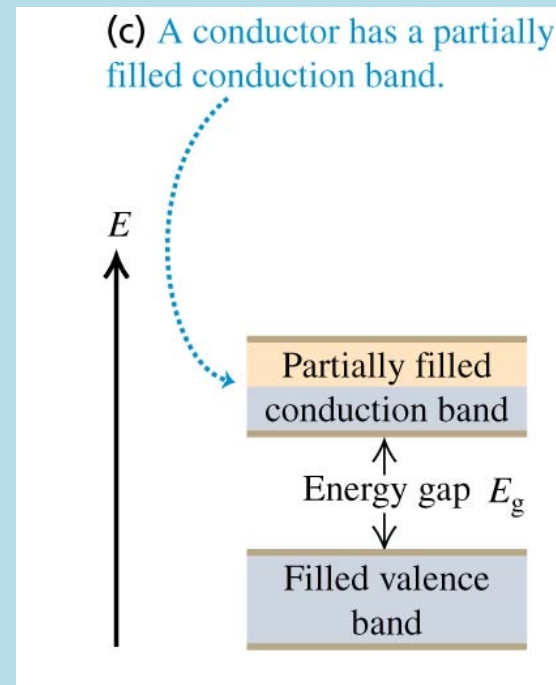
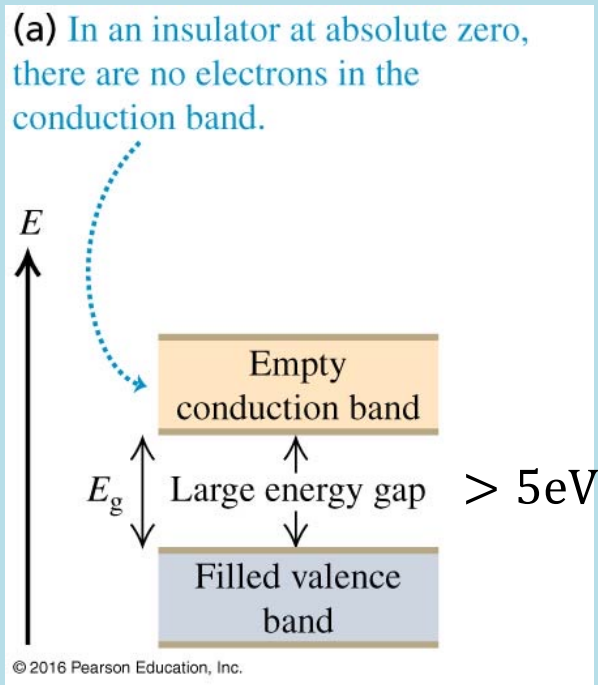
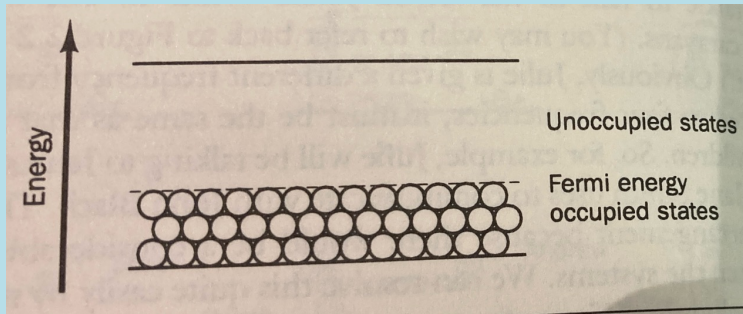


图 3.33 Dirac 梳

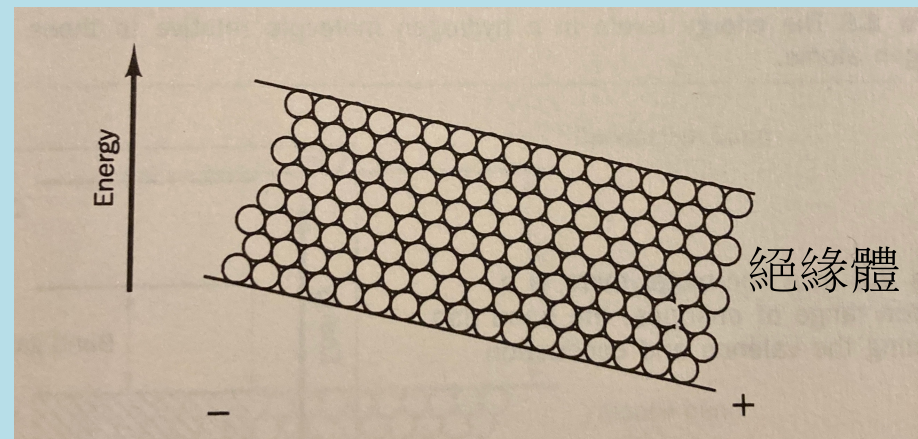
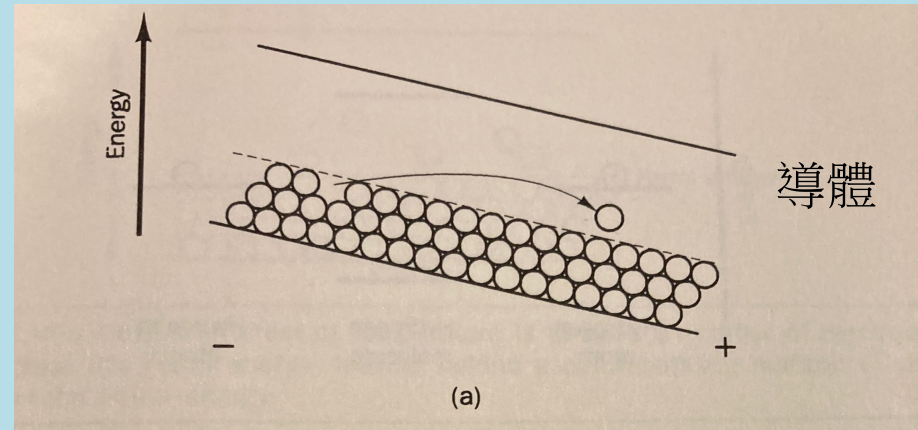
如果電子恰好填滿一個能帶（Valence），這些能帶中的電子無處可去！如同單一原子內的電子，需要很大能量才能克服間隙，改變狀態。如此電子即使不再被束縛於單一原子旁，但也不是機動的。這樣的固體無法導電，是絕緣體。



但如果電子未填滿能帶(稱Conduction)，未滿能帶內的電子很容易改變狀態。只要些許能量就能讓它激發到較高的能態。這些電子非常機動而自由，稱為導電電子。這樣的固體就可以導電，就是導體。於是連續卻有間隙的能帶energy band是固體導電性的關鍵。

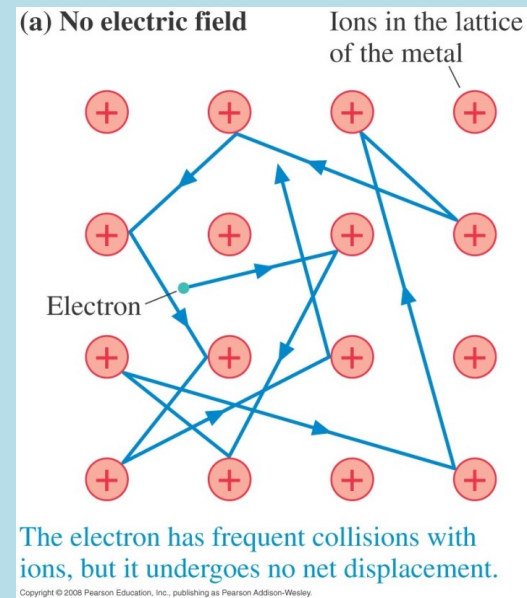
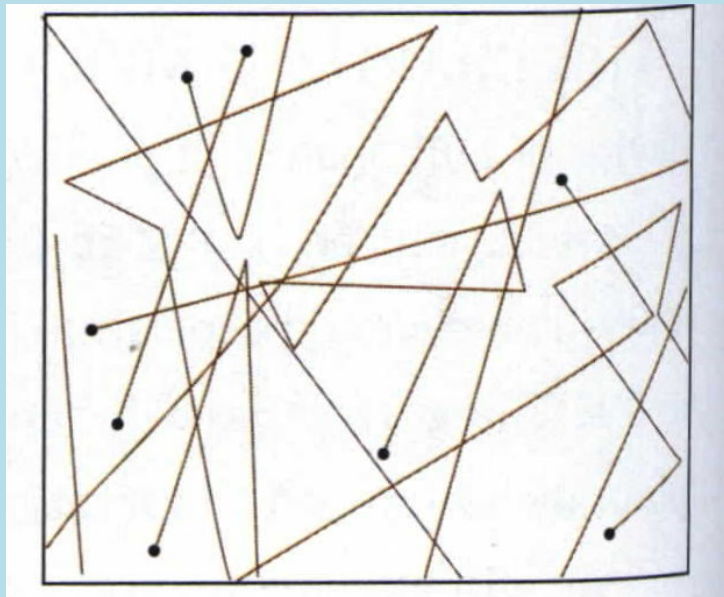


未加電壓



加電壓

自由電子模型



這就稱為**自由電子模型**。

電子在導體中是如氣體分子般混亂地運動！

有時又稱為**無相互作用的理想電子氣體**。

注意是週期分布的離子使電子如同自由一般，因此右圖本質上是錯的。

但電子在自由運動間，會與破壞週期性的雜質散射，猶如右圖中撞到離子一般。

Electrons in Metals: Drude Theory

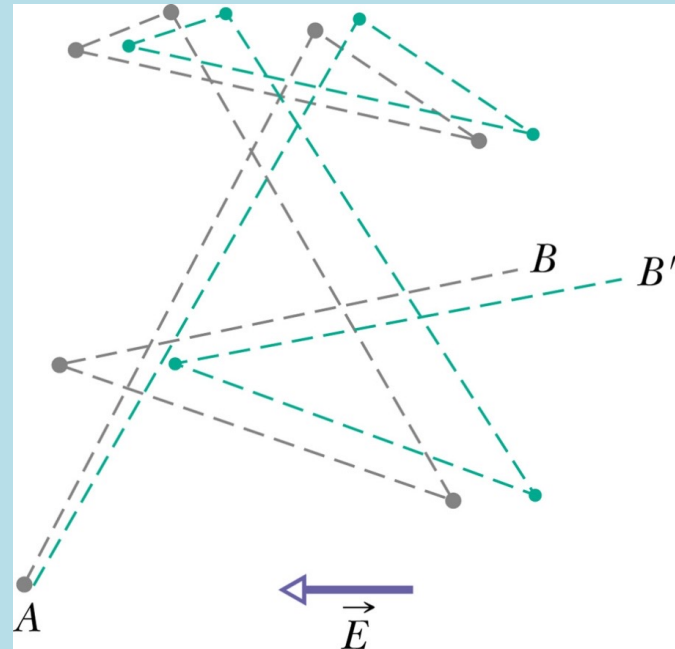
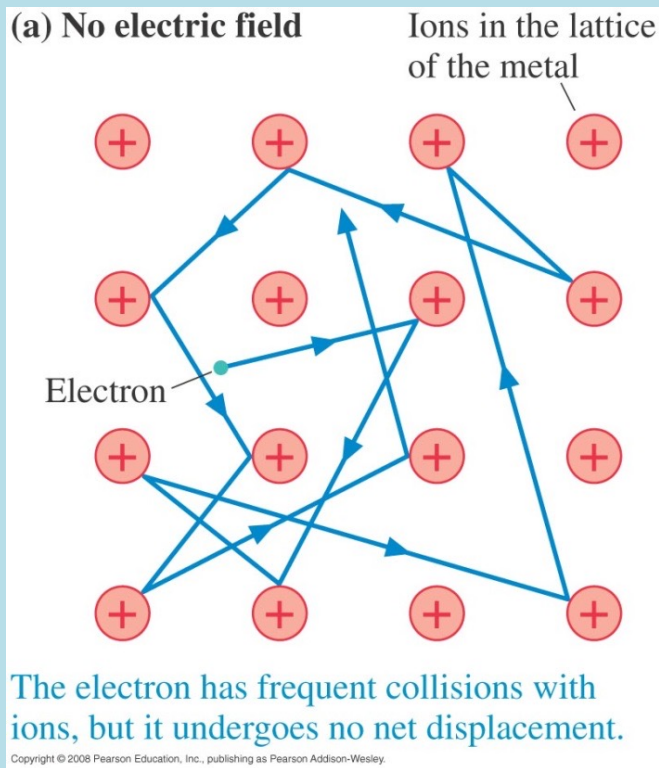
J.J. Thomson's 1896 discovery of the electron ("corpuscles of charge" that could be pulled out of metal) raised the question of how these charge carriers might move within the metal. In 1900 Paul Drude² realized that he could apply Boltzmann's kinetic theory of gases to understanding electron motion within metals. This theory was remarkably successful, providing a first understanding of metallic conduction.³

Having studied the kinetic theory of gases in previous courses, Drude theory should be very easy to understand. We will make three assumptions about the motion of electrons

- (1) Electrons have a scattering⁴ time τ . The probability of scattering within a time interval dt is dt/τ .
- (2) Once a scattering event occurs, we assume the electron returns to momentum $\mathbf{p} = 0$.
- (3) In between scattering events, the electrons, which are charge $-e$ particles, respond to the externally applied electric field \mathbf{E} and magnetic field \mathbf{B} .

The first two of these assumptions are exactly those made in the kinetic theory of gases.⁵ The third assumption is just a logical generalization to account for the fact that, unlike gas molecules, electrons are charged and must therefore respond to electromagnetic fields.





即使沒有外加電場，導體中電子也不是靜止不動的！

電子在導體中如氣體分子般混亂地移動！

但每一個電子的位移彼此無關，平均總位移為零！也就沒有電流。

若是加上一個電場，所有自由電子在同一方向會多一個位移！

電子平均總位移不為零！也就產生電流。

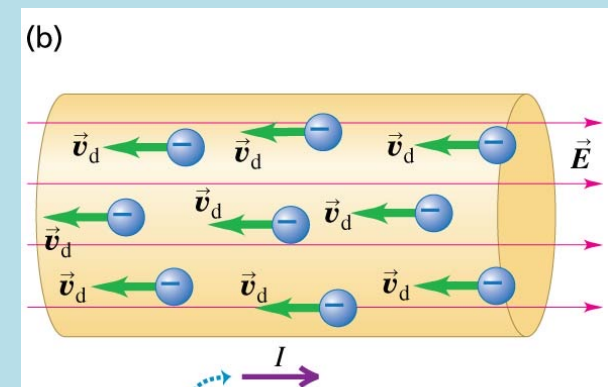
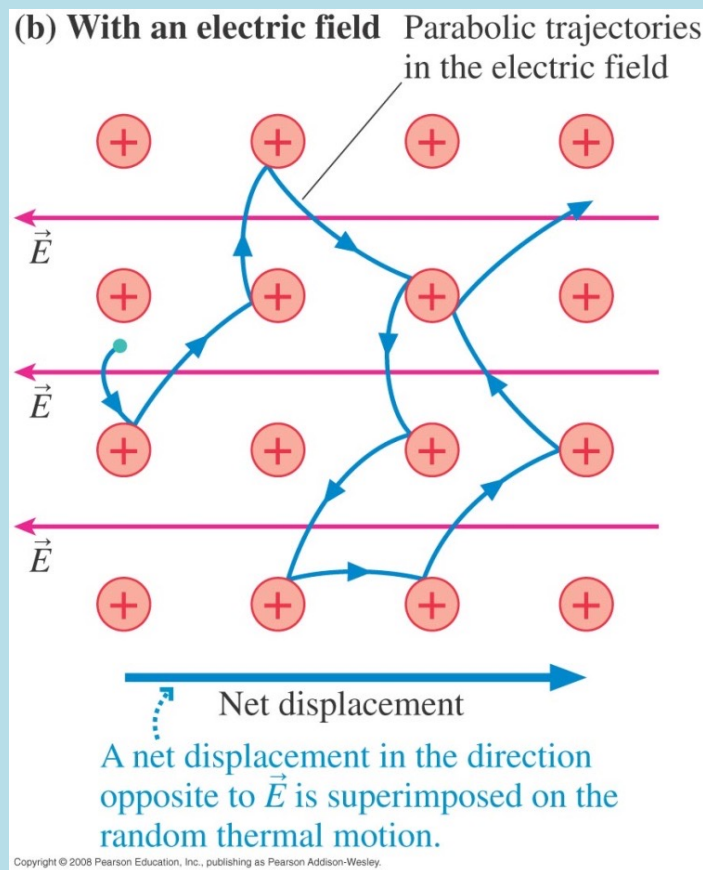
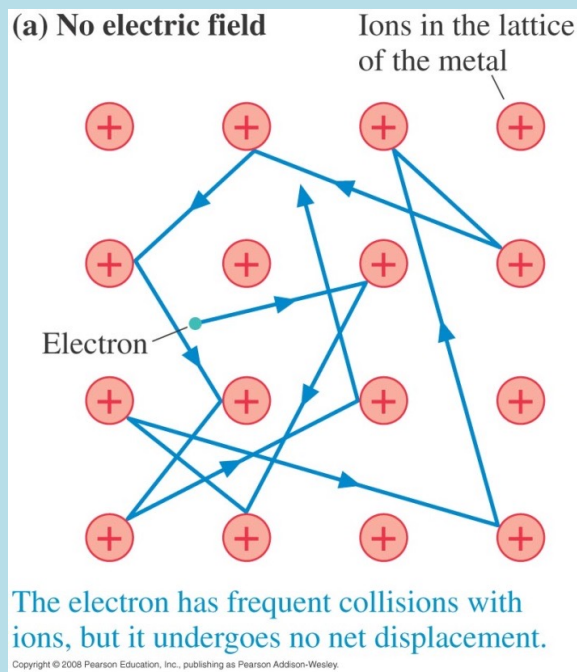
我們可以估計電子平均動得多快！

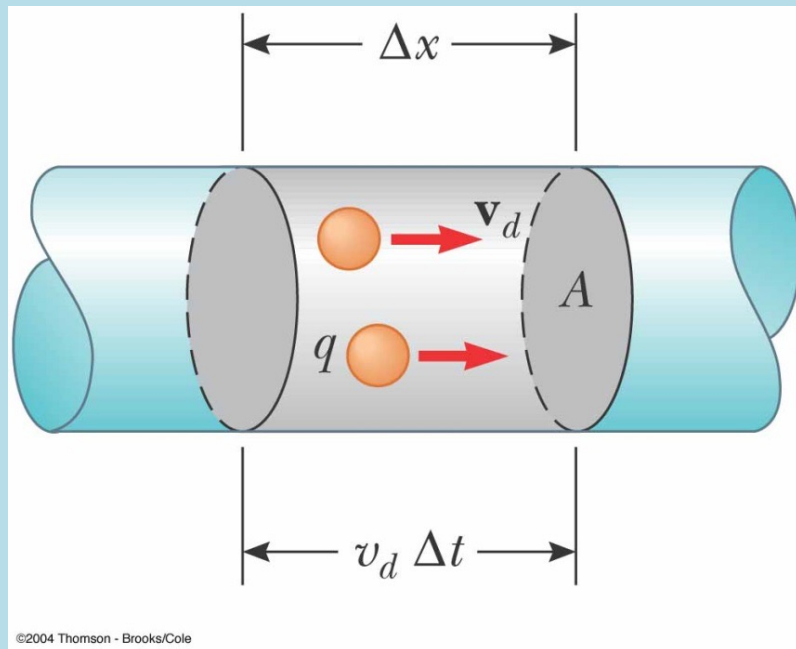
電場對電子產生一加速度：
$$a = \frac{F}{m} = \frac{eE}{m}$$

這是等加速度運動，電子速度一直增加，直到與離子碰撞後大致歸零。
我們可用兩次碰撞間，電子的平均速度，來估計電子漂移的平均速度。

平均漂移速度
$$v_d = a\tau = \frac{e\tau}{m} E$$
 τ 是兩次碰撞間的平均間隔時間

平均漂移速度與電場成正比。





漂移速度決定電流大小：

取 Δt ，在此時間內通過截面 A 的電荷：

一定就在左圖灰色體積範圍內：

$$q = (A\Delta x) \cdot ne = neAv_d\Delta t$$

$$i = \frac{q}{\Delta t} = neAv_d$$

電流密度為單位面積的電流。

$$j = \frac{i}{A} = nev_d$$

電流密度與平均漂移速度成正比。

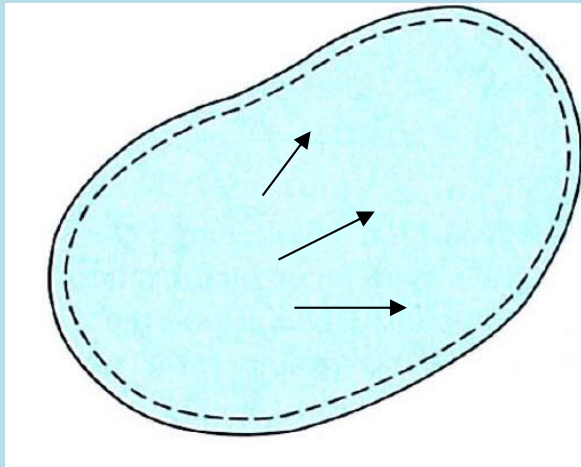
平均漂移速度與電場成正比。

電流密度與平均漂移速度成正比。

$$v_d = a\tau = \frac{e\tau}{m} E$$

$$j = \frac{i}{A} = nev_d$$

↓ τ 與外加電場無關，可視為一個常數。



$$j = \left(\frac{e^2 n \tau}{m} \right) E$$

歐姆定律

$$E = \left(\frac{m}{e^2 n \tau} \right) j$$

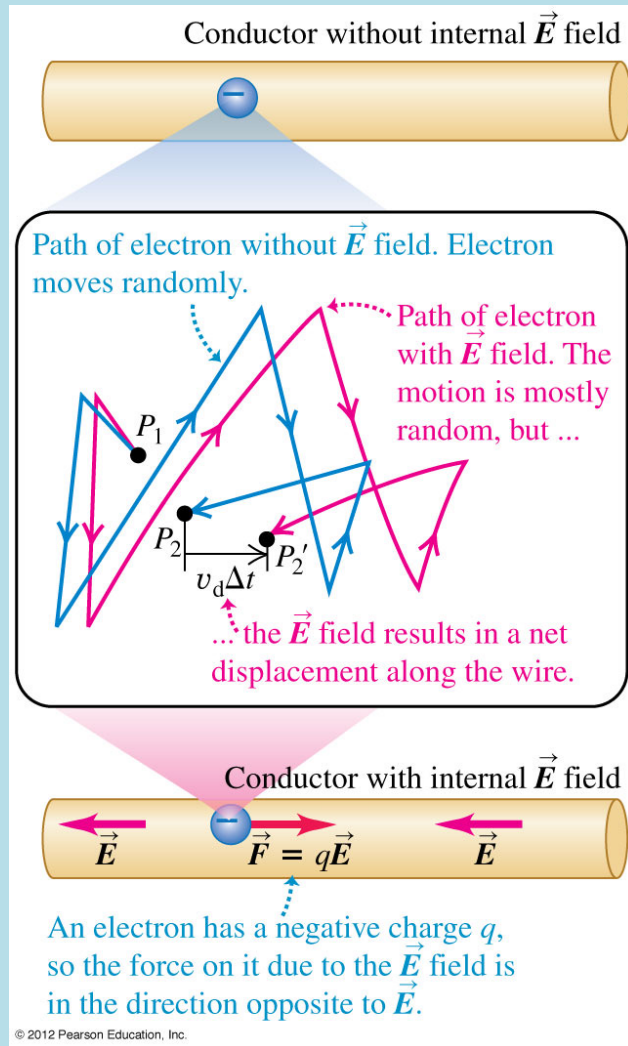
Georg Simon Ohm



$$\vec{E} = \rho \vec{j}$$

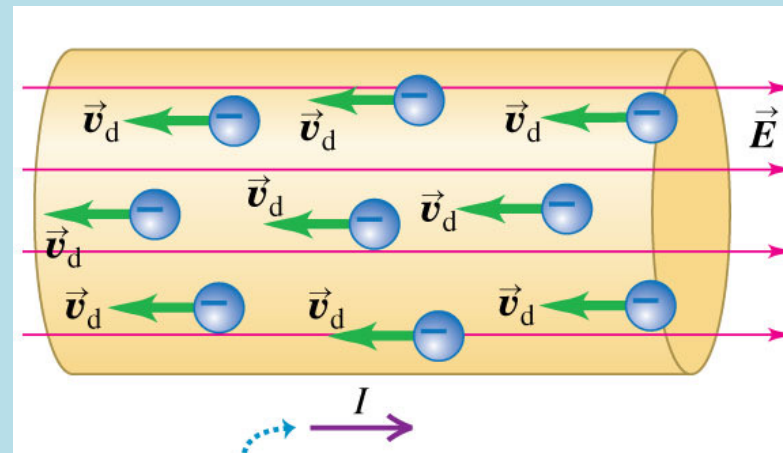
$$\rho = \frac{m}{e^2 n \tau}$$

ρ 是電阻率 Resistivity，是材料的性質



$$v_{\text{rms}} \sim 10^6 \text{ m/s}$$

但電子的熱運動方向隨機，因此互相抵消。
討論導電性時，可以忽略而等價以下圖表示。



$$v_d \sim 10^{-4} \text{ m/s} \ll v_{\text{rms}}$$

τ 由極快的 v_{rms} 決定，與外加電場無關。
因此 τ 可視為一個常數。

TABLE 25.1 Resistivities at Room Temperature (20°C)

Substance		ρ ($\Omega \cdot \text{m}$)	Substance		ρ ($\Omega \cdot \text{m}$)	
Conductors			Semiconductors			
Metals	Silver	1.47×10^{-8}	Pure carbon (graphite)		3.5×10^{-5}	
	Copper	1.72×10^{-8}	Pure germanium		0.60	
	Gold	2.44×10^{-8}	Pure silicon		2300	
	Aluminum	2.75×10^{-8}	Insulators			
	Tungsten	5.25×10^{-8}	Amber		5×10^{14}	
	Steel	20×10^{-8}	Glass		$10^{10} - 10^{14}$	
	Lead	22×10^{-8}	Lucite		$> 10^{13}$	
	Mercury	95×10^{-8}	Mica		$10^{11} - 10^{15}$	
	Alloys	Manganin (Cu 84%, Mn 12%, Ni 4%)	44×10^{-8}	Quartz (fused)		75×10^{16}
		Constantan (Cu 60%, Ni 40%)	49×10^{-8}	Sulfur		10^{15}
Nichrome		100×10^{-8}	Teflon		$> 10^{13}$	
			Wood		$10^8 - 10^{11}$	

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$$\rho = \frac{m}{e^2 n \tau}$$

傳導電子似乎就是價電子！

3.1 Comparison of the valence of various atoms to the valence predicted from the measured Hall coefficient.

Material	$\frac{1}{-eR_H n_{atomic}}$	Valence
Li	.8	1
Na	1.2	1
K	1.1	1
Cu	1.5	1
Be	-0.2*	2
Mg	-0.4	2
Ca	1.5	2

Here n_{atomic} is the density of atoms in the metal and R_H is the measured Hall coefficient. In Drude theory, the middle column should give the number of electrons per atom, i.e., the valence. For monovalent atoms, the agreement is fairly good. But for divalent atoms, the sign can even come out wrong! The * next to Be indicates that its Hall coefficient is anisotropic. Depending on which angle you run the current you can get either sign of the Hall coefficient!

⁸In any experiment there will also be some amount of thermal conductivity from structural vibrations of the material as well—so-called phonon thermal conductivity (we will meet phonons in Chapter 9). However, for most metals, the thermal conductivity is mainly due to electron motion and not from vibrations.

⁹The thermal conductivity κ is defined by $\mathbf{j}_q = \kappa \nabla T$ where \mathbf{j}_q is the heat current density. The rough intuition for Eq. 3.3 is that a density n of electrons each carries an amount of heat $c_v T$ at a velocity $\langle v \rangle$ for a distance λ before scattering.

Aside: One can also consider turning this experiment on its head. If you know the density of electrons in your sample you can use a Hall measurement to determine the magnetic field. This is known as a Hall sensor. Since it is hard to measure small voltages, Hall sensors typically use materials, such as semiconductors, where the density of electrons is low so R_H and hence the resulting voltage is large.

Let us then calculate $n = -1/(eR_H)$ for various metals and compare it to the density of atoms n_{atomic} (see Table 3.1). This should give us the number of free electrons per atom. Later on we will see that this is frequently not so hard to estimate the number of electrons in a system. A short description is that electrons bound in the core shells of the atom are never free to travel throughout the crystal, whereas the electrons in the outer shell may be free (we will discuss in Chapter 16 when the valence electrons are free and when they are not). The number of electrons in the outermost shell is known as the *valence* of the atom.

We see from Table 3.1 that for many metals this Drude theory and simple theory seems to make sense—the “valence” of lithium, sodium, and potassium (Li, Na, and K) are all one, which agrees roughly with the measured number of electrons per atom. The effective valence of copper (Cu) is also one, so it is not surprising either. However, something has clearly gone seriously wrong for Be and Mg. In this case, the sign of the Hall coefficient has come out incorrect. From this result, one might conclude that the charge carrier for beryllium and magnesium (Be and Mg) is the opposite charge from that of the electron! We will see in Section 17.1.1 that this is indeed true and is a result of the so-called band structure of these materials. However, for many metals, simple Drude theory gives quite reasonable results. We will see in Chapter 17 that Drude theory is particularly good for describing semiconductors.

If we believe the Hall effect measurement of the density of electrons in metals, using Eq. 3.2 we can then extract a scattering time from the expression for the conductivity. The Drude scattering time comes out to be in the range of $\tau \approx 10^{-14}$ seconds for most metals near room temperature.

3.2 Thermal Transport

$$\tau \sim 10^{-14} \text{ s}$$

Drude was brave enough to attempt to further calculate the thermal conductivity κ due to mobile electrons⁸ using Boltzmann’s kinetic theory. Without rehashing the derivation, this result should look familiar to you from your previous encounters with the kinetic theory of gases.

$$\kappa = \frac{1}{3} n c_v \langle v \rangle \lambda$$

where c_v is the heat capacity per particle, $\langle v \rangle$ is the average thermal velocity and $\lambda = \langle v \rangle \tau$ is the scattering length. For a conventional (monatomic) gas the heat capacity per particle is

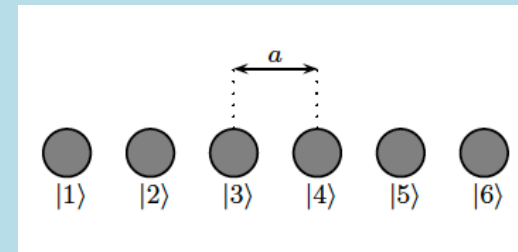
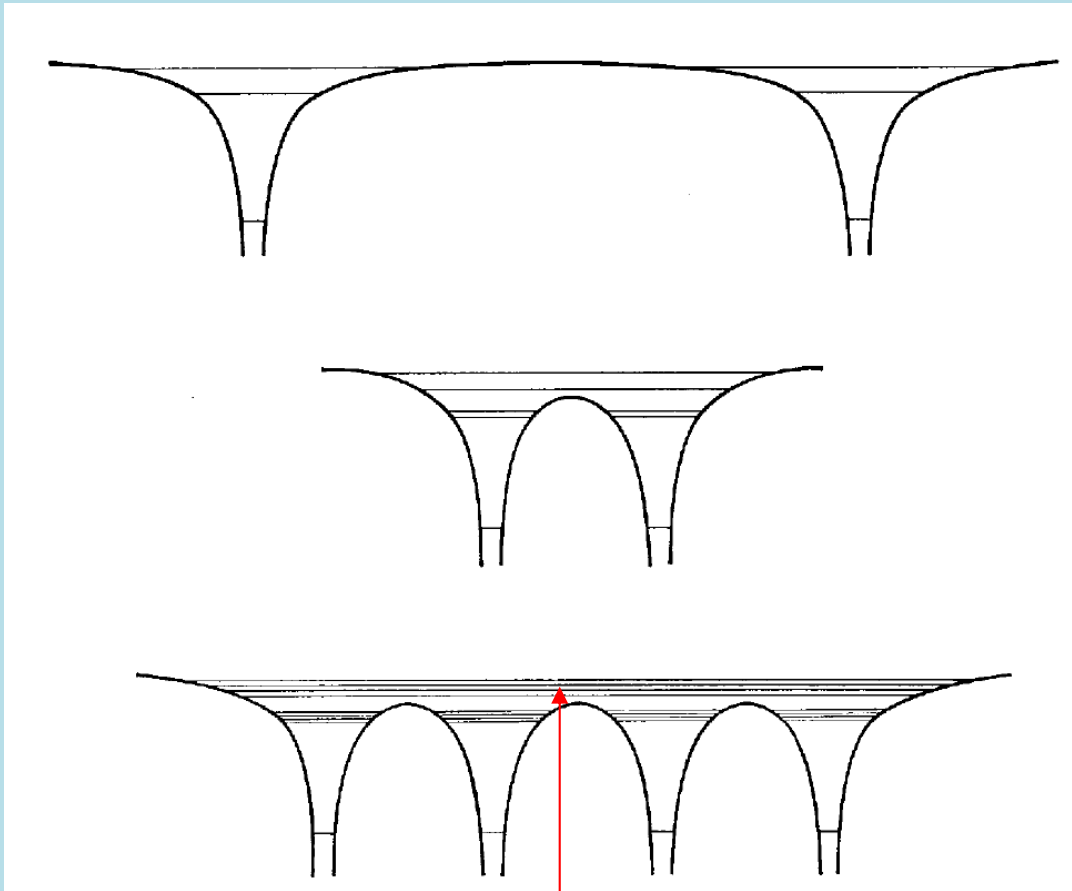
$$c_v = \frac{3}{2} k_B$$

$$v_{rms} \sim 10^6 \text{ m/s}$$

$$\text{自由徑} \sim 10^{-8} \text{ m}$$

$$\text{原子間距} \sim 10^{-10} \text{ m}$$

Nearly free electron model and energy band



當原子彼此靠近，某些態將跨越原子間的位能。

這些原來屬於私人的電子現在是**公共財產**！

因為能量超越位能，這些電子基本的本質會很像自由的粒子（未微擾）。

晶格上週期排列的離子，產生的週期性位能，可以以微擾項來處理。

One can gain substantial insight into the structure imposed on the electronic energy levels by a periodic potential, if that potential is very weak. This approach might once have been regarded as an instructive, but academic, exercise. We now know, however, that in many cases this apparently unrealistic assumption gives results surprisingly close to the mark. Modern theoretical and experimental studies of the metals found in groups I, II, III, and IV of the periodic table (i.e., metals whose atomic structure consists of s and p electrons outside of a closed-shell noble gas configuration) indicate that the conduction electrons can be described as moving in what amounts to an almost constant potential. These elements are often referred to as “nearly free electron” metals, because the starting point for their description is the Sommerfeld free electron gas, modified by the presence of a *weak* periodic potential. In this chapter we shall examine some of the broad general features of band structure from the almost free electron point of view. Applications to particular metals will be examined in Chapter 15.

It is by no means obvious why the conduction bands of these metals should be so free-electron-like. There are two fundamental reasons why the strong interactions of the conduction electrons with each other and with the positive ions can have the net effect of a very weak potential.

1. The electron-ion interaction is strongest at small separations, but the conduction electrons are forbidden (by the Pauli principle) from entering the immediate neighborhood of the ions because this region is already occupied by the core electrons.
2. In the region in which the conduction electrons are allowed, their mobility further diminishes the net potential any single electron experiences, for they can *screen* the fields of positively charged ions, diminishing the total effective potential.

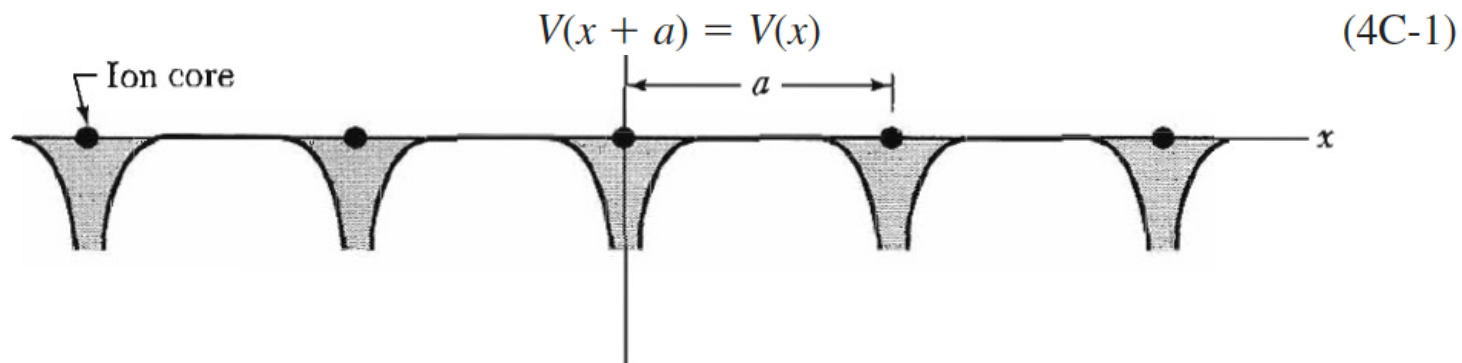
Supplement 4-C

Periodic Potentials

Metals generally have a crystalline structure; that is, the ions are arranged in a way that exhibits a spatial periodicity. In our one-dimensional discussion of this topic, we will see that this periodicity has two effects on the motion of the free electrons in the metal. One is that for a perfect *lattice*—that is, for ions spaced equally—the *electron propagates without reflection*; the other is that there are restrictions on the energies allowed for the electrons; that is, *there are allowed and forbidden energy “bands.”*

We begin with a discussion of the consequences of perfect periodicity.

The periodicity will be built into the potential, for which we require that

$$V(x + a) = V(x) \quad (4C-1)$$


The diagram illustrates a periodic potential $V(x)$ along the x -axis. The potential consists of a series of identical, shaded, downward-pointing wells. Each well represents the potential energy of an electron near an ion core. The ion cores are marked with black dots on the x -axis. The distance between two adjacent ion cores is labeled as a . The equation $V(x + a) = V(x)$ is written above the diagram, indicating the periodicity of the potential. The x -axis is labeled at the right end.

Nearly free electron model

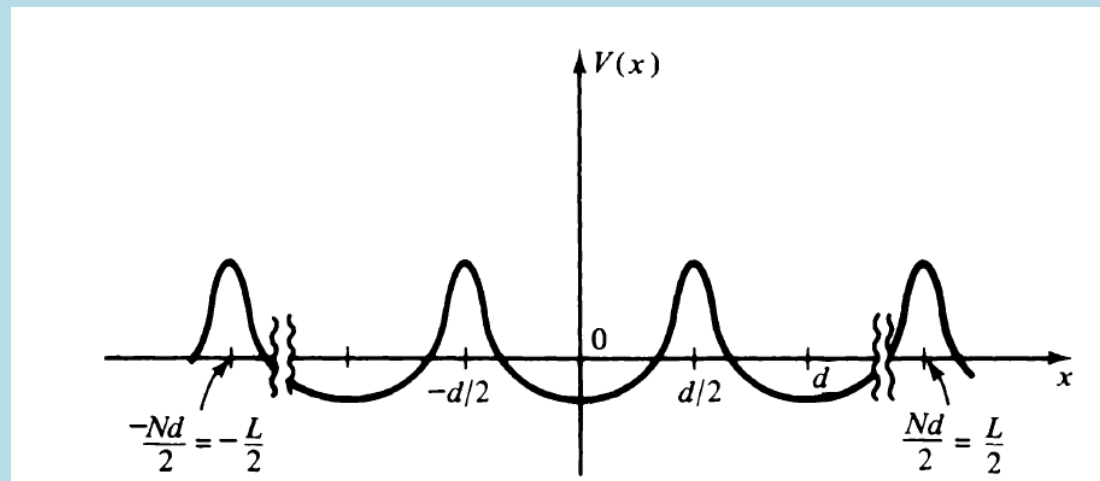
考慮一維空間，將自由電子視為未微擾模型，加入一週期性位能 $V(x)$ 作為微擾！

$$H_0 = \frac{p^2}{2m}$$

$$H_1 = V(x)$$

$$V(x+a) = V(x)$$

例如：



未微擾自由電子能量： $H_0 = \frac{p^2}{2m}$

未微擾能量本徵態，即是平面波 $|k\rangle$ （設一維空間有一長度 L ）：

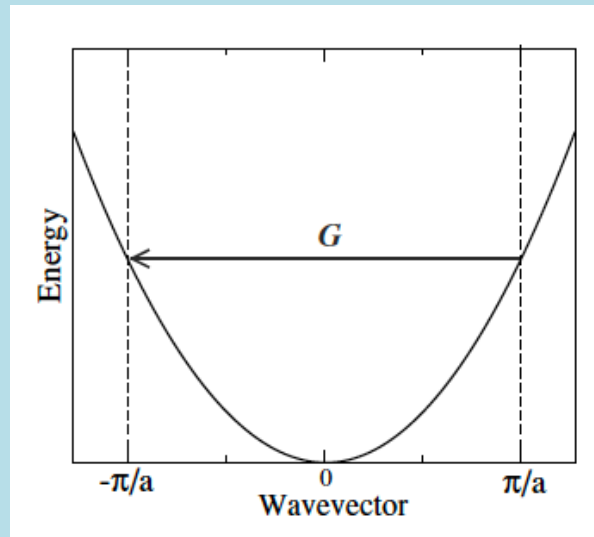
波函數以角波數 k ，即動量標定：

$$|k\rangle \sim \frac{1}{\sqrt{L}} e^{-ikx}$$

對應的本徵值：

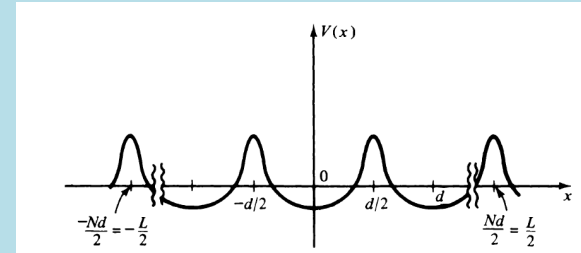
$$E^{(0)} = \frac{\hbar^2 k^2}{2m}$$

零階本徵值能量 $E_k^{(0)}$ 對 k 作圖



微擾的週期性位能可以作傅立葉分析，

$$V(x) = \sum_{n=-\infty}^{\infty} V_n e^{i2\pi n \left(\frac{x}{a}\right)}$$



係數 V_n 也可以代表此位能。位能應該是實數，因此：

$$V_{-n} = V_n^*$$

先計算微擾項 $V(x)$ 在未微擾本徵態間的矩陣元：

$$\langle q|V|k\rangle = \frac{1}{L} \int dx e^{iqx} \sum_{n=-\infty}^{\infty} V_n e^{i2\pi n \left(\frac{x}{a}\right)} e^{-ikx}$$

積分與求和交換次序！得到虛數指數函數積分，這是一 δ 函數！

$$\sum_{n=-\infty}^{\infty} \left(V_n \cdot \frac{1}{L} \int dx e^{-i\left(k - q + \frac{2\pi n}{a}\right)x} \right) = \sum_{n=-\infty}^{\infty} \left[V_n \cdot \delta\left(k - q + \frac{2\pi n}{a}\right) \right]$$

微擾項矩陣元只有在兩邊 k 相差 $\frac{2n\pi}{a}$ 才不為零！這是位能週期性的表現。

以下我們以 V_1 的貢獻為例，以簡化符號。其他 V_n 可以用同樣方式直接加入。

$$\langle q|V|k\rangle = V_1 \cdot \delta\left(k - q + \frac{2\pi}{a}\right)$$

這個量會直接出現在我們計算中。

$$\langle q|V|k\rangle = V_1 \cdot \delta\left(k - q + \frac{2\pi}{a}\right)$$

矩陣元只有在兩邊 k 相差 $\frac{2\pi}{a}$ 才不為零！

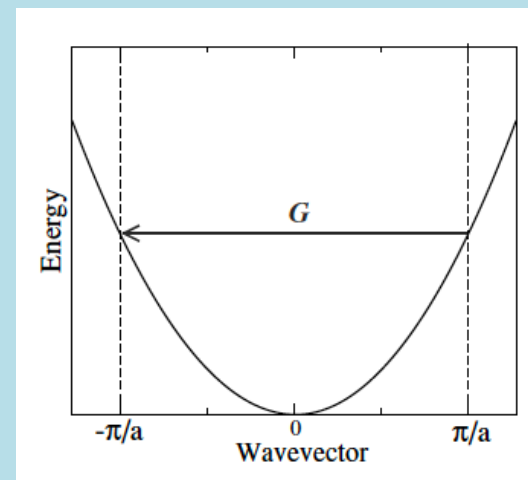
計算對平面波態 $|k\rangle$ ，能量的一階修正，代入公式： $E_n^{(1)} = \langle \phi_n | H_1 | \phi_n \rangle$

$$E_n^{(1)} = \langle k | V | k \rangle = V_1 \cdot \delta\left(k - k + \frac{2\pi}{a}\right) = 0$$

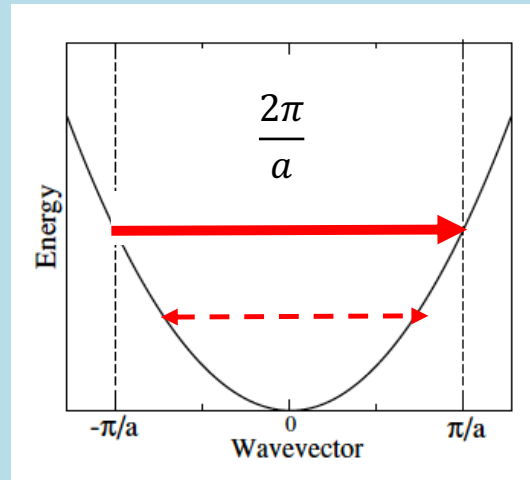
能量的一階修正為零。

$$E^{(0+1)} = \frac{\hbar^2 k^2}{2m}$$

零階加一階本徵值能量 $E_k^{(0+1)}$ 對 k 作圖



“幾乎自由電子”與自由電子差距極小！
因此似乎電子還是近似處於自由狀態！
這個結果大部分對，但不完全！



零階本徵值能量 $E_k^{(0)}$ 對 k 作圖

自由電子的能量有一個簡併，正負 k 能量相等：

$$E_k^{(0)} = E_{-k}^{(0)}$$

$|k\rangle \sim e^{-ikx}$ 與 $|-k\rangle \sim e^{ikx}$ 能量相同，因此簡併！

但這個簡併對微擾一般來說不重要，週期性位能不會混雜這兩個簡併的態。

週期性位能 V_1 只會混雜 k 相差 $\frac{2\pi}{a}$ 的平面波：

$$\langle q|V|k\rangle = V_1 \cdot \delta\left(k - q + \frac{2\pi}{a}\right)$$

但如果

$$k = -\frac{\pi}{a}$$

$$E_{\frac{\pi}{a}}^{(0)} = E_{\frac{\pi}{a}}^{(0)}$$

$e^{-i\frac{\pi}{a}x}$ 與 $e^{i\frac{\pi}{a}x}$ 簡併！

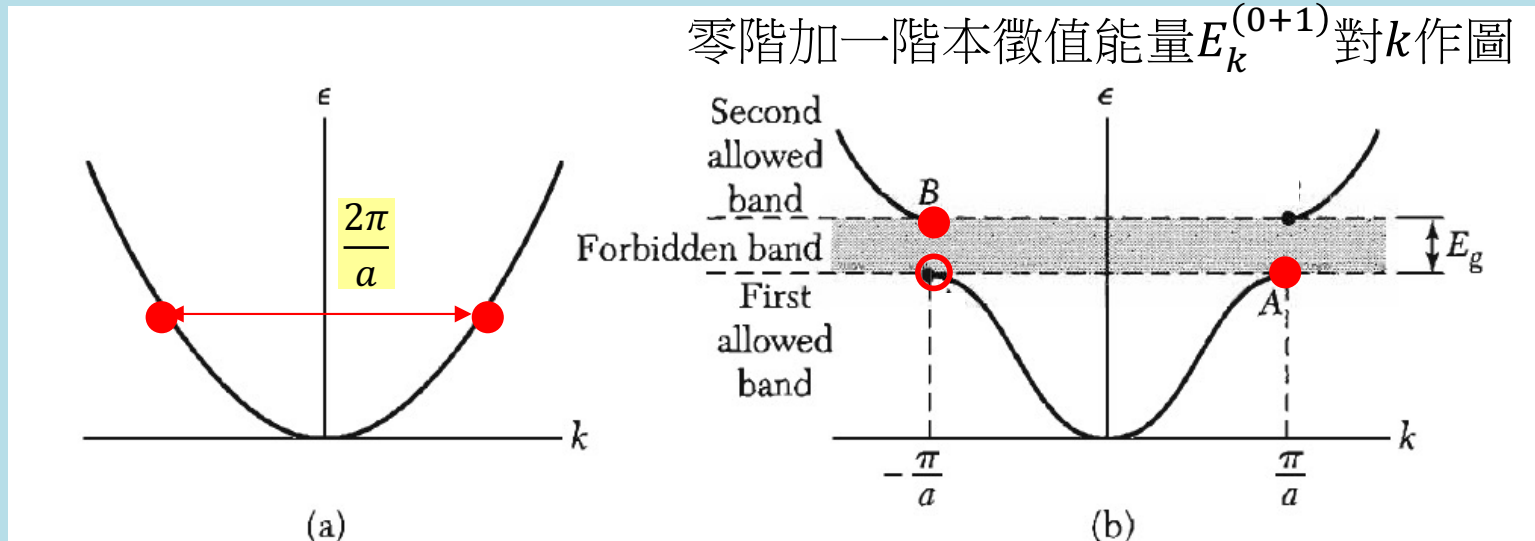
而且週期性位能會混雜這兩個簡併的態，因為 k 恰好相差 $\frac{2\pi}{a}$ 。

此時一般微擾公式的分母為零，混雜是無限大，就不能用了。

這又是兩個簡併態會被微擾所混雜的例子！

回到簡併微擾

零階加一階本徵值能量 $E_k^{(0+1)}$ 對 k 作圖



$$k = -\frac{\pi}{a}$$

Band Edge

$e^{-i\frac{\pi}{a}x}$ 與 $e^{i\frac{\pi}{a}x}$ 簡併！

$$E_{-\frac{\pi}{a}}^{(0)} = E_{\frac{\pi}{a}}^{(0)}$$

只有兩個簡併態，還沒有算，已經從經驗可以猜到答案了！

微擾會消除簡併！在Band Edge上的簡併態，微擾後會分裂為A,B兩個能量不等的態！

而接近Band Edge的態能量，微擾後應該也要隨著上述的分裂而跟著改變。

最自然的：Band Edge內 $k \leq \frac{\pi}{a}$ 能量曲線，會下彎至Band Edge上的A點。

$k \geq \frac{\pi}{a}$ ，由Band Edge上較大本徵值B點出發，能量曲線彎回到拋物線。

因此原來能量值是連續的，在Band Edge處因微擾出現不連續的間隙Energy Gap。

Band Edge上的嚴格計算：

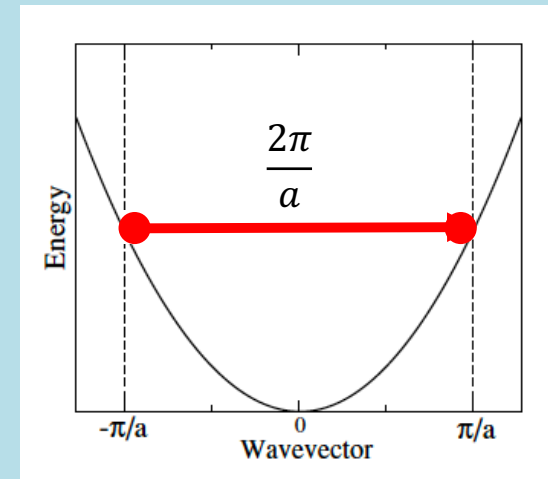
微擾能量矩陣元不為零的 $\left|k = -\frac{\pi}{a}\right\rangle$ 與 $\left|k + \frac{2\pi}{a} = \frac{\pi}{a}\right\rangle$ ，兩者能量相等，

這兩個態處於簡併。考慮二維簡併空間：設微擾計算的零階項可以寫成：

$$\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} \sim \alpha_1 \left| \frac{\pi}{a} \right\rangle + \alpha_2 \left| -\frac{\pi}{a} \right\rangle$$

零階項滿足微擾項的本徵態方程式：

$$\begin{pmatrix} \left\langle \frac{\pi}{a} \right| V \left| \frac{\pi}{a} \right\rangle & \left\langle \frac{\pi}{a} \right| V \left| -\frac{\pi}{a} \right\rangle \\ \left\langle -\frac{\pi}{a} \right| V \left| \frac{\pi}{a} \right\rangle & \left\langle \frac{\pi}{a} \right| V \left| \frac{\pi}{a} \right\rangle \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E_n^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$



$$\langle q|V|k\rangle = V_1 \cdot \delta\left(k - q + \frac{2\pi}{a}\right) \quad \text{設 } V_1 > 0$$

位能矩陣元只有兩邊狀態動量相差 $\frac{2\pi}{a}$ 時才不為零！

$$\left\langle \frac{\pi}{a} \right| V \left| \frac{\pi}{a} \right\rangle = \left\langle \frac{\pi}{a} \right| V \left| -\frac{\pi}{a} \right\rangle = 0$$

$$\left\langle -\frac{\pi}{a} \right| V \left| \frac{\pi}{a} \right\rangle = \left\langle \frac{\pi}{a} \right| V \left| -\frac{\pi}{a} \right\rangle = V_1$$

$$\begin{pmatrix} 0 & V_1 \\ V_1 & 0 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E_n^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

這又是已經解過： σ_x 的本徵態問題。

$$\begin{pmatrix} 0 & V_1 \\ V_1 & 0 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E_n^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

本徵值與本徵態如預期有兩組。

$$E_n^{(1)} = V_1$$

$$\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

或者

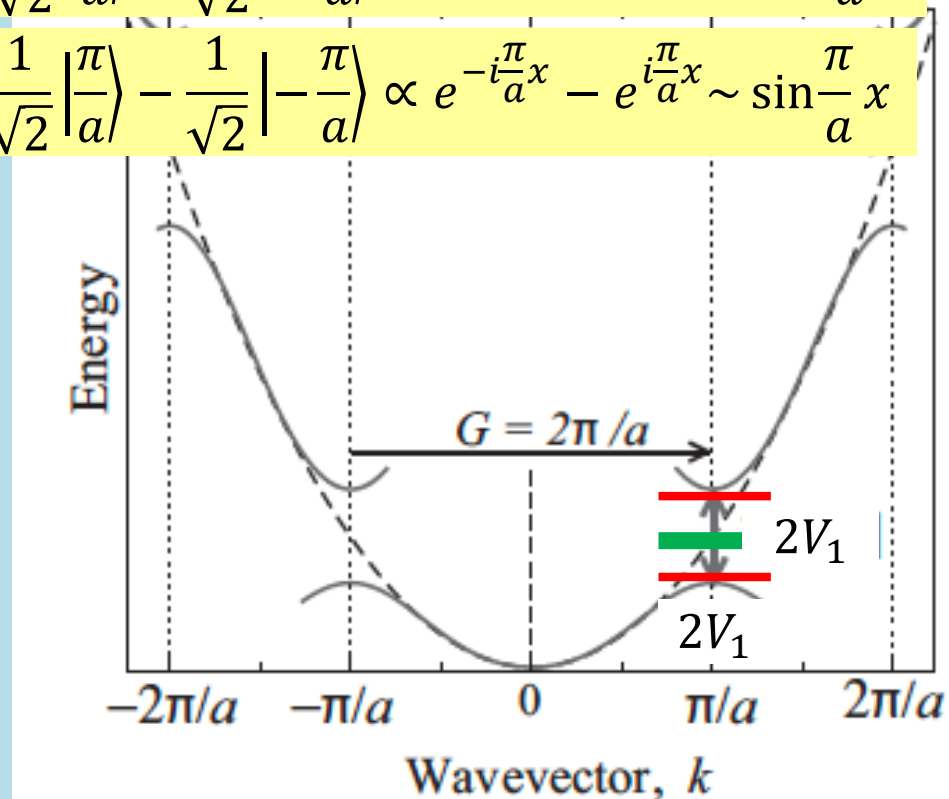
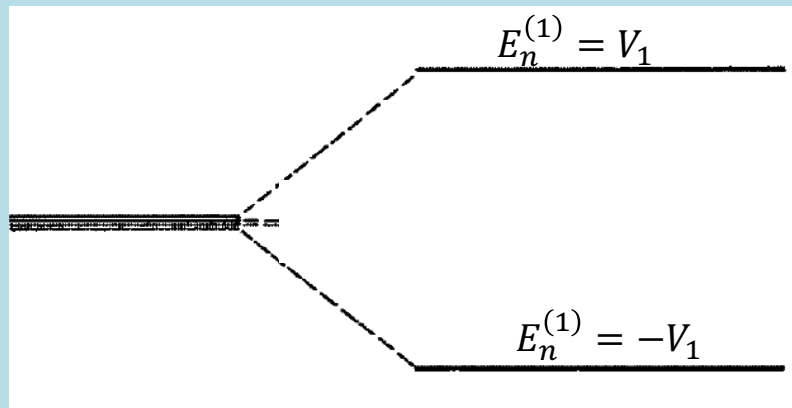
$$E_n^{(1)} = -V_1$$

$$\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\langle x | k \rangle = \frac{1}{\sqrt{L}} e^{-ikx}$$

$$\frac{1}{\sqrt{2}} \left| \frac{\pi}{a} \right\rangle + \frac{1}{\sqrt{2}} \left| -\frac{\pi}{a} \right\rangle \propto e^{-i\frac{\pi}{a}x} + e^{i\frac{\pi}{a}x} \sim \cos \frac{\pi}{a} x$$

$$\frac{1}{\sqrt{2}} \left| \frac{\pi}{a} \right\rangle - \frac{1}{\sqrt{2}} \left| -\frac{\pi}{a} \right\rangle \propto e^{-i\frac{\pi}{a}x} - e^{i\frac{\pi}{a}x} \sim \sin \frac{\pi}{a} x$$



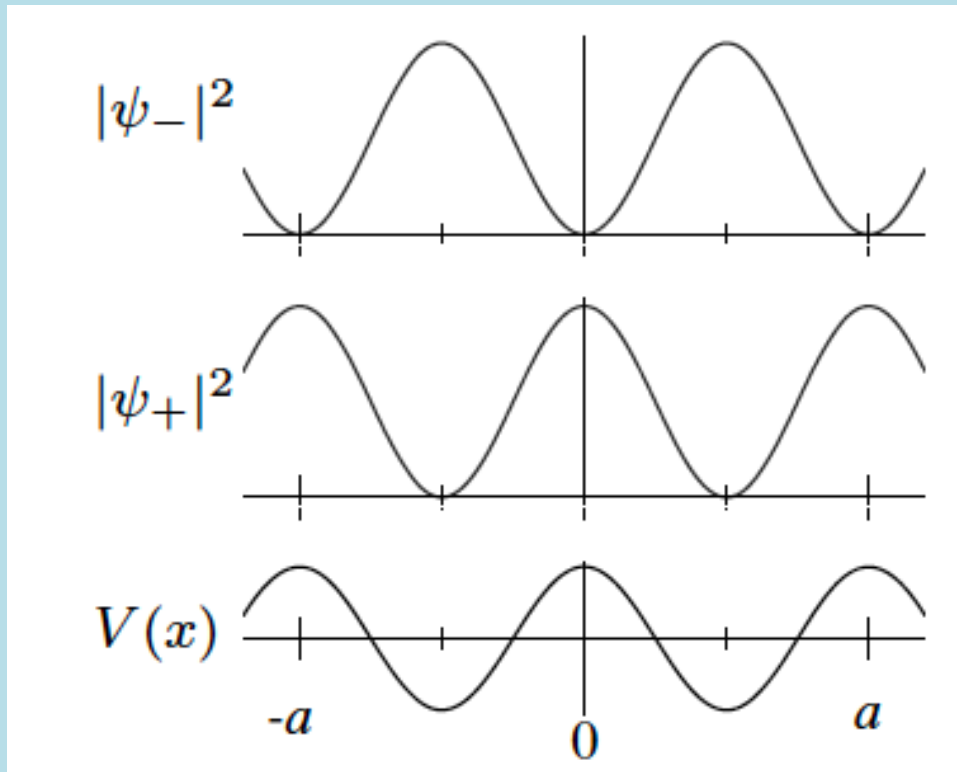
$k = \frac{\pi}{a}$ 在 k 空間稱為 Band Edge。

Band Edge 上兩能量相等的簡併態，會因微擾分裂為兩個能量不等的定態！

在 Band Edge 處因微擾出現不連續的間隙 Energy Gap $2V_1$ 。

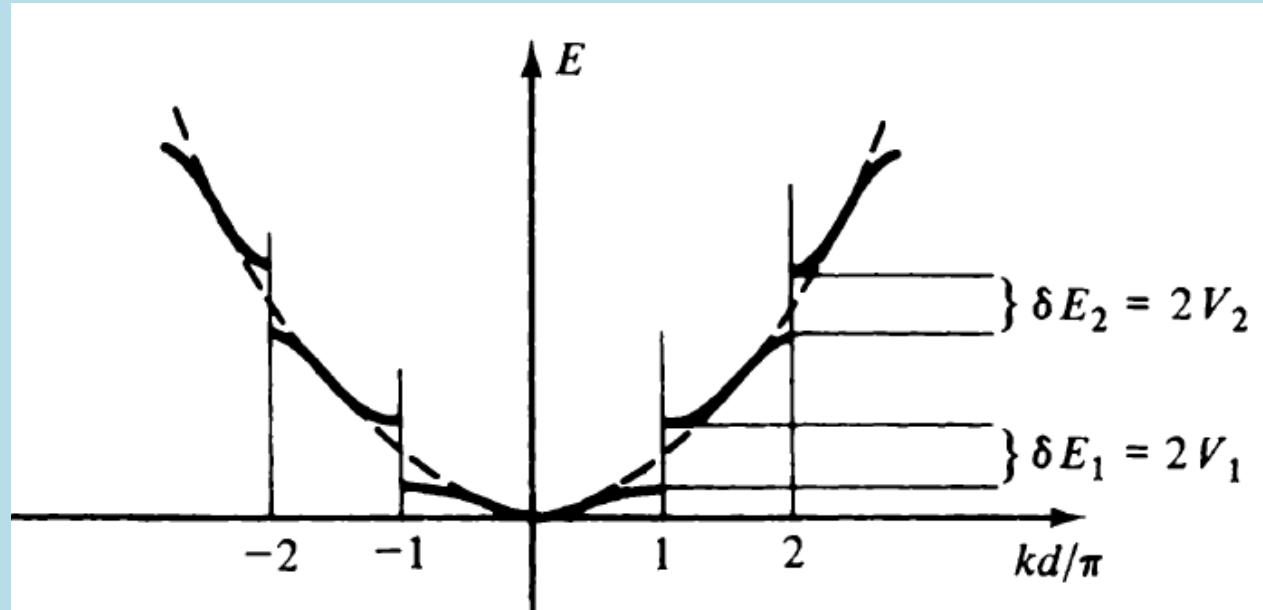
這兩個能量不等的態，是原本兩個簡併態 $e^{-i\frac{\pi}{a}x}$ 與 $e^{i\frac{\pi}{a}x}$ ，相加與相減形成的疊加態！

電子的機率密度分別集中與遠離，離子附近位能較低的區域，造成能量差異。



$$\frac{1}{\sqrt{2}} \left| \frac{\pi}{a} \right\rangle - \frac{1}{\sqrt{2}} \left| -\frac{\pi}{a} \right\rangle \sim \sin \frac{\pi}{a} x$$

$$\frac{1}{\sqrt{2}} \left| \frac{\pi}{a} \right\rangle + \frac{1}{\sqrt{2}} \left| -\frac{\pi}{a} \right\rangle \sim \cos \frac{\pi}{a} x$$



若是考慮所有 V_n ，每一個 V_n 會對應一個 Band Edge。

每一個 Band Edge，都會出現間隙 Gap。大小為 $2V_n$ 。

這與真實可解的Dirac梳週期性位能非常類似！

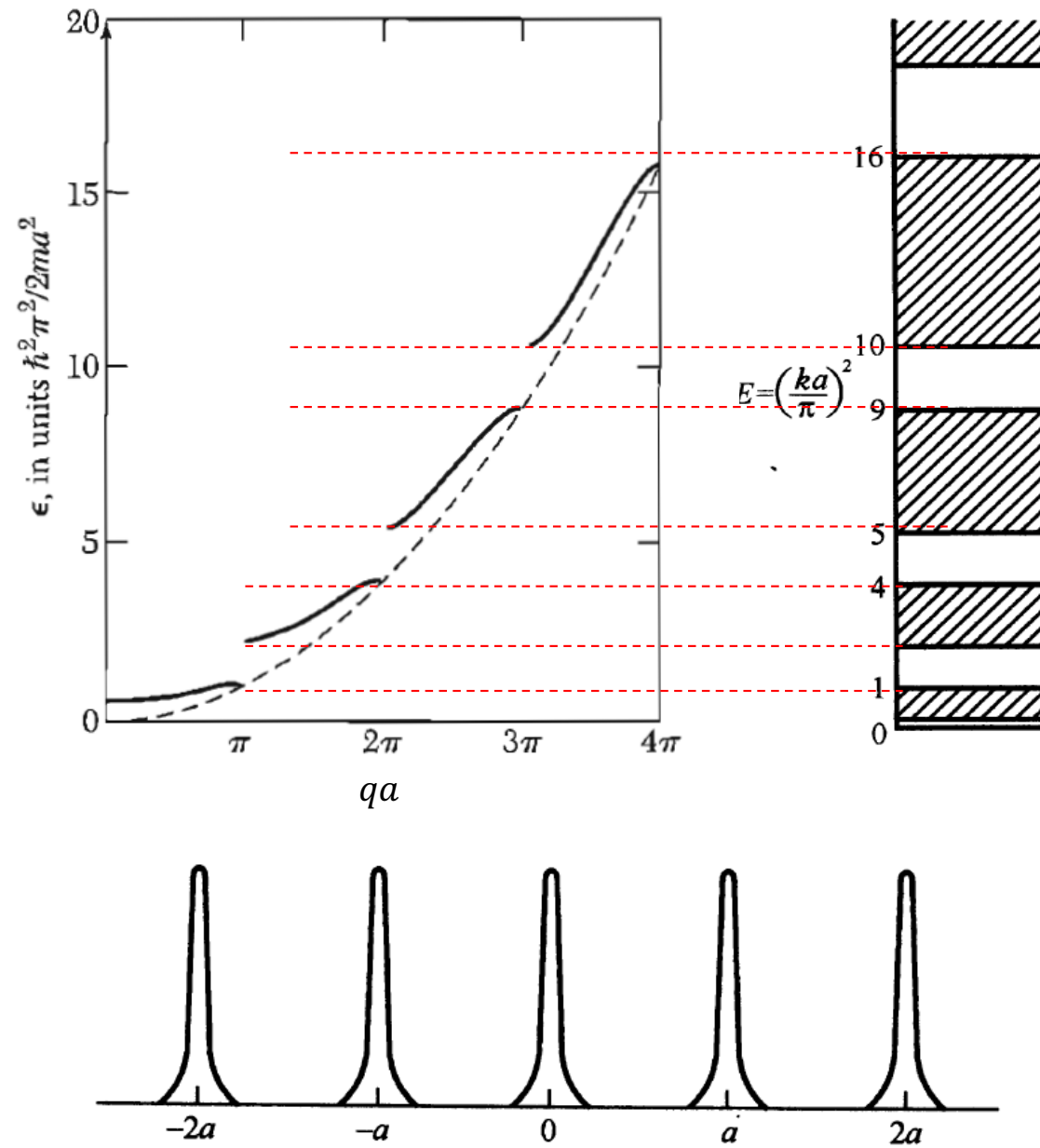


图 3.33 Dirac 梳

現在考慮在第一個Band Edge附近的平面波態： $k = -\frac{\pi}{a} - \delta$ 。

位能矩陣元會混雜動量相差 $\frac{2\pi n}{a}$ 的兩個狀態！

詳細計算能帶的形狀！

但現在 $|k = -\frac{\pi}{a} - \delta\rangle$ 與 $|k + \frac{2\pi}{a} = \frac{\pi}{a} - \delta\rangle$ 兩者能量不完全相等，分別是：

$$E^{(0)} = \frac{\hbar^2 \left(\frac{\pi}{a} \pm \delta\right)^2}{2m} \sim \frac{\hbar^2 \left(\frac{\pi}{a}\right)^2}{2m} \pm \frac{\hbar^2 \pi \delta}{ma}$$

所以嚴格說，這不是簡併微擾。

但若 δ 很小， δ 的貢獻也構成微擾的一部分。

於是這兩個態的 δ 零階能量就相等，因此簡併！

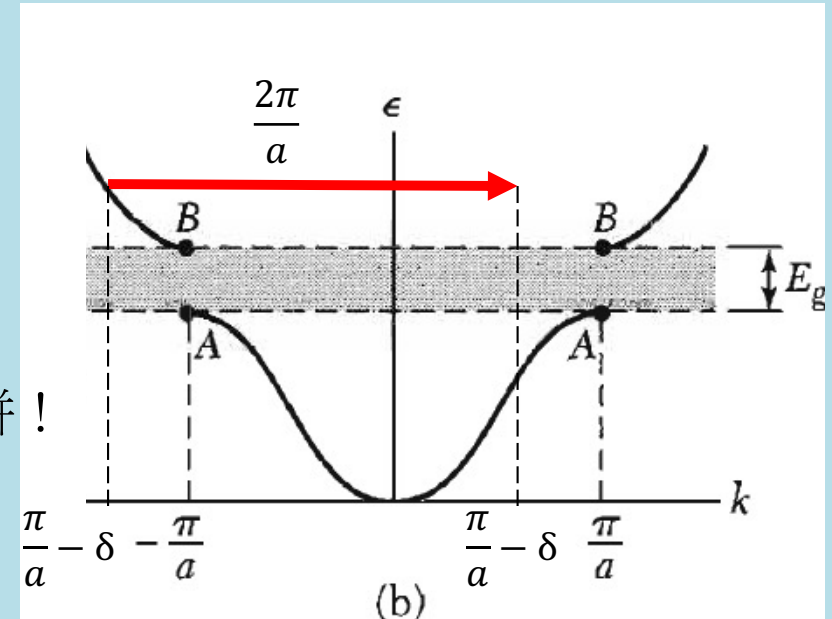
就應該把兩個態的混合也考慮進去。

$$\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} \sim \alpha_1 \left| \frac{\pi}{a} - \delta \right\rangle + \alpha_2 \left| -\frac{\pi}{a} - \delta \right\rangle$$

兩個態與 δ 零階能量，即 $\left| \frac{\pi}{a} \right\rangle$ 的能量，能量差是 δ 的一次項，歸到微擾一次展開。

能量差是能量本徵值的一部分，不是混雜，因此會出現在矩陣的對角元素！

$$\begin{pmatrix} \frac{\hbar^2 \pi \delta}{ma} & V_1 \\ V_1 & -\frac{\hbar^2 \pi \delta}{ma} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E_n^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$



$$\begin{pmatrix} \frac{\hbar^2 \pi \delta}{ma} & V_1 \\ V_1 & -\frac{\hbar^2 \pi \delta}{ma} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E_n^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

這個矩陣經常出現，值得以簡化的代號求解：

$$\begin{pmatrix} \Delta & V_1 \\ V_1 & -\Delta \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = c \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

$$\Delta \equiv \frac{\hbar^2 \pi \delta}{ma}$$

設本徵值為 c ，本徵態： $\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$ ：

$$\begin{vmatrix} \Delta - c & V_1 \\ V_1 & -\Delta - c \end{vmatrix} = 0$$

$$c^2 = \Delta^2 + V_1^2$$

若 $\Delta \gg V_1$ ：微擾可以忽略，能量維持原來形式！

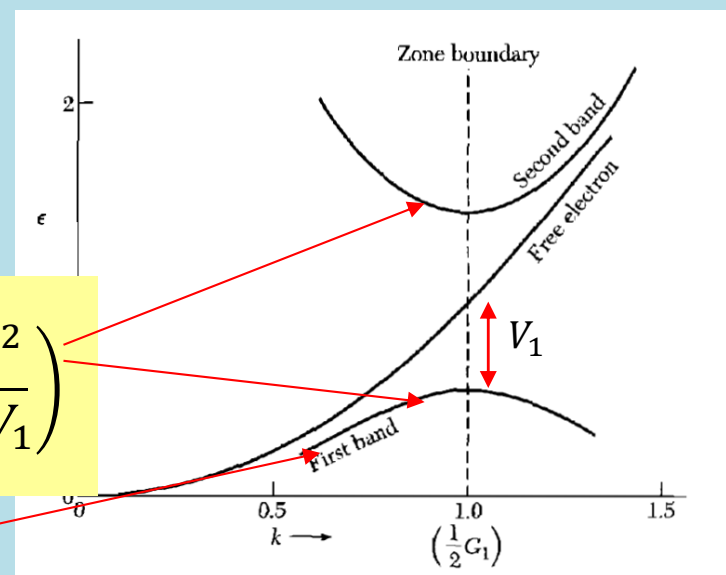
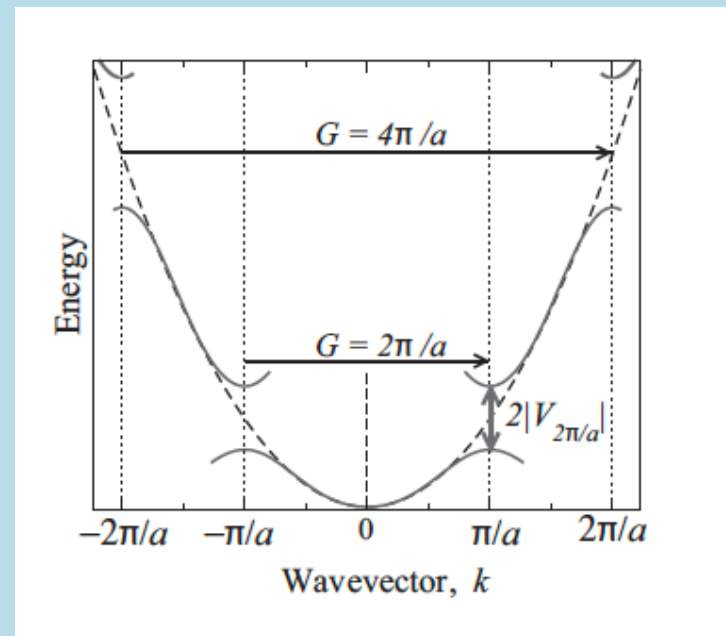
考慮 $\Delta \ll V_1$ ：

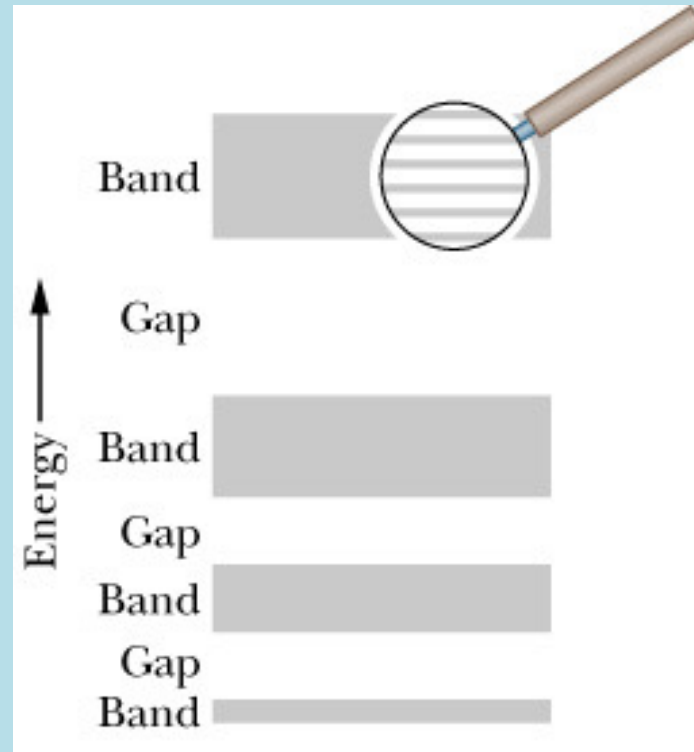
$$c = \pm \sqrt{\Delta^2 + V_1^2} = \pm \left(V_1 \sqrt{1 + \frac{\Delta^2}{V_1^2}} \right) = \pm \left(V_1 + \frac{\Delta^2}{2V_1} \right)$$

以能量較低的能態為例：

$$E_n^{(1)} = - \left(V_1 + \frac{\hbar^2 \pi^2}{2V_1 m^2 a^2} \delta^2 \right)$$

因此在band edge附近，能量是一條拋物曲線 $\sim \delta^2$ 。此曲線會趨近band edge上已經下降 V_1 的能量值。





所以固體中的電子能態(能量本徵值)，形成一個個能帶，能帶之間可能有間隙！

固態物理之父Bloch

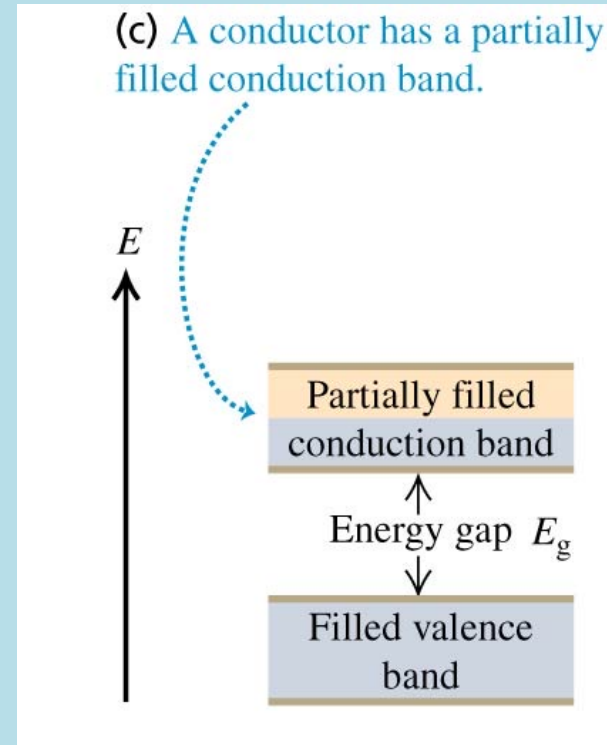
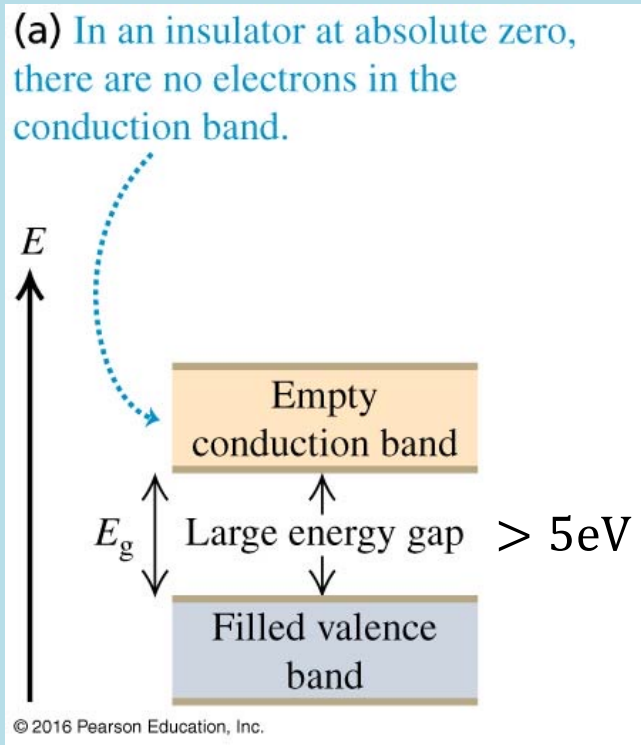
現在要幫電子往能態裡面填。



如果電子恰好填滿一個能帶（稱Valence），這些能帶中的電子無處可去！

需要很大能量才能克服間隙，才能改變狀態。

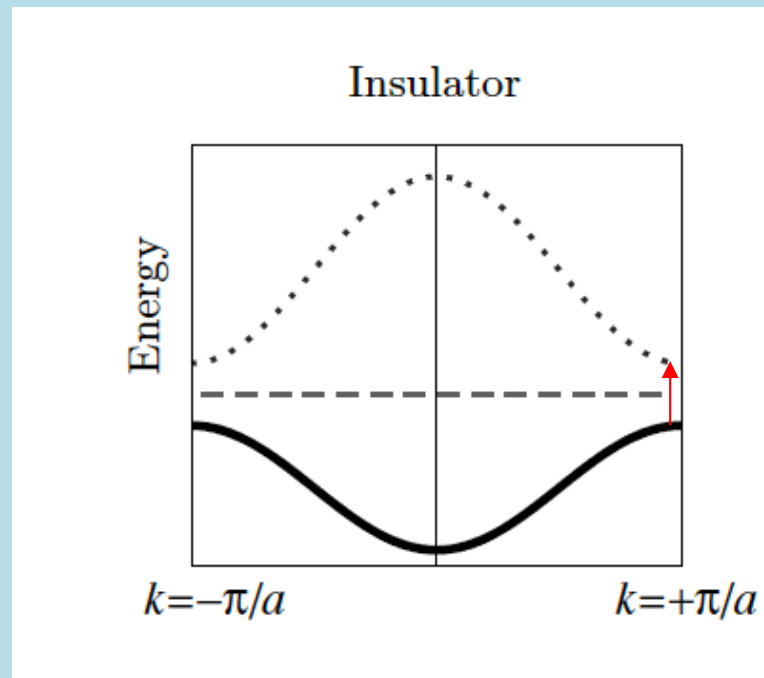
如此電子即使不再被束縛，但完全不能自由。這樣的固體無法導電，是絕緣體。



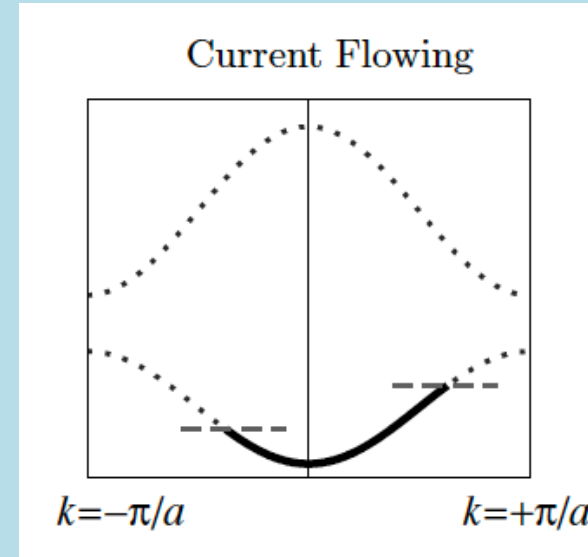
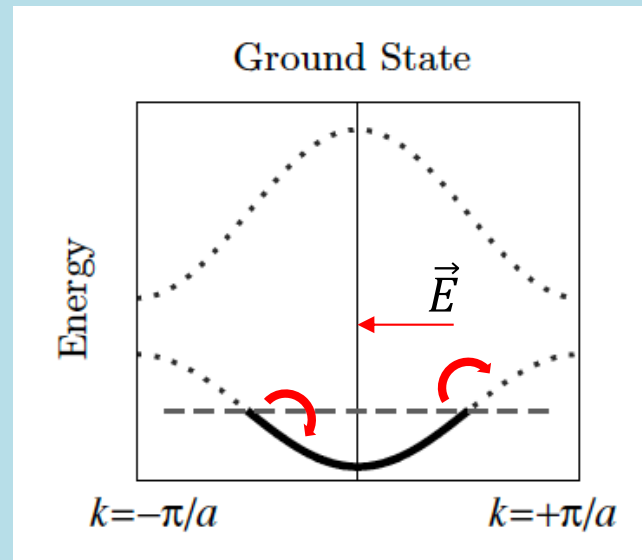
如果電子未填滿能帶（稱Conduction），未滿能帶內的電子很容易改變狀態。

只要些許能量就能讓它激發到其他能態。

這些電子非常自由，可以移動。這樣的固體就可以導電，就是導體。



在填滿的能帶內的電子，完全無法改變狀態，除非付出很高的能量，跳到下一能帶。這些電子便與導電無關，稱為價電子Valance。絕緣體便是所有能帶都被填滿的固體。



在半滿的能帶中，電子便有狀態可以供它改變運動狀態。

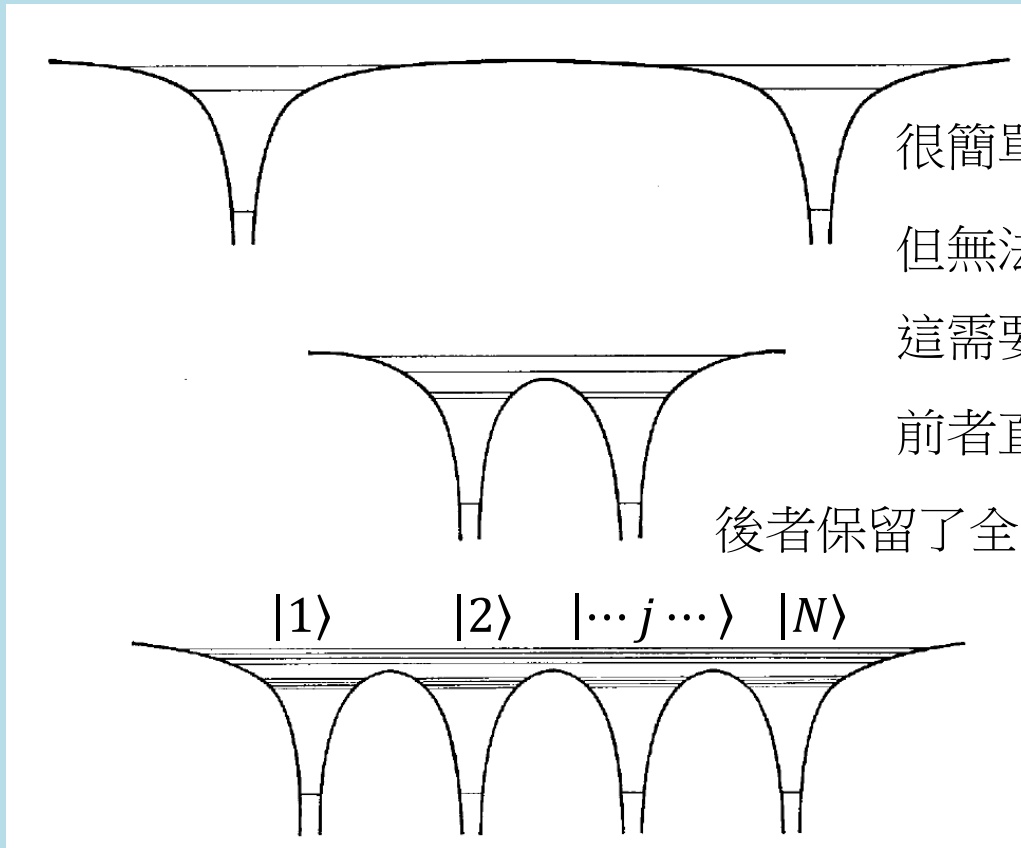
加上電場後，可以證明所有電子的晶體動量 k 會如圖隨時間增加： $\delta k = -\frac{eE}{\hbar} t$ 。

如此往電場反向的晶體動量會大於正向，電子密度總和是向反向運動的。

所以這樣半滿能帶中的電子，便能導電，稱傳導電子，此能帶就稱傳導能帶。

Tight Binding Model 参考

Tight Binding Model



Nearly Free Electron Model

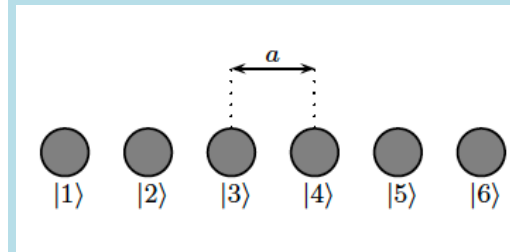
很簡單的解出能帶結構。

但無法說明為何不同元素導電度的差異。

這需要Tight Binding Model。

前者直接由全球化的電子出發。

後者保留了全球化的電子與家的聯繫、在地性！



將第 j 個原子內的某一特定能態(例如3s)標為 $|j\rangle$ 。

每一個原子內都有此能態(例如3s)，因此共有 N 個狀態 $|j\rangle, j = 1 \dots N$ 。

如果原子足夠靠近，一個原子的電子會感受到旁邊原子的位能。

於是第 j 個原子的位能可以同時影響 $|j\rangle$ 、 $|j + 1\rangle$ 、 $|j - 1\rangle$ 。

此位能應可以微擾處理。

而未微擾前，這些態是同一能階，能量相等，所以這是簡併下微擾。

而未微擾前，這些態是同一能階，能量相等，所以這是簡併下微擾。

簡併態 $|j\rangle, j = 1 \dots N$ ，數量為原子數 N 。所以簡併空間是 $|j\rangle$ 所展開 N 維空間。

因此我們要解 H_1 矩陣 $N \times N$ 的本徵問題：

設本徵態寫成： $\sum_{j=1}^N c_j |j\rangle$ 可表為行向量： $\begin{pmatrix} c_1 \\ \vdots \\ c_j \\ \vdots \\ c_N \end{pmatrix}$

H_1 矩陣元如同簡併微擾時：

$$H_{1ij} = \langle i | H_1 | j \rangle$$

$$H_{1ij} = \begin{pmatrix} 0 & -t & 0 & \dots & 0 \\ -t & 0 & -t & 0 & 0 \\ 0 & -t & 0 & -t & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 0 \end{pmatrix}$$

這裡假設 $|j\rangle$ 只能感受到 $j - 1$ 及 $j + 1$ 原子核的位能。此位能以一個數 $-t$ 代表。

本徵方程式： $H_{1,jj+1} = \langle j | H_1 | j + 1 \rangle = -t$

$$\begin{pmatrix} 0 & -t & 0 & \dots & 0 \\ -t & 0 & -t & 0 & 0 \\ 0 & -t & 0 & -t & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_j \\ \vdots \\ c_N \end{pmatrix} = E_0^{(1)} \begin{pmatrix} c_1 \\ \vdots \\ c_j \\ \vdots \\ c_N \end{pmatrix}$$

本徵方程式：

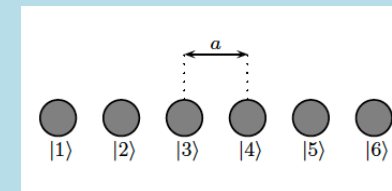
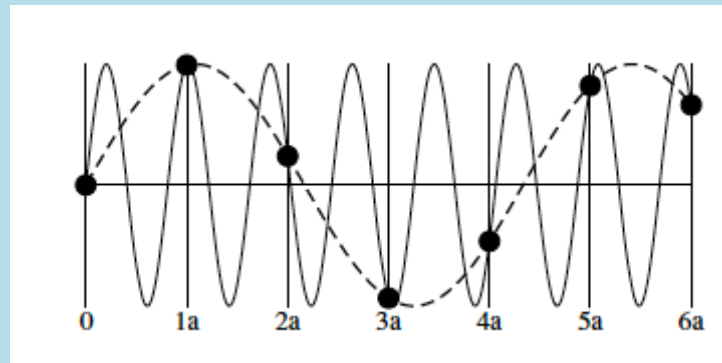
$$\begin{pmatrix} 0 & -t & 0 & \dots & 0 \\ -t & 0 & -t & 0 & 0 \\ 0 & -t & 0 & -t & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_j \\ \vdots \\ c_N \end{pmatrix} = E_0^{(1)} \begin{pmatrix} c_1 \\ \vdots \\ c_j \\ \vdots \\ c_N \end{pmatrix}$$

$$\sim \begin{pmatrix} e^{-ika} \\ e^{-i2ka} \\ \vdots \\ e^{-i(j-1)ka} \\ e^{-ijk a} \\ e^{-i(j+1)ka} \\ \vdots \\ e^{-iNka} \end{pmatrix}$$

*因為此式有平移對稱，解已經可以猜出來：

$c_j \sim e^{-ijk a} = e^{-ikja}$ 第個原子上的電子所占分量，就是平面波在此原子位置的值。

實數部可以這樣理解：



常數 k 稱晶格動量，一不同的 k 對應一特定的態，*總共會有 N 個本徵態。

但如果將 $k + \frac{2\pi}{a}$ ， $kja \rightarrow kja + 2j\pi$ ， e^{-ikja} 對應完全一樣的函數。

因此會將限制在一個範圍內：

$$-\frac{\pi}{a} < k < \frac{\pi}{a}$$

本徵方程式：

$$c_j \sim e^{-ijka}$$

$$\begin{pmatrix} 0 & -t & 0 & \dots & 0 \\ -t & 0 & -t & 0 & 0 \\ 0 & -t & 0 & -t & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_j \\ \vdots \\ c_N \end{pmatrix} = E_0^{(1)} \begin{pmatrix} c_1 \\ \vdots \\ c_j \\ \vdots \\ c_N \end{pmatrix}$$

$$\sim \begin{pmatrix} e^{-ika} \\ e^{-i2ka} \\ \vdots \\ e^{-i(j-1)ka} \\ e^{-ijka} \\ e^{-i(j+1)ka} \\ \vdots \\ e^{-iNka} \end{pmatrix}$$

這個解的特徵是鄰近的兩個分量比例沿整個固體都相等：

$$\frac{c_{j+1}}{c_j} \sim e^{-ika}$$

可以說是等比數列！這正適合連接相鄰原子的位能矩陣。

例如上式第 j 個元素的等式： $-tc_{j-1} - tc_{j+1} = E_0^{(1)} c_j$

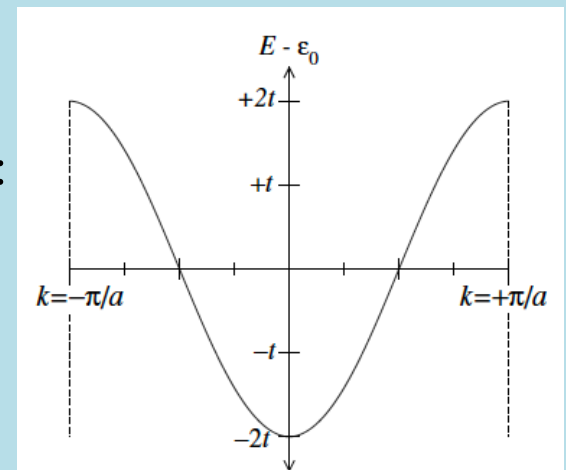
整式除以 c_j ，得： $-te^{+ika} - te^{-ika} = E_0^{(1)}$ 且與 j 無關。

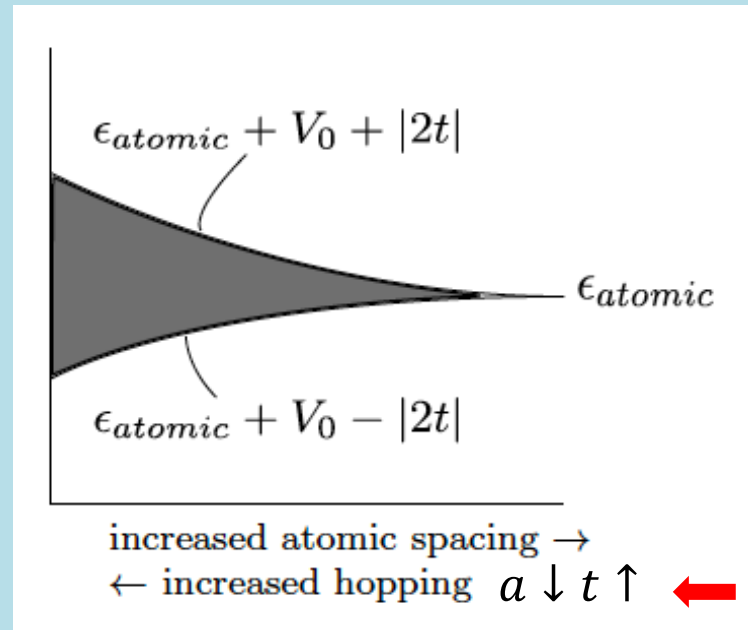
代入就可以解出能量本徵值： $E_0^{(1)} = 2t \cos ka$

注意能量有極大值 $2t$ ，及極小值 $-2t$ ，而且在 $-2t, 2t$ 之間任何值都有能態，

加上未微擾電子 $|j\rangle$ 態在原來第 j 個原子中的能量 V_0 ，得：

$$E = V_0 + 2t \cos ka$$





能態的總數量 N 極龐大，**能量間隙** $= 4t$ 微小，因此相鄰能態能量差很小。

形成一近似是連續的能帶 Energy Band。

這個結果應該在預料之中！

這裡有 N 個簡併態，受到週期性位能微擾而混雜。

標準的微擾計算結果就是簡併破壞，而分裂為能量不同的 N 個能態。

分裂後的能量寬度大致就與位能大小 t 相當，

一般來說， $a \downarrow$ ， $t \uparrow$ 。原子越靠近，能帶就越寬。

原子內的一個能階，在晶體中就會形成一近似是連續的能帶Energy Band。

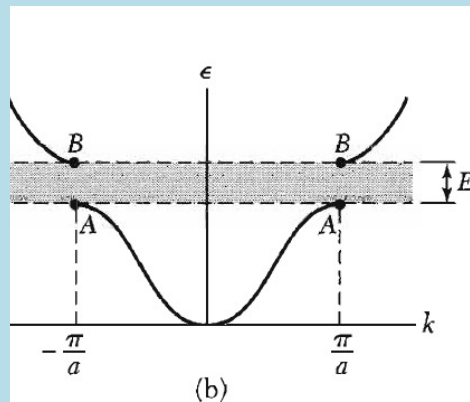
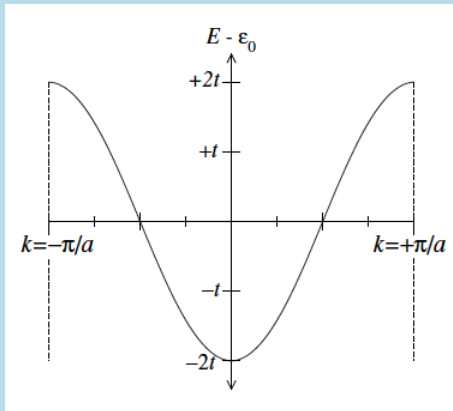
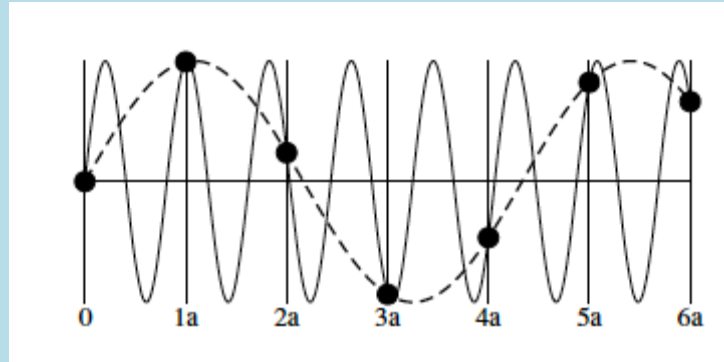
$$\sum_{j=1}^N e^{-ikja} |j\rangle$$

$$c_j \sim e^{-ikja}$$

很像平面波。這是屬於個別原子的 $|j\rangle$ 的線性疊加。
這些原來屬於私人的電子現在是**公共財產**！

保留了在地性的全球化電子！

實數部可以這樣理解：



在接近底部處， $E \sim E(0) + ta^2 k^2$ 如同一自由電子，

$$E^{(0)} = \frac{\hbar^2 k^2}{2m}$$

這就是Nearly Free Electron Model會成功的原因，但質量必須取有效質量：

$$m^* = \frac{\hbar^2}{2ta^2}$$

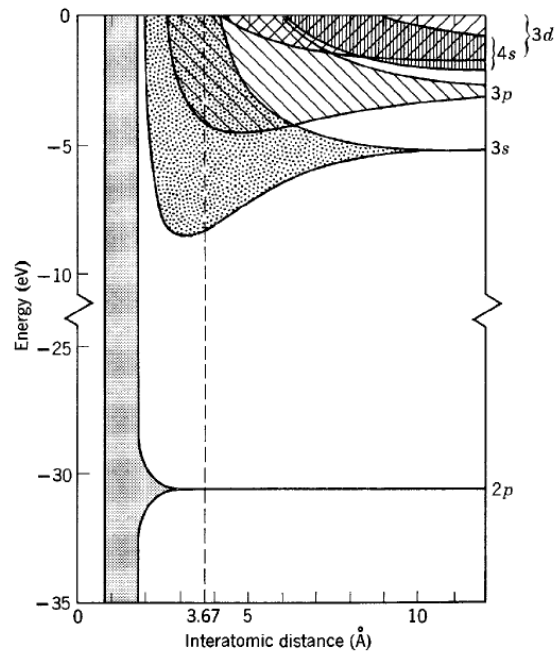
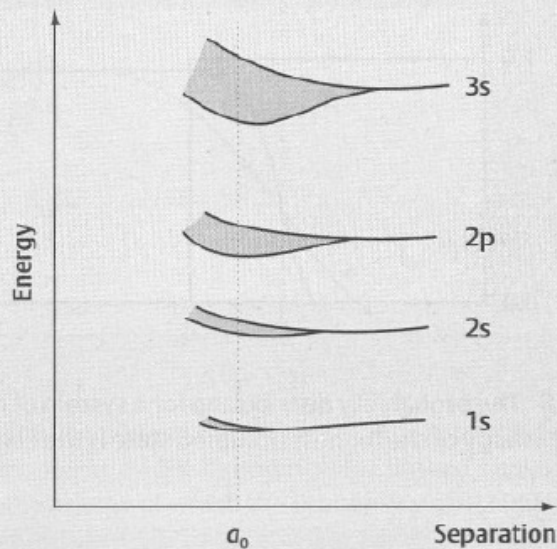
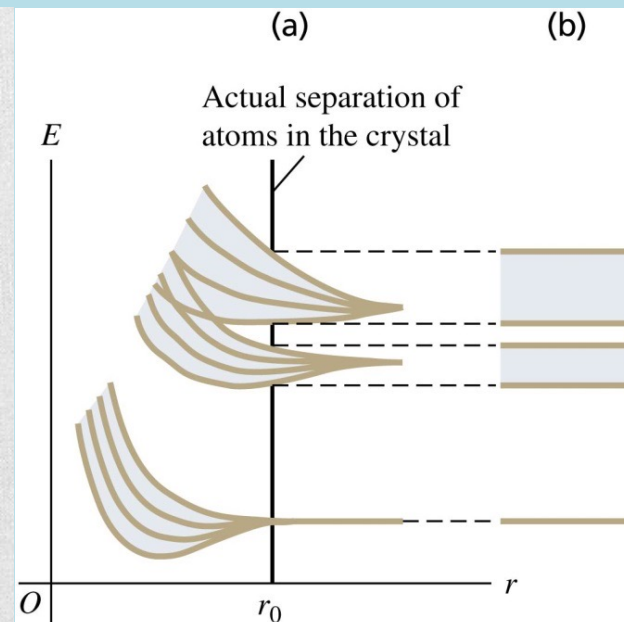


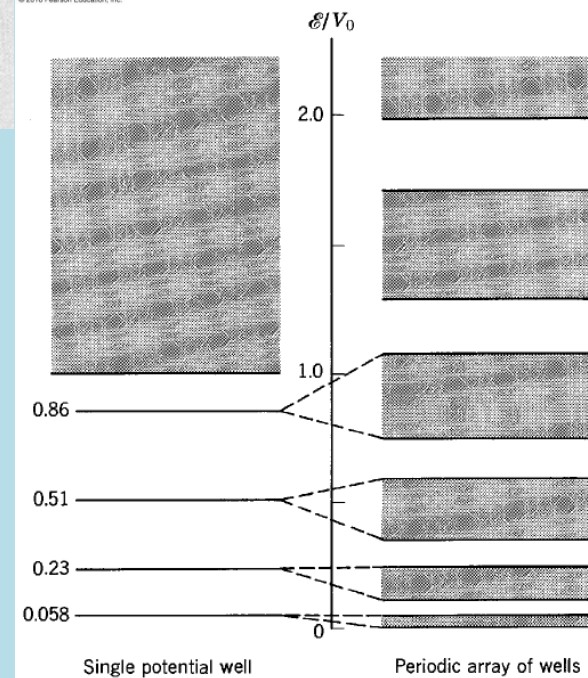
Figure 13-3 Showing the formation of energy bands for sodium atoms as the interatomic separation decreases. The observed interatomic separation in solid sodium is indicated. The energy levels that constitute each *p* or *d* band are not indicated.



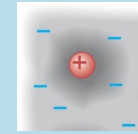
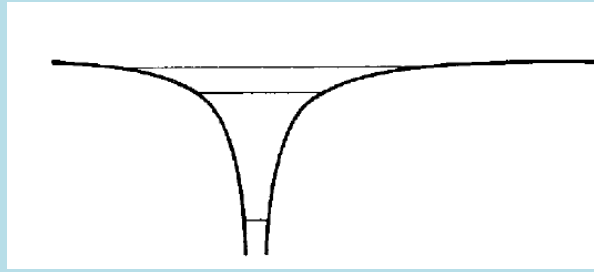
1.15 The formation of 1s, 2s, 2p and 3s energy bands in sodium. Bands become progressively narrower for electrons which are more bound to the parent nucleus.



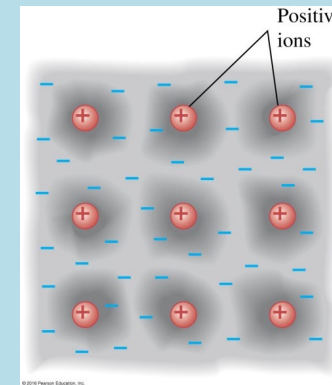
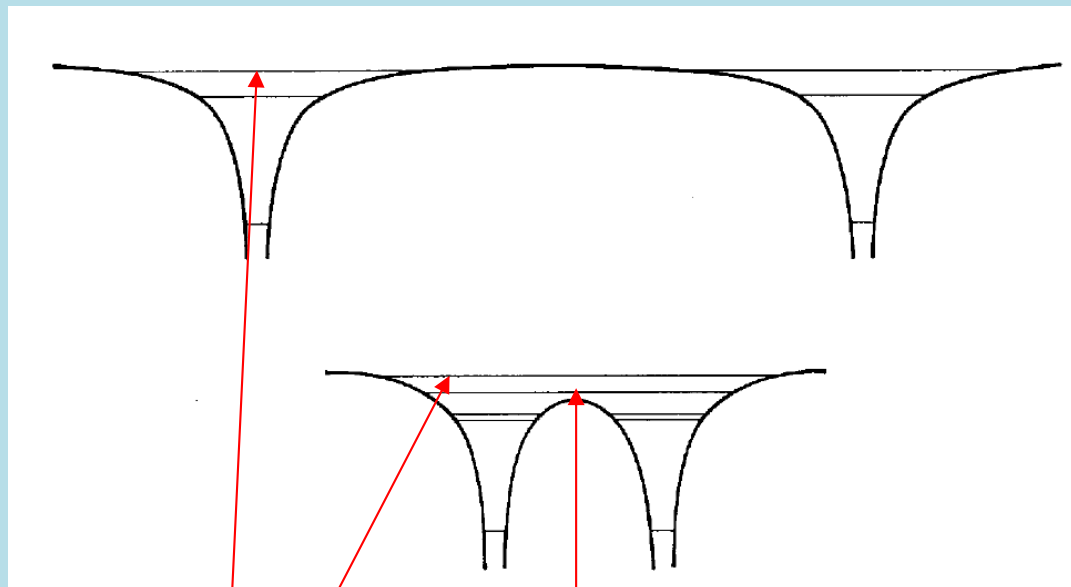
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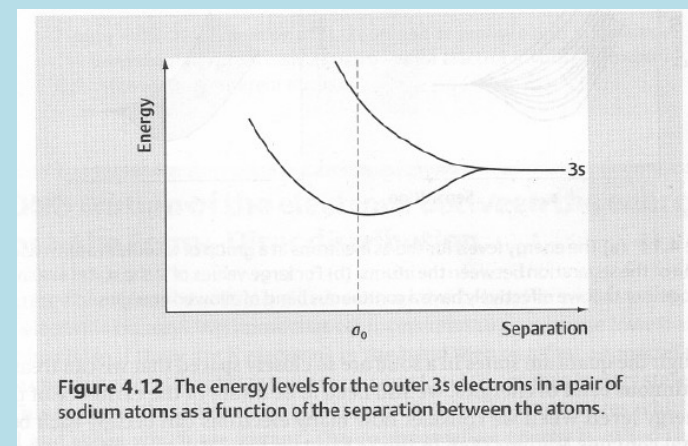
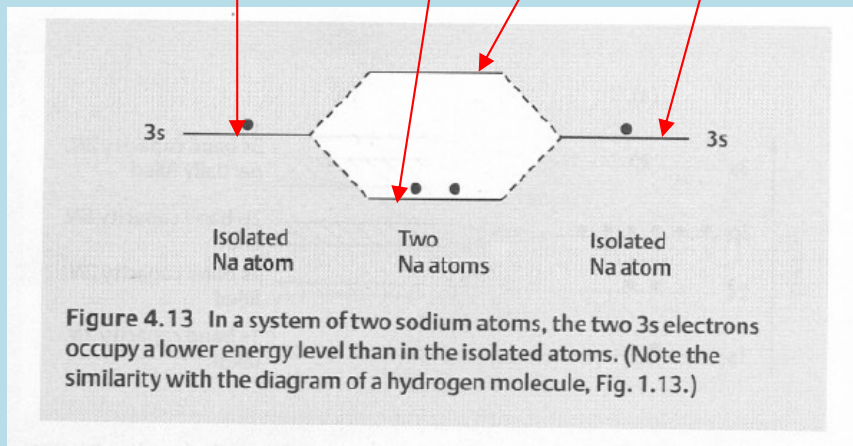
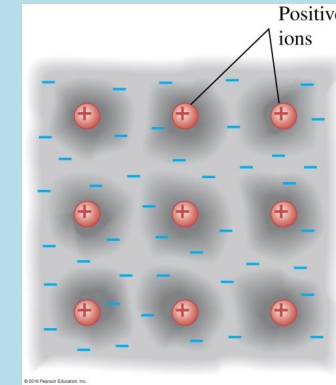
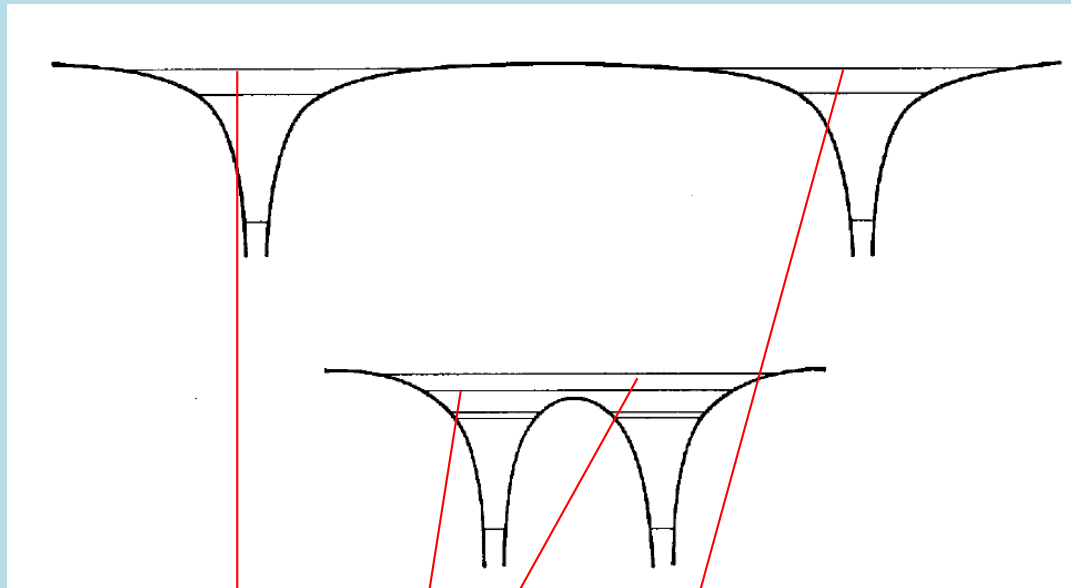
這是固態鈉的能帶。



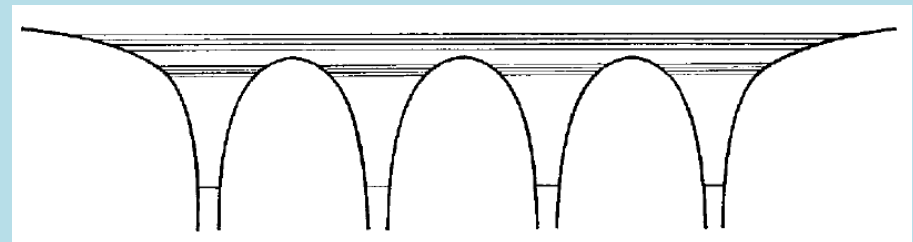
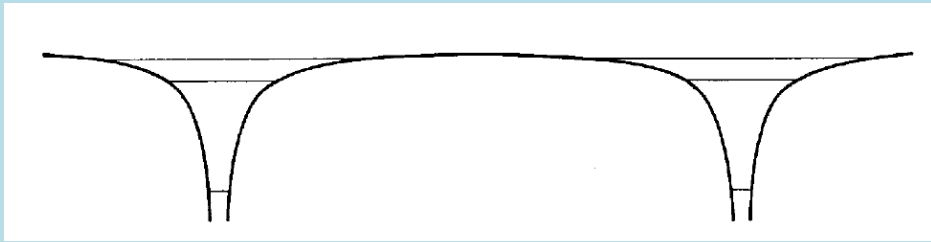
在獨立的原子中，位能為庫倫位能，電子的能態形成分離的能階。
 當原子彼此靠近時，多個原子核的庫倫位能都必須考慮，
 也就是，電子會同時感覺多個原子核的電力。



原子間的庫倫電位能疊加後會下降，
 能量比較高的能態，就可能跨越原子間的位能。



跨越原子間的位能後，
 這兩個來自兩個原子，但原本能量相同的態會彼此混合，
 然後分裂為兩個能量相近的態。
 能量差會隨距離靠近而增加、但相對小於原來能階能量差。

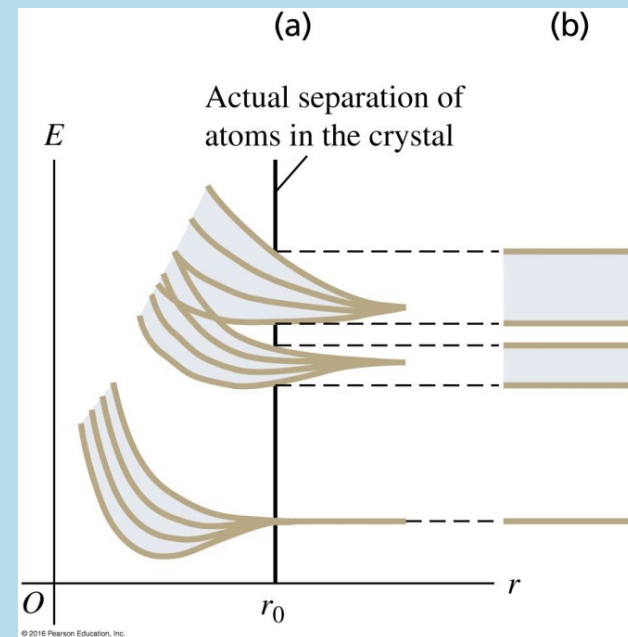
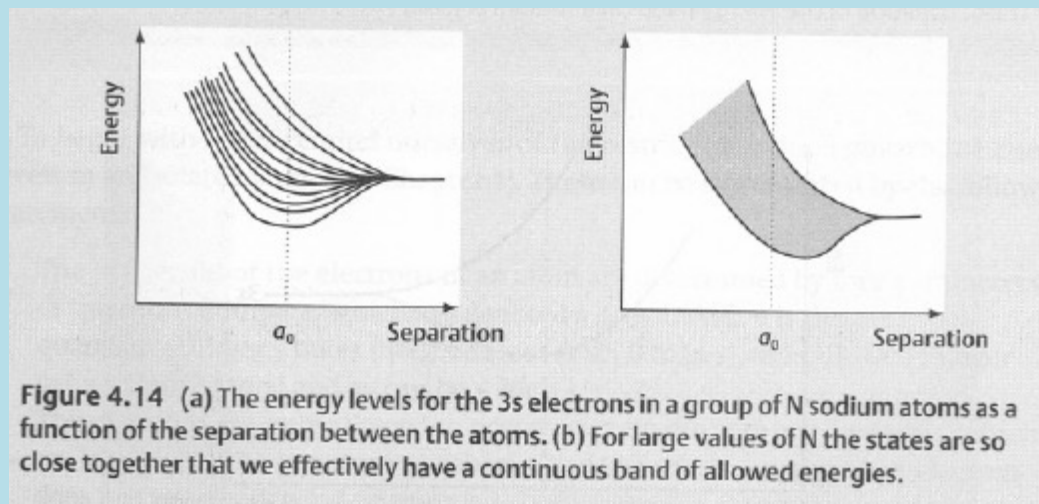


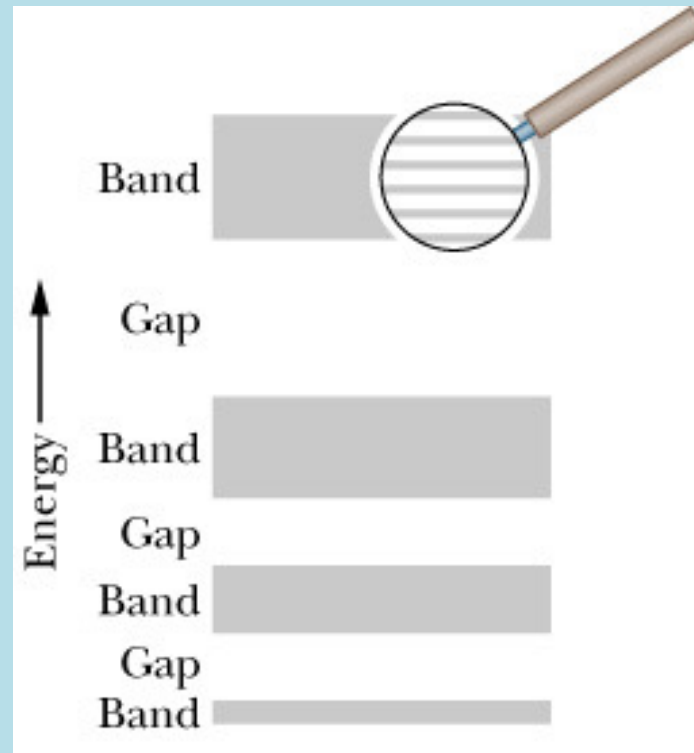
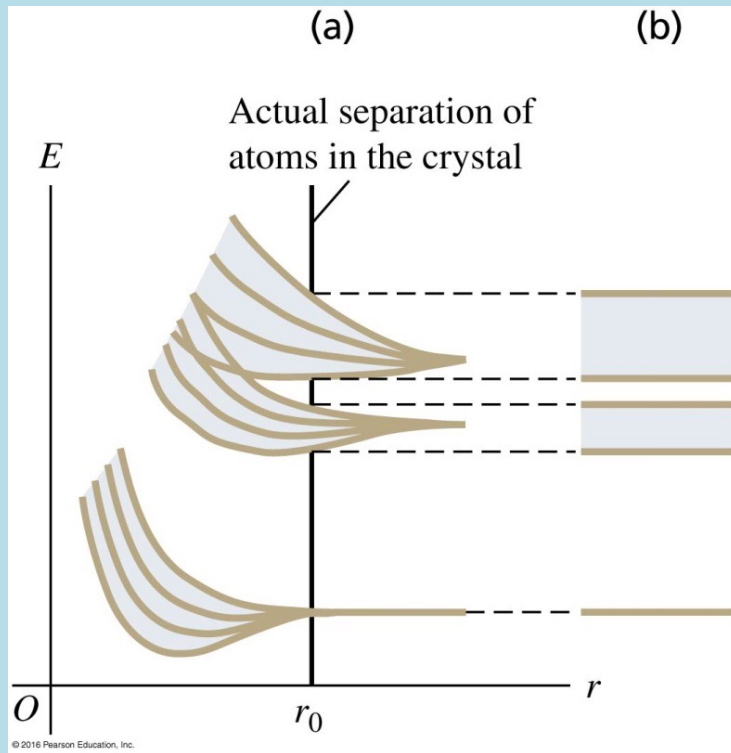
這些跨越原子間的能態，原來是來自能量相等的、束縛於單一原子中的能態，因此能態總數等於原子數目，數量龐大！

當原子距離縮小後，它們的能量會彼此出現些微差距，差距隨距離縮小而變大。

大量能階擠入微小的能量差距，這些能階就形成了幾乎連續的能帶 **Energy Band**！

在計算時，將距離取為真實的原子間距，就得到真實的電子能態所形成的能帶。





所以固體中的電子能態(能量本徵值)，形成一個個能帶，能帶之間可能有間隙！

固態物理之父Bloch

現在要幫電子往能態裡面填。



如同在原子中，將電子一個個在能階圖由下往上填。

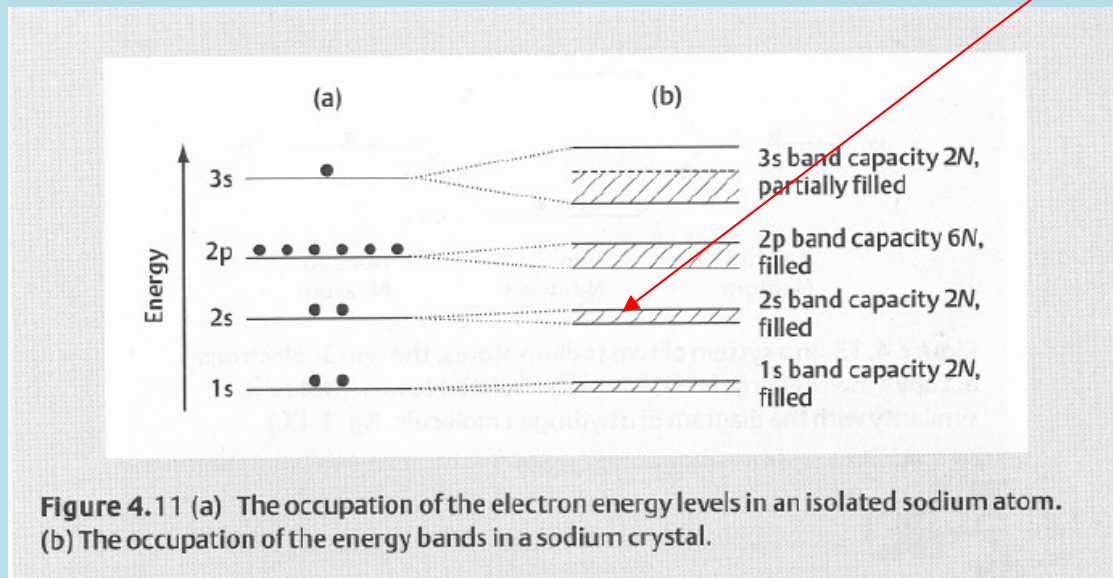
在固體中也是將電子在能帶中一個個由下往上填。

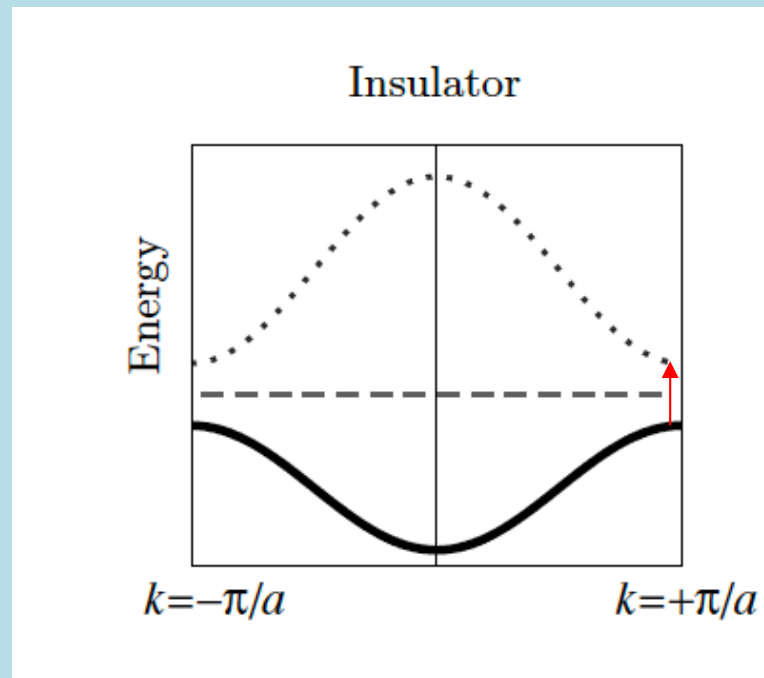
能帶是 N 個原子原本獨立的原子能階混雜而成，

可以嚴格證明一個能帶內有 N 個狀態。考慮兩個自旋，能帶中的狀態數是 $2N$ 。

固體鈉 $2s$ 的能帶來自原子鈉 $2s$ 的能階。

原來原子鈉 $2s$ 的能階有二個電子，因此有 $2N$ 顆電子可以填。正好填滿！





在填滿的能帶內的電子，完全無法改變狀態，除非付出很高的能量，跳到下一能帶。這些電子便與導電無關，稱為價電子Valance。絕緣體便是所有能帶都被填滿的固體。

原子鈉 $3s$ 的能階只有一個電子，
因此固體鈉 $3s$ 的能帶只有 N 顆電子可以填，無法填滿能帶內 $2N$ 個態！

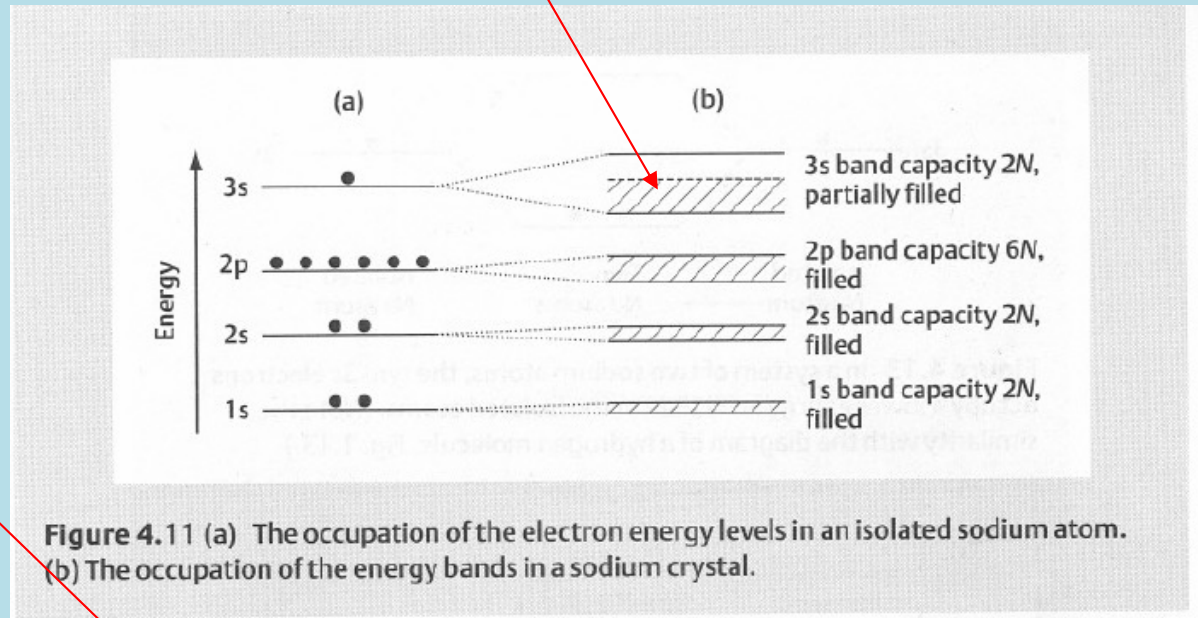
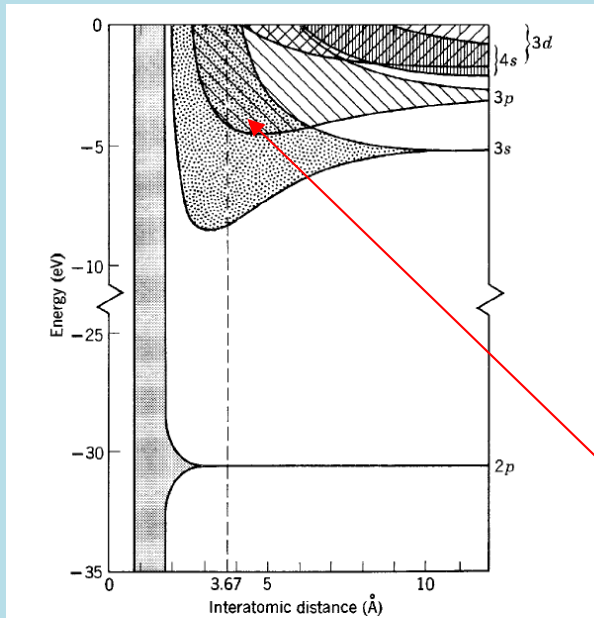
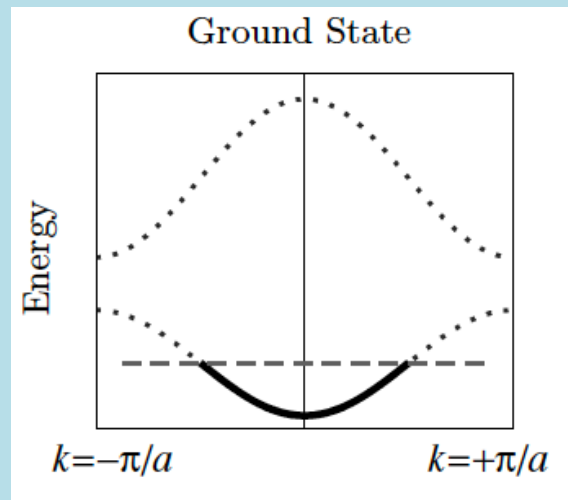
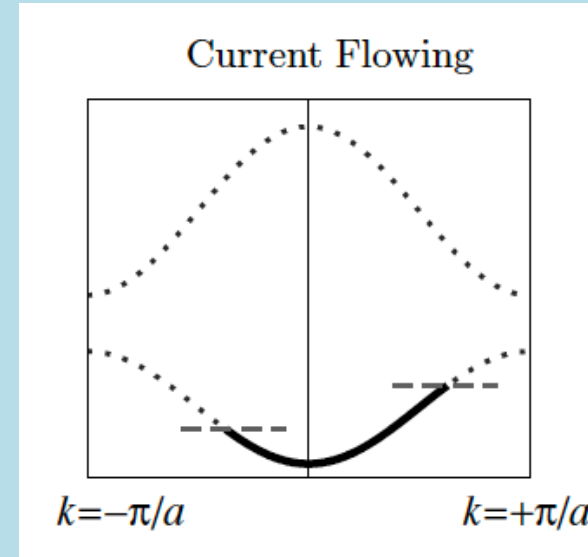
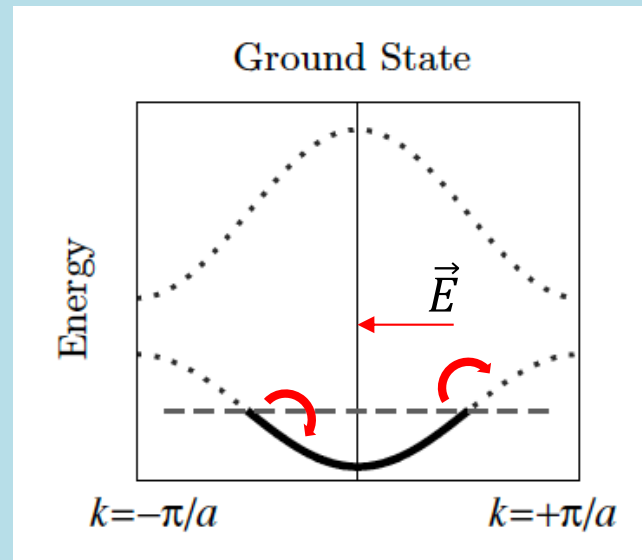


Figure 4.11 (a) The occupation of the electron energy levels in an isolated sodium atom. (b) The occupation of the energy bands in a sodium crystal.

固體鈉 $3s$ 的能帶甚至是原子鈉 $3s$ 及 $3p$ 的能階的混合。能帶中的狀態數大於 $2N$ 。

這個能帶將會是未填滿！



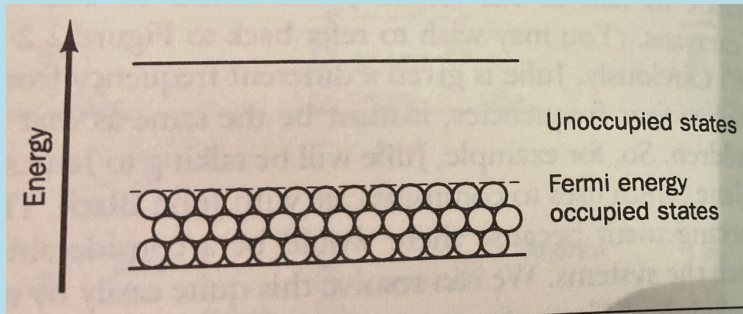


在半滿的能帶中，電子便有狀態可以供它改變運動狀態。

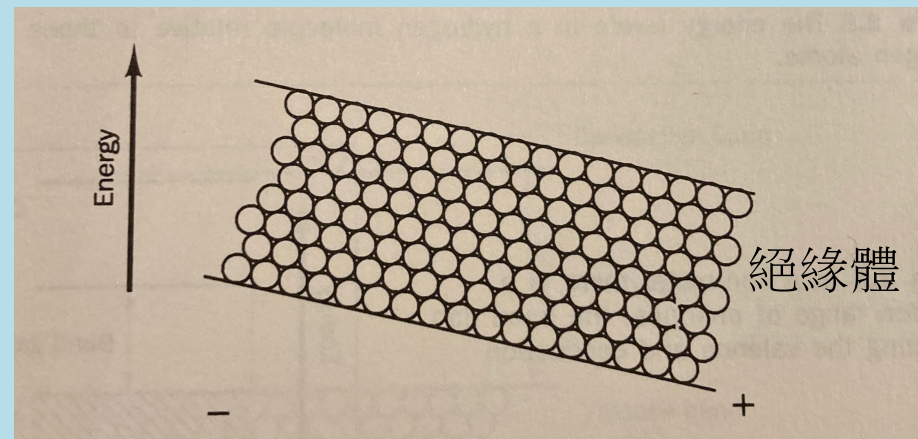
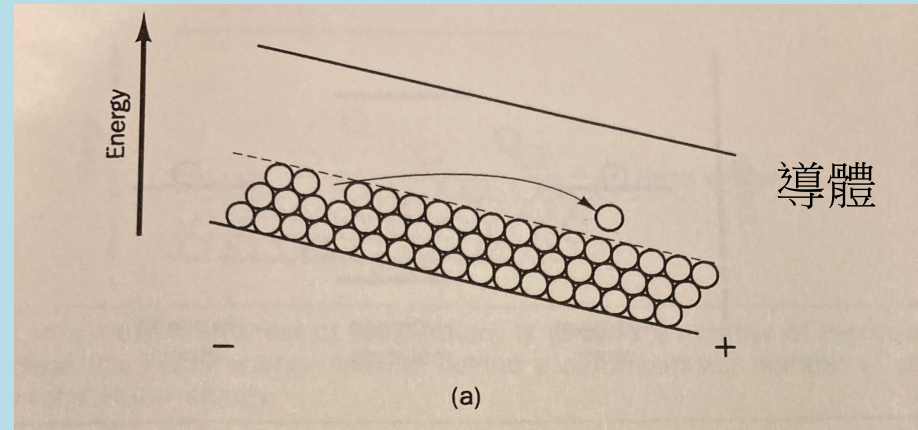
加上電場後，可以證明所有電子的晶體動量 k 會如圖隨時間增加： $\delta k = -\frac{eE}{\hbar} t$ 。

如此往電場反向的晶體動量會大於正向，電子密度總和是向反向運動的。

所以這樣半滿能帶中的電子，便能導電，稱傳導電子，此能帶就稱傳導能帶。

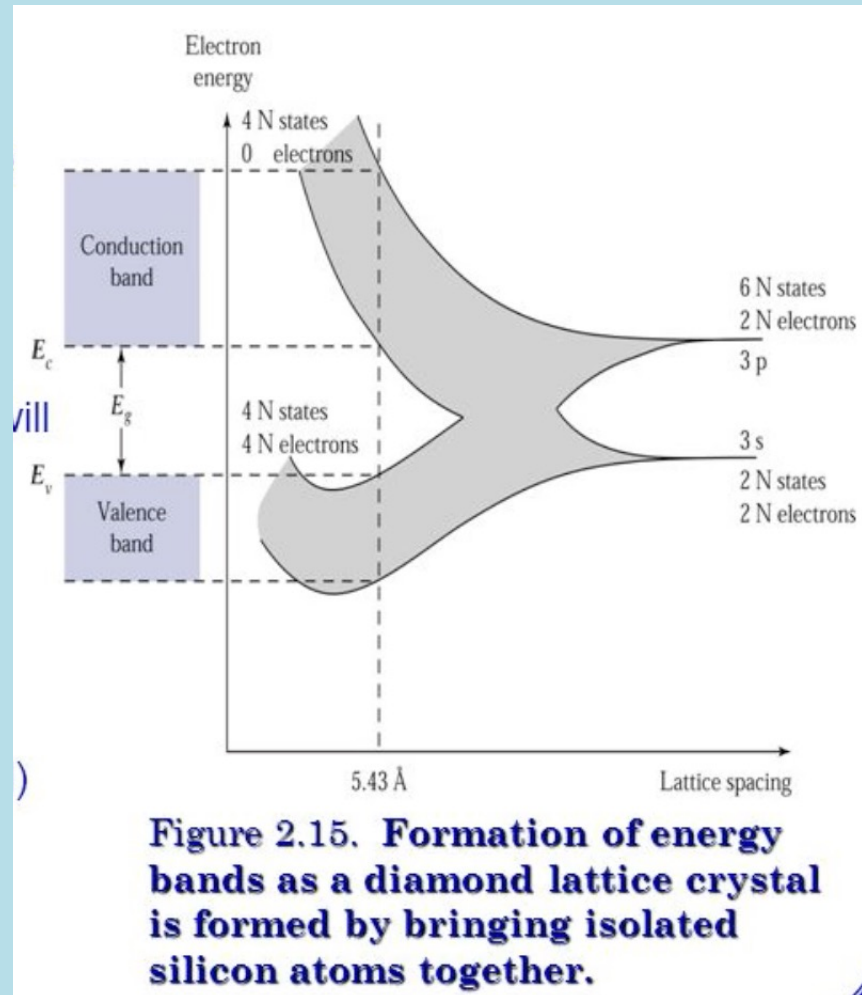


未加電壓

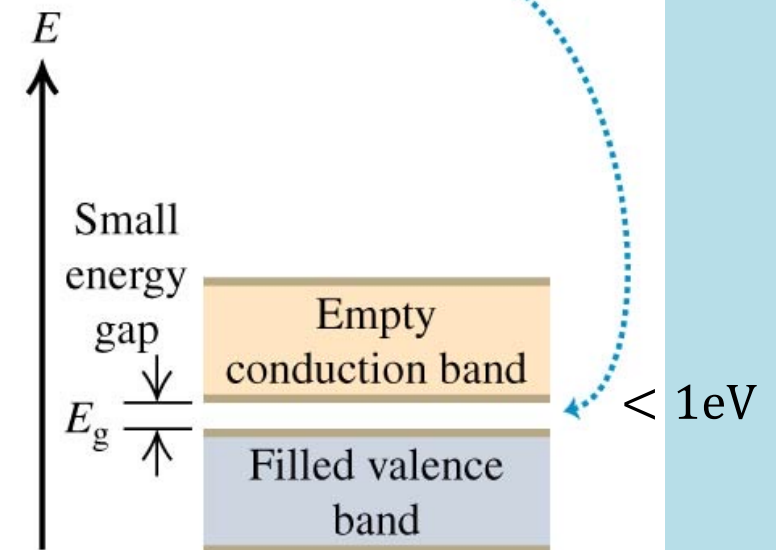


加電壓

半導體 Semiconductor



(b) A semiconductor has the same band structure as an insulator but a smaller gap between the valence and conduction bands.



若全滿的Valence能帶與全空的Conduction能帶間隙很小時，情況與絕緣體很不一樣！

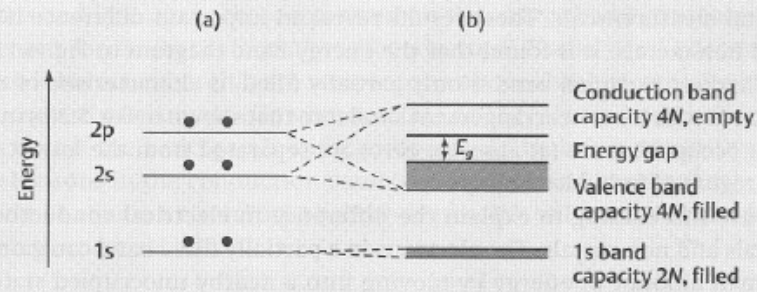


Figure 5.2 The occupation of (a) the energy levels in an isolated carbon atom, and (b) the energy bands in a diamond crystal. Notice that there is an energy range E_g separating the highest occupied states (in the valence band) from the lowest vacant states (in the conduction band). This is a characteristic feature of all insulators.

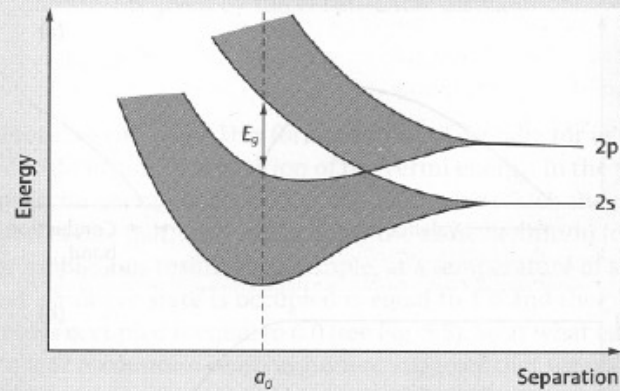
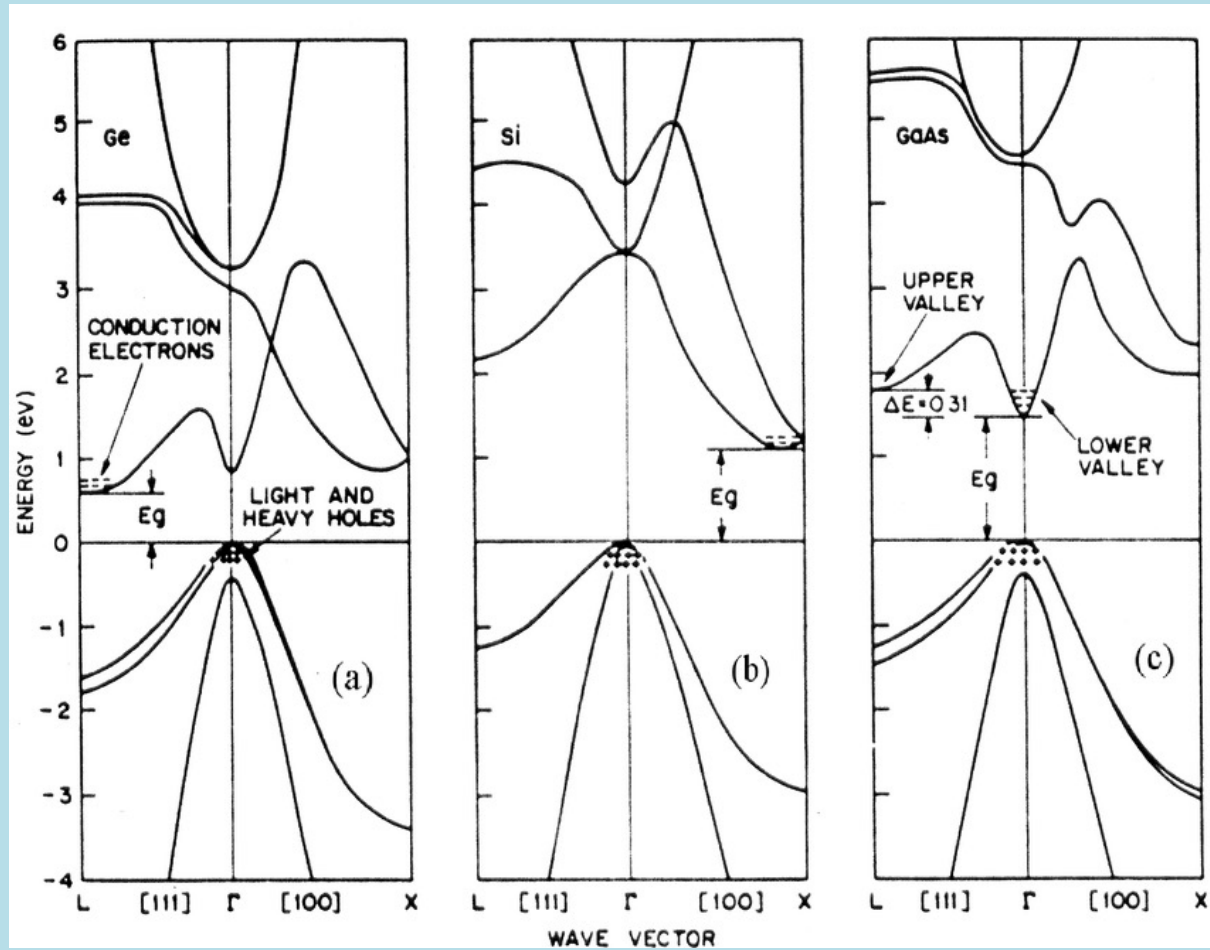
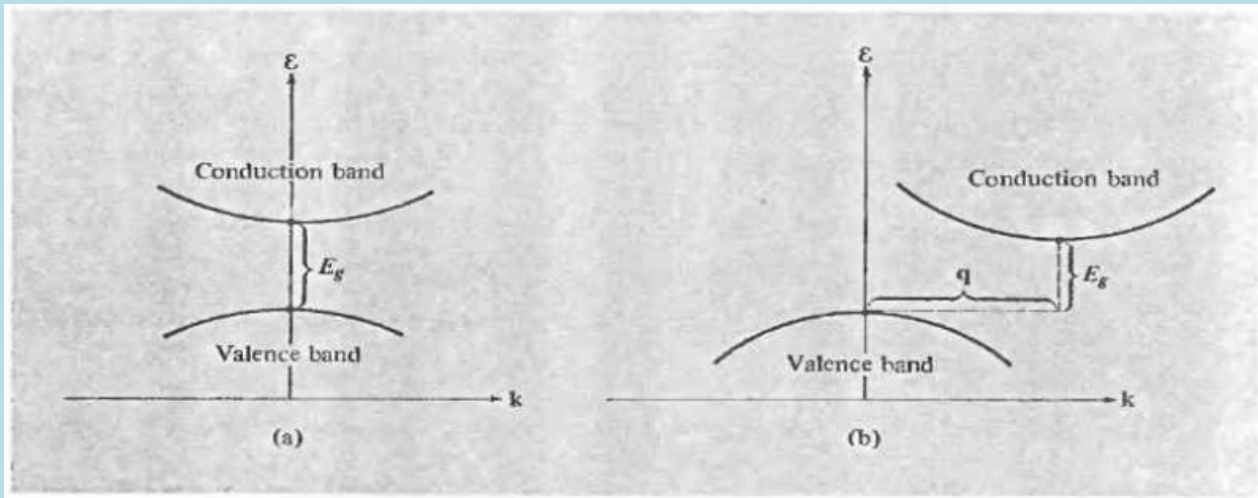
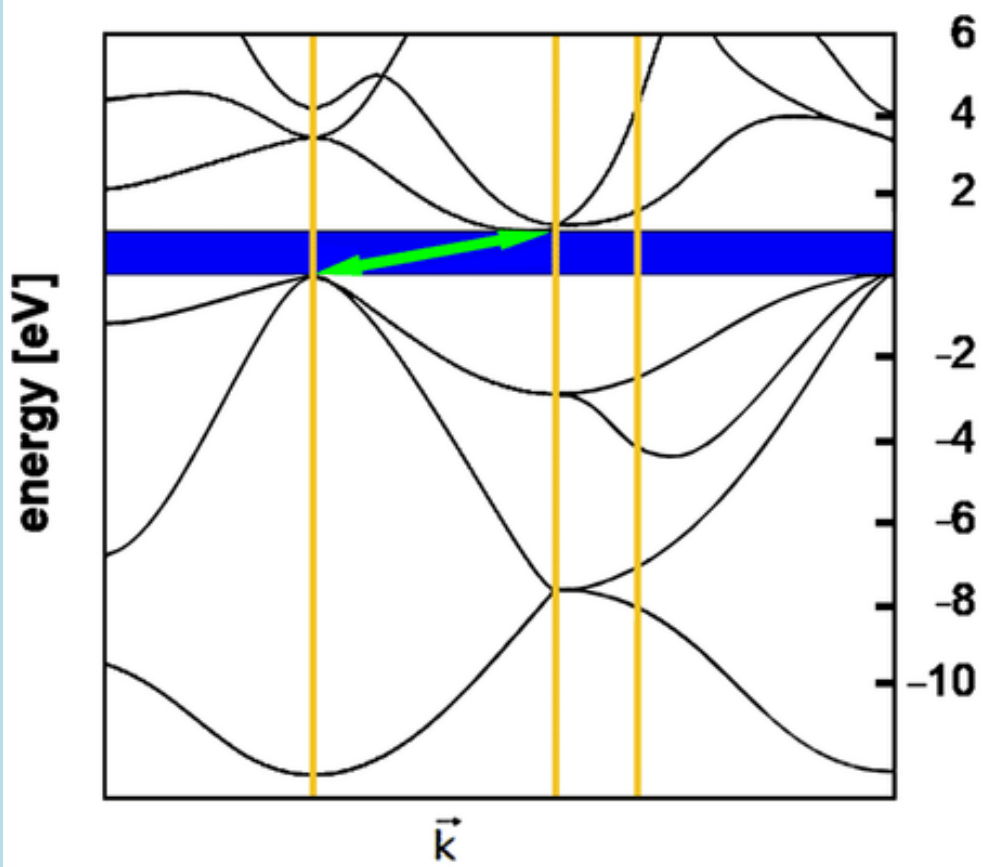


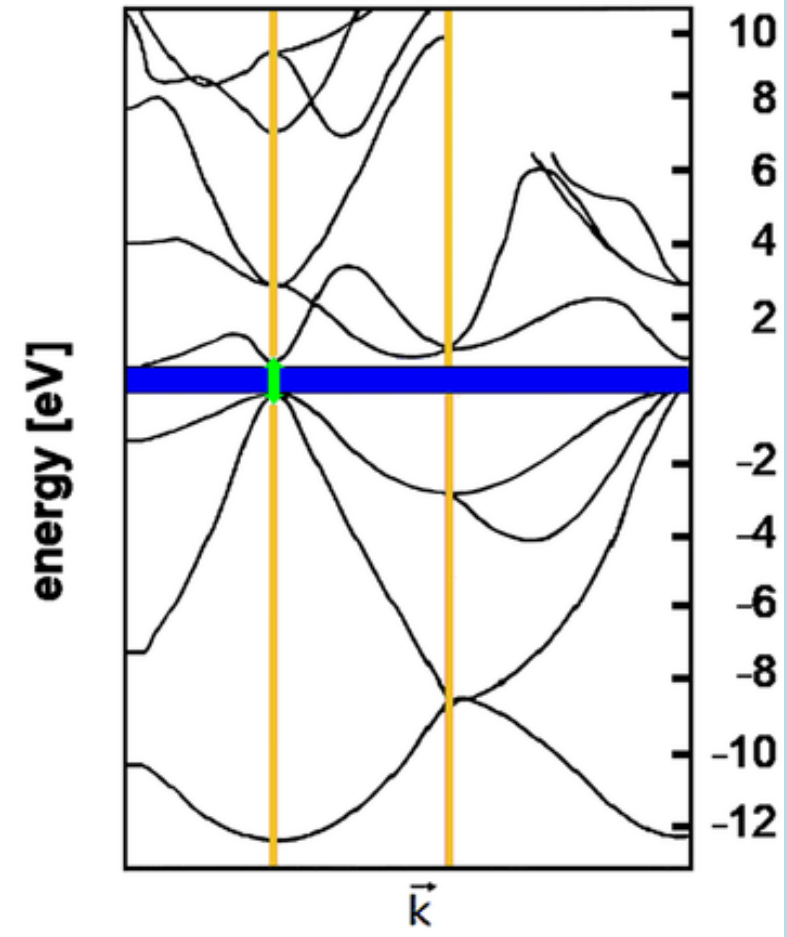
Figure 5.3 The energy levels of the 2s and 2p states for a group of N carbon atoms as a function of the separation of the atoms.

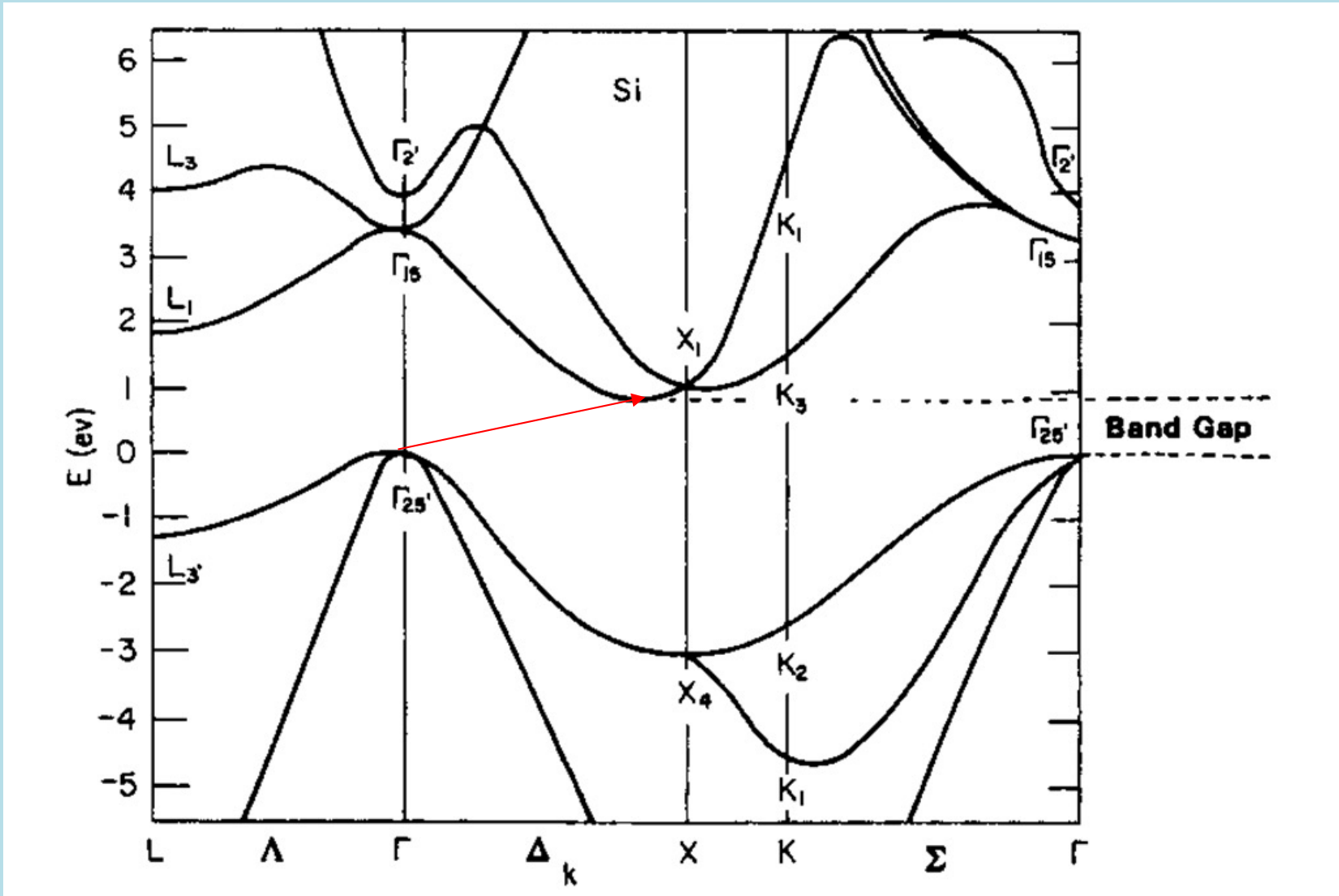


Silicon

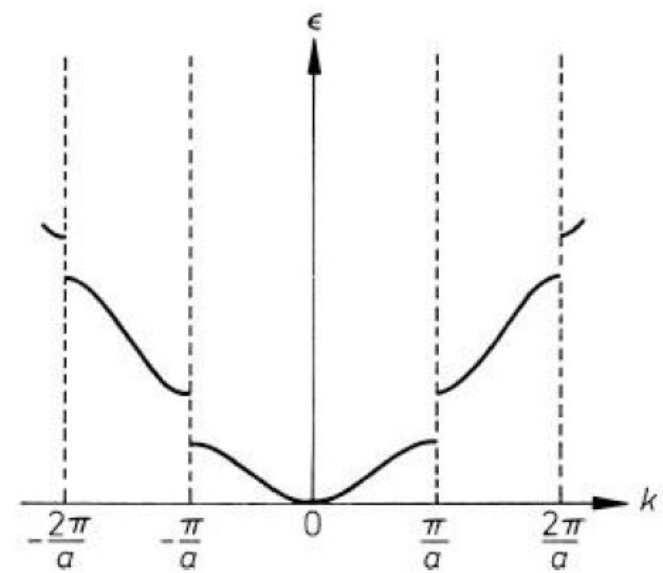
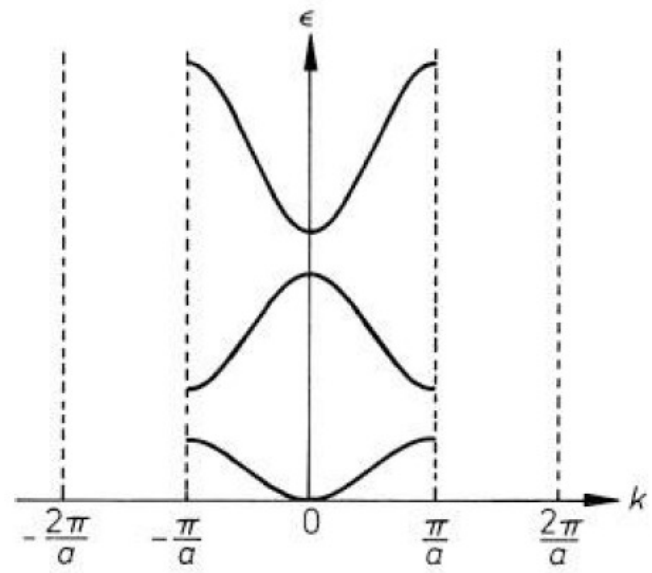


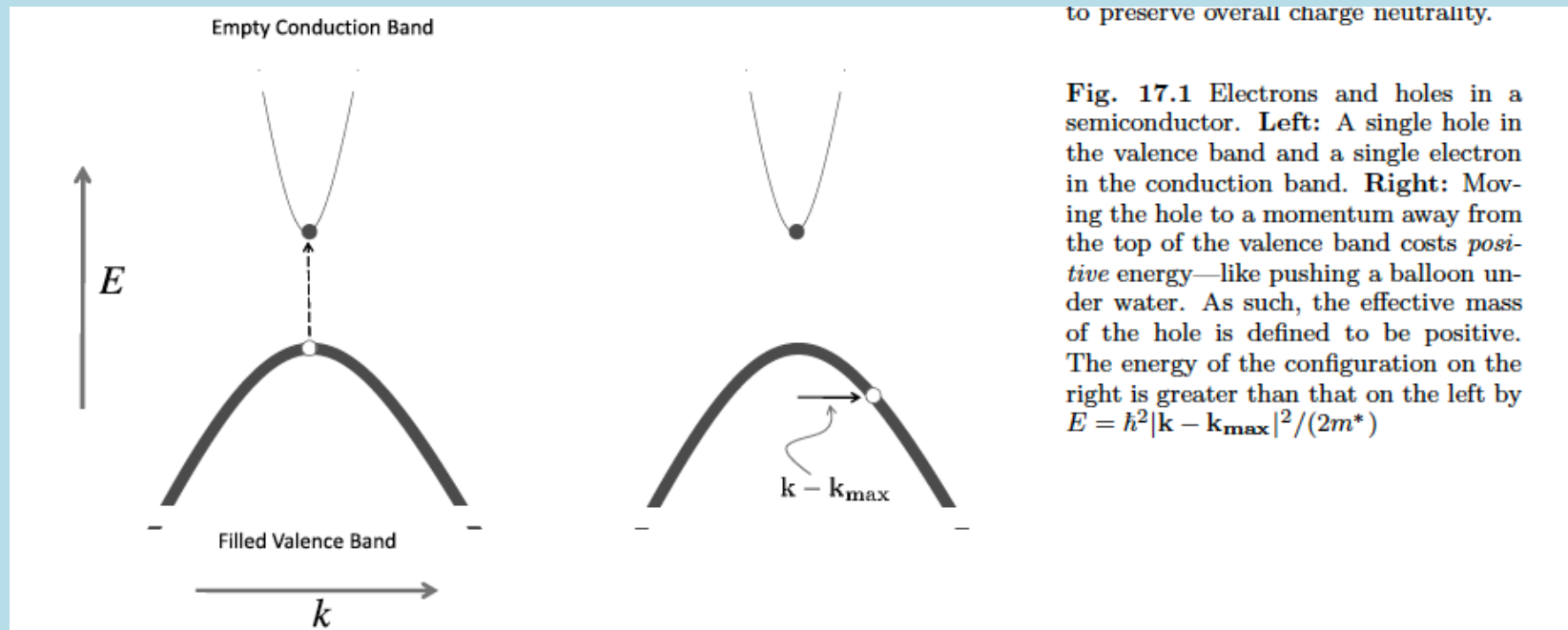
Germanium





橫軸是態波函數的晶體動量





to preserve overall charge neutrality.

Fig. 17.1 Electrons and holes in a semiconductor. **Left:** A single hole in the valence band and a single electron in the conduction band. **Right:** Moving the hole to a momentum away from the top of the valence band costs *positive* energy—like pushing a balloon under water. As such, the effective mass of the hole is defined to be positive. The energy of the configuration on the right is greater than that on the left by $E = \hbar^2|\mathbf{k} - \mathbf{k}_{\max}|^2/(2m^*)$

Analogously we can define an effective mass for holes. Here things get a bit more complicated. For the top of the valence band, the energy dispersion for electrons would be

$$E = E_{\max} - \alpha|\mathbf{k} - \mathbf{k}_{\max}|^2 + \dots \quad (17.3)$$

with $\alpha > 0$. The modern convention is to *define the effective mass for holes at the top of a valence band to be always positive*⁸

$$\frac{\hbar^2}{m_{\text{hole}}^*} = -\frac{\partial^2 E}{\partial k^2} = 2\alpha. \quad (17.4)$$

The convention of the effective mass being positive makes sense because the energy to boost the hole from zero velocity ($\mathbf{k} = \mathbf{k}_{\max}$ at the top of the valence band) to finite velocity is positive. This energy is naturally given by

$$E_{\text{hole}} = \text{constant} + \frac{\hbar^2|\mathbf{k} - \mathbf{k}_{\max}|^2}{2m_{\text{hole}}^*}.$$