

# Stationary State in 1Dimension Periodic Potential

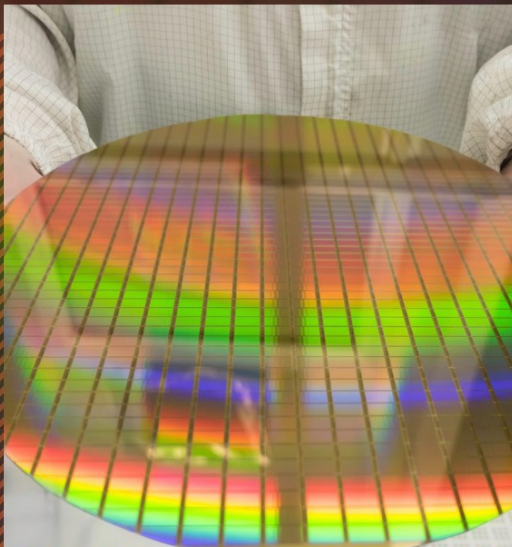
## 一維固態物理初步



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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

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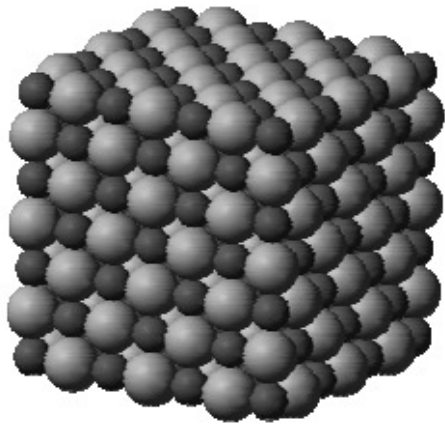
#科學 #張嘉泓 #物理好好玩 #晶圓 #半導體  
#矽島 #台積電 #電洞 #自動計算機



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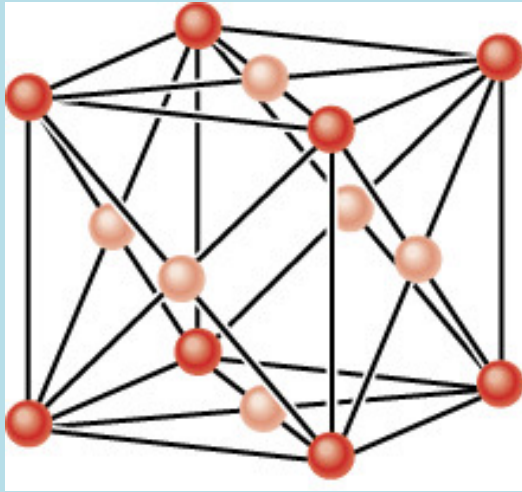
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## 固體是原子組成的晶格 Lattice

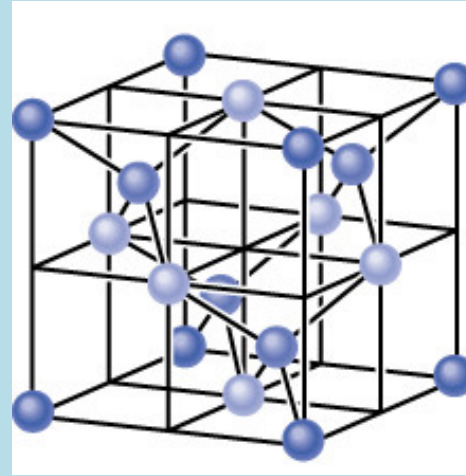


**Fig. 7.1:** **Left:** Small units reproduced periodically to form a crystal. This particular figure depicts NaCl (table salt), with the larger spheres being  $\text{Cl}^-$  ions and the smaller spheres being  $\text{Na}^+$  ions. **Right:** The macroscopic morphology of a crystal often will reflect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

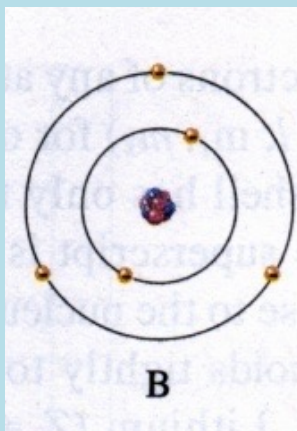
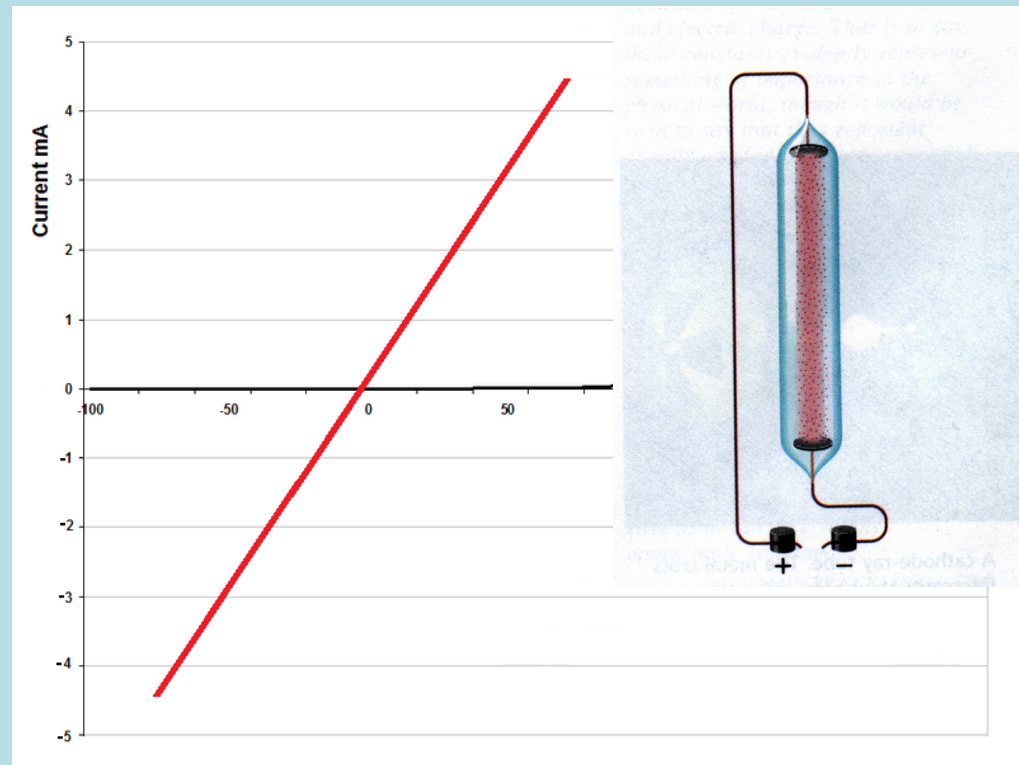
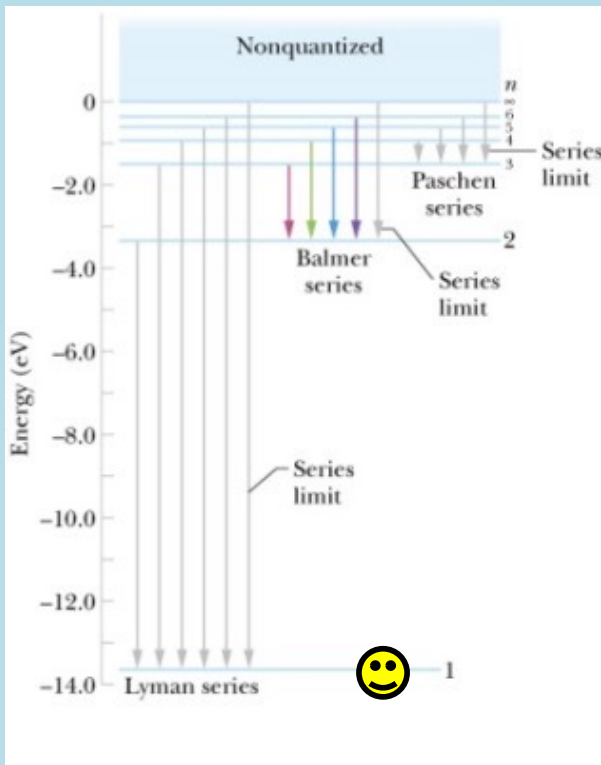
三維的晶體比較複雜，因此先從一維出發！



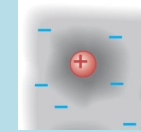
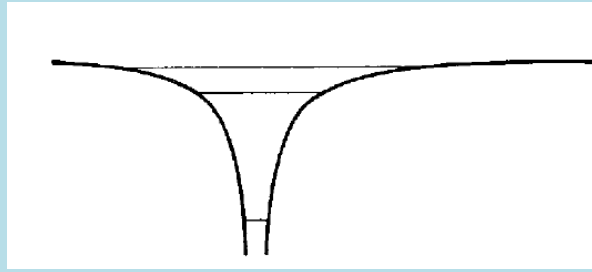
Copper fcc



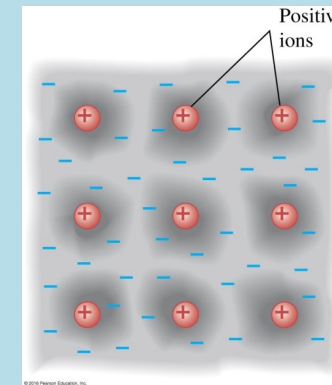
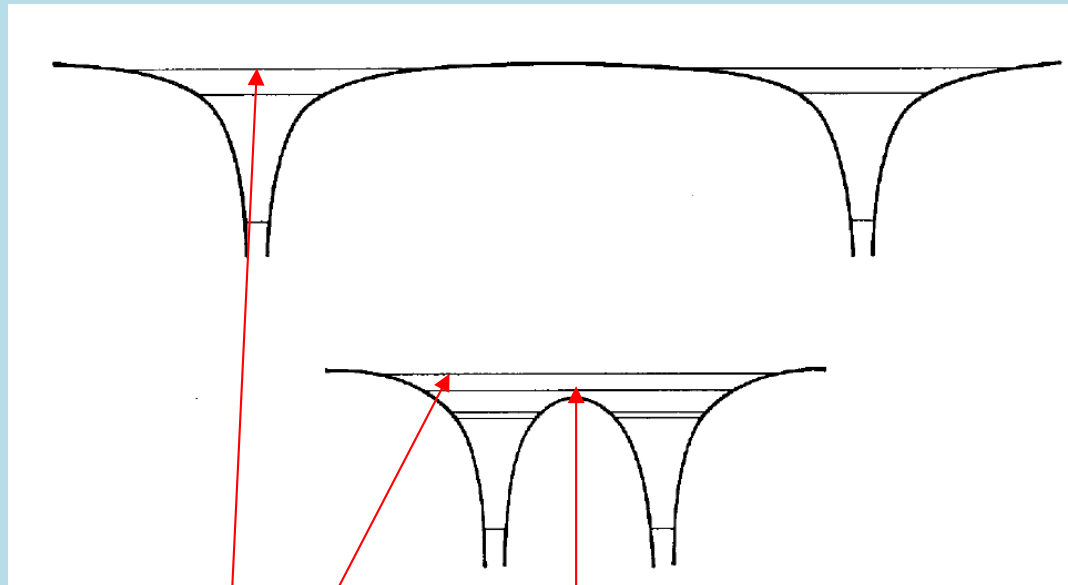
Silicon and Carbon



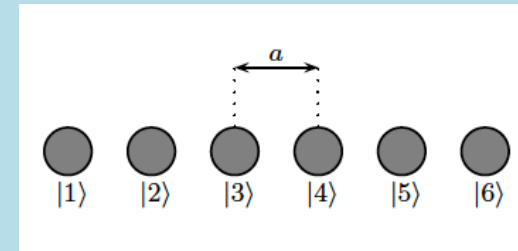
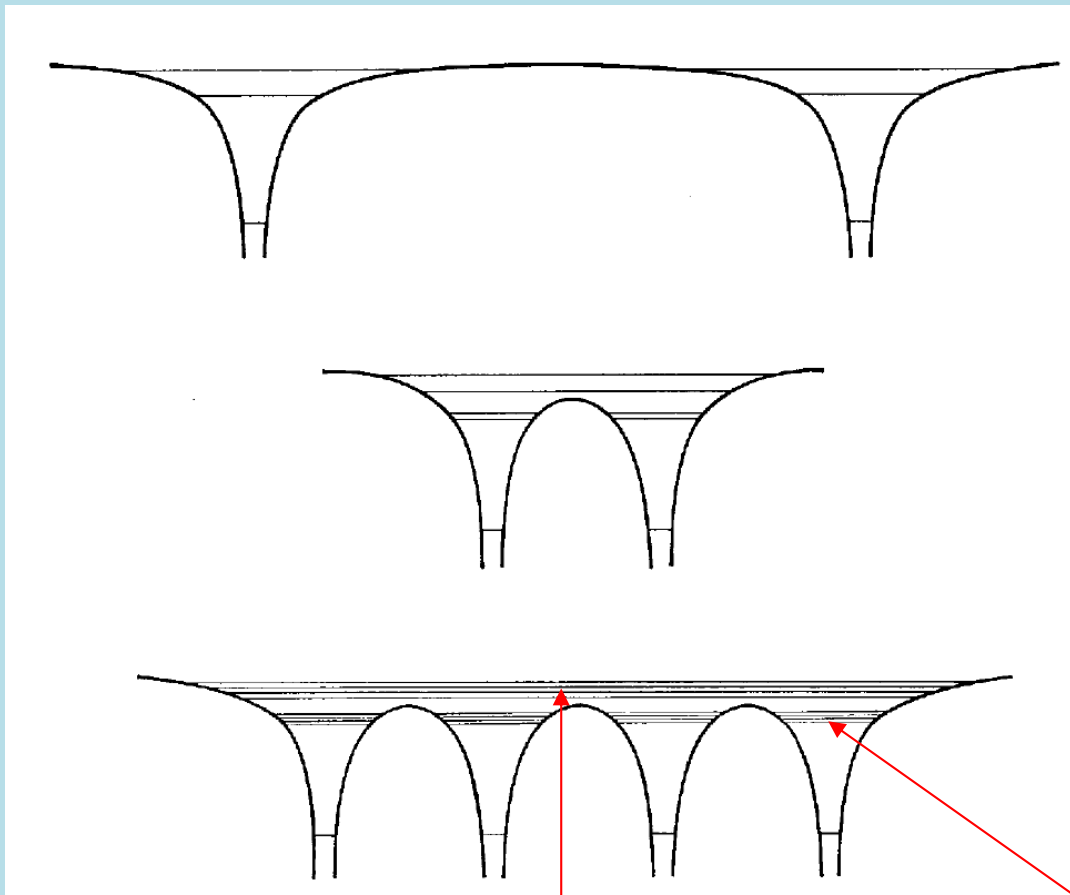
在原子中，電子被束縛在原子核旁邊。能量呈現能階的形式。要讓原來處於基態的電子離開原子核，至少需要13伏特的電壓。這對氣態的原子的確是對的！稱為氣體放電。但在固態導體中，顯然很小的電壓就能產生電流。歐姆定律。導體內為何有機動的mobile電荷可以自由流動？絕緣體內為何又沒有電荷可以流動呢？



在獨立的原子中，位能為庫倫位能，電子處於分離的能態。  
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，  
能量比較高的能態，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

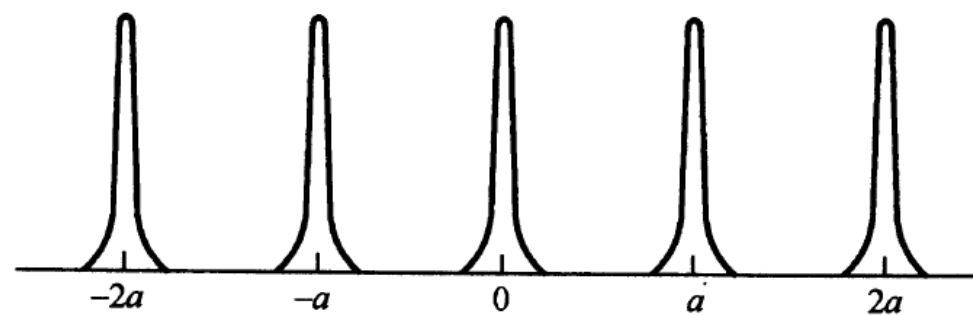
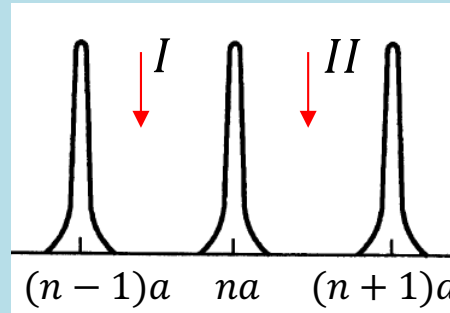


图 3.33 Dirac 梳



## 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在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：

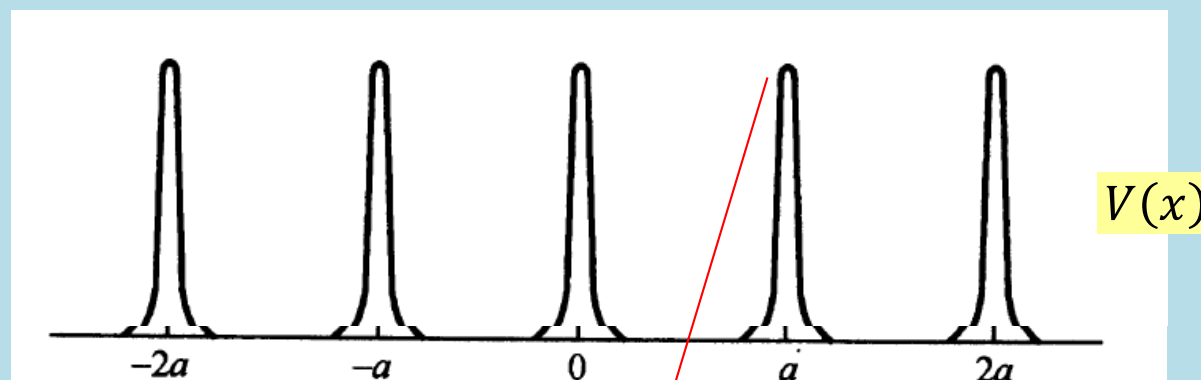
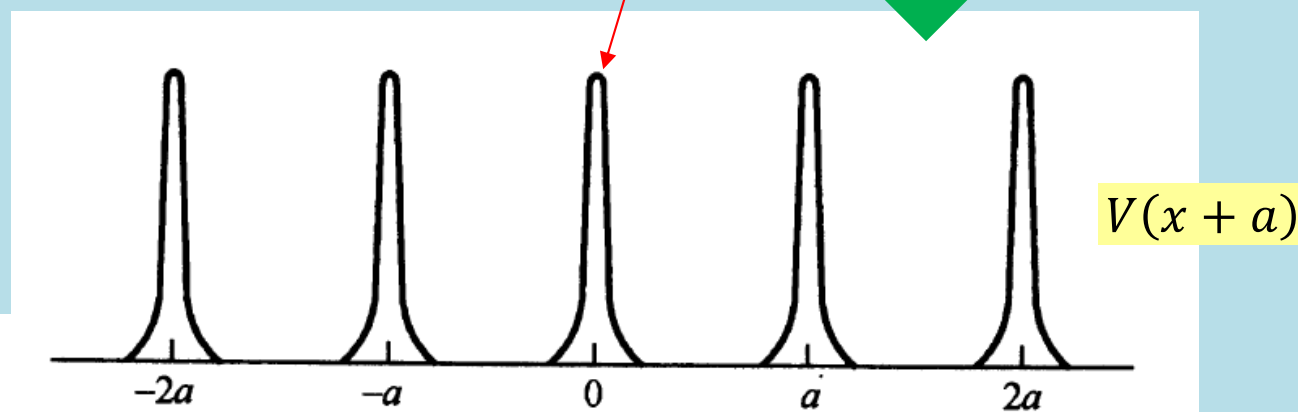


图 3.33 Dirac 梳

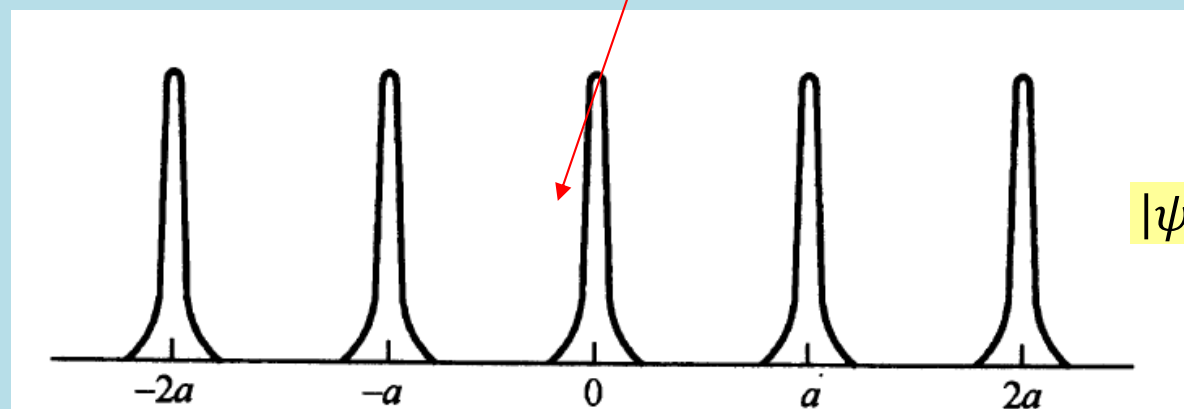
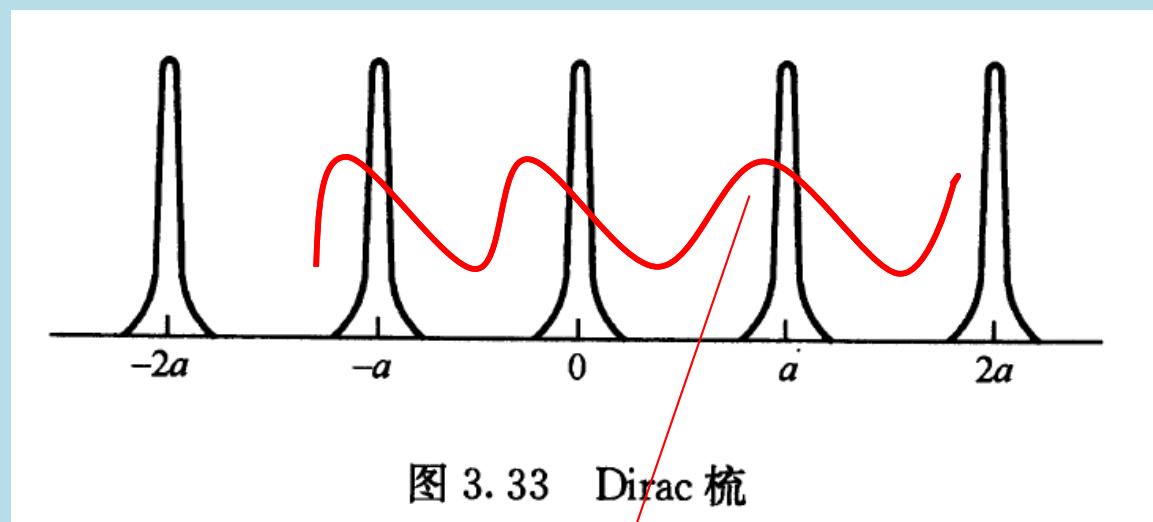


週期位能：

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

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：

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



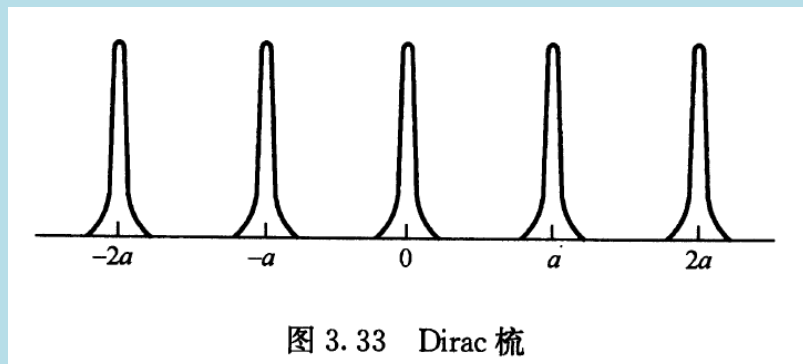


图 3.33 Dirac 梳

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：

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

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：

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

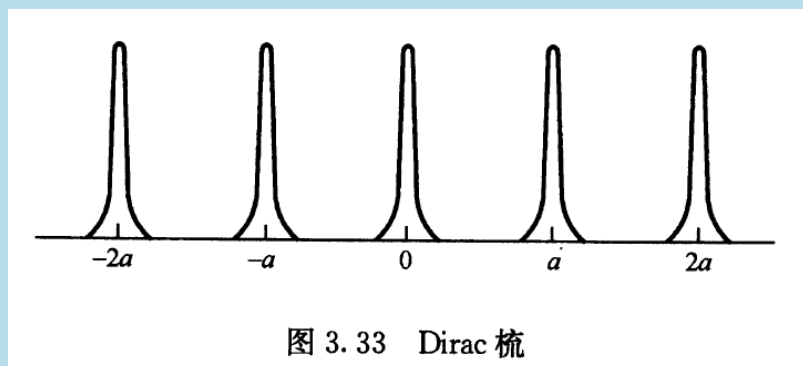


图 3.33 Dirac 梳

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  $\lambda_a$  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：

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

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！

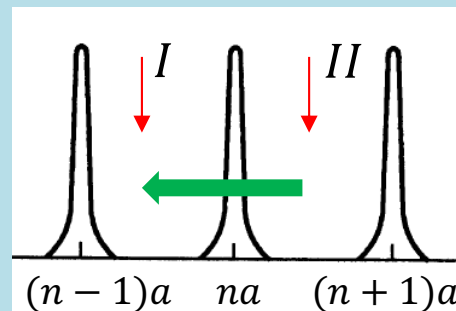
這樣的函數稱為 **Block Function**。自然滿足：

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

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

$$\begin{aligned} -A_{n+1} \sin ka + B_{n+1} \cos ka &= B_n \\ \left(\frac{du}{dx}\right)_\varepsilon - \left(\frac{du}{dx}\right)_{-\varepsilon} &= \int_{-\varepsilon}^{\varepsilon} dx \frac{d}{dx} \frac{du}{dx} \\ &= \int_{-\varepsilon}^{\varepsilon} dx \frac{2m}{\hbar^2} [V(x) - E] u(x) = 0 \end{aligned} \quad (4-12)$$

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 ( $x = na$ )

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

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  $g = \lambda/ka$ .

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

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

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

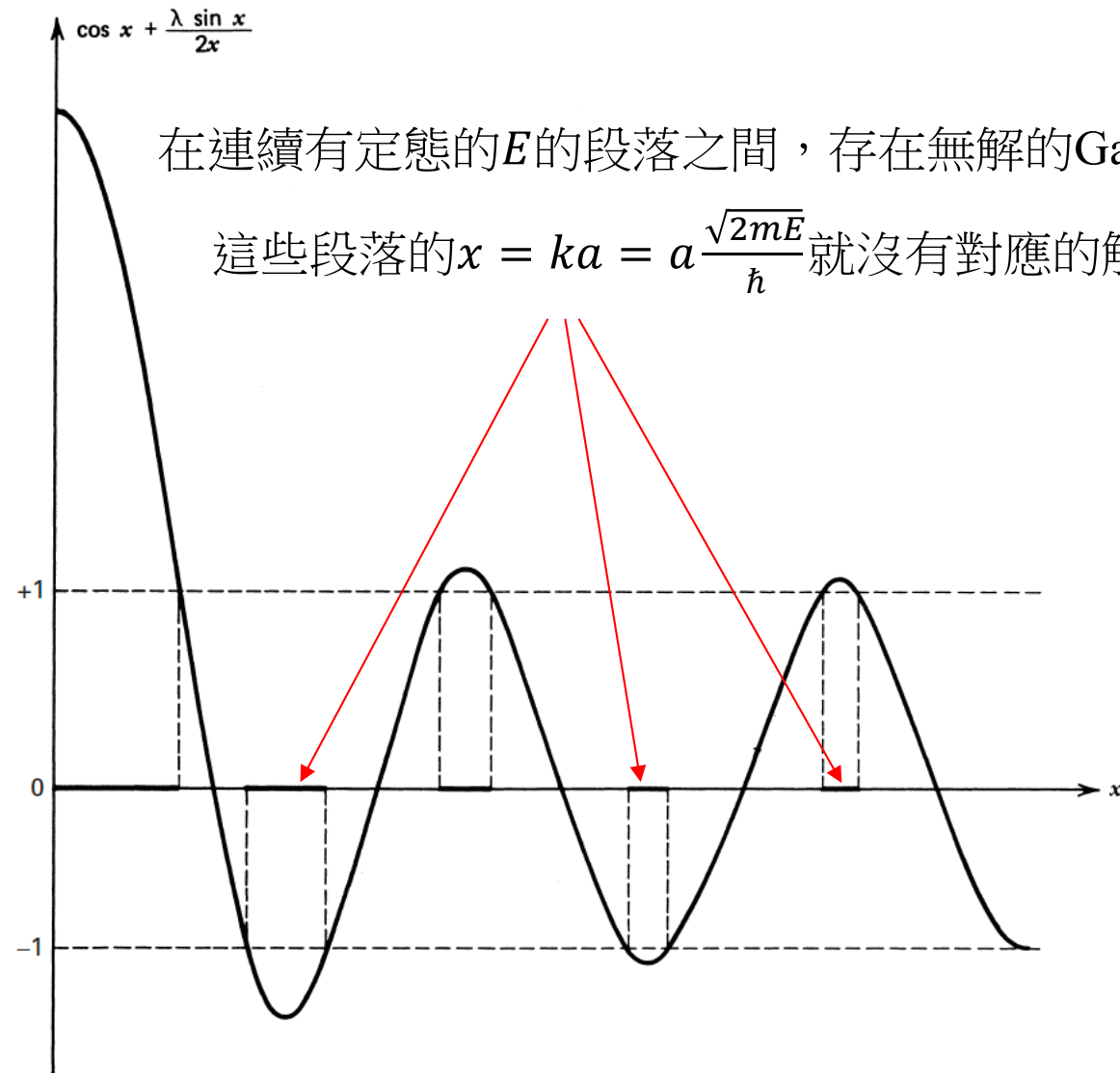
This quadratic equation can be solved, and both real and imaginary parts lead to the condition

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

補充教材

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

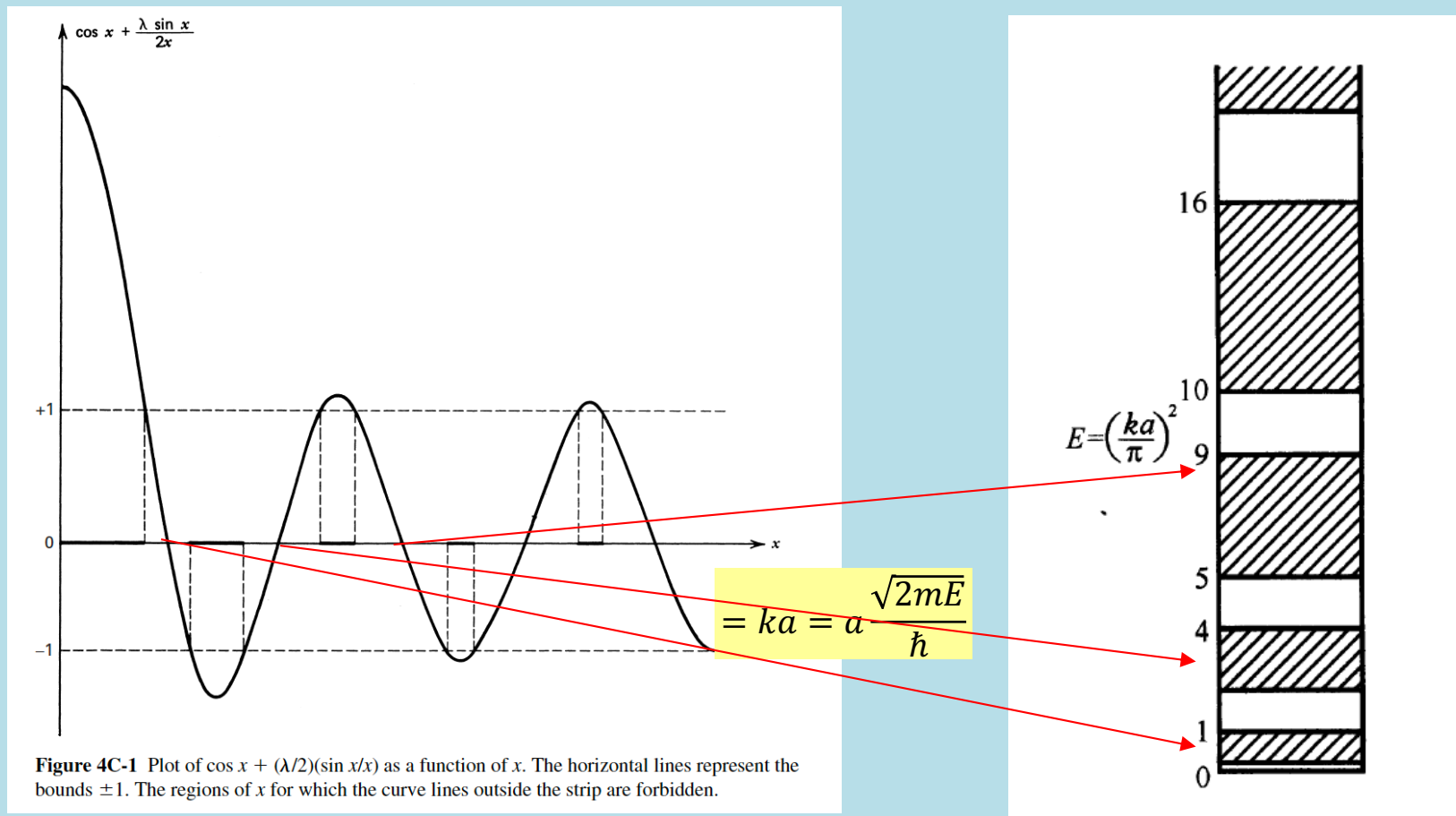
此式有解的 $ka \sim \sqrt{E}$ 才對應有定態！  
左邊 $\cos qa$ 只能在 $-1$ 與 $1$ 之間！



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

**Figure 4C-1** Plot of  $\cos x + (\lambda/2)(\sin x/x)$  as a function of  $x$ . The horizontal lines represent the bounds  $\pm 1$ . 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！

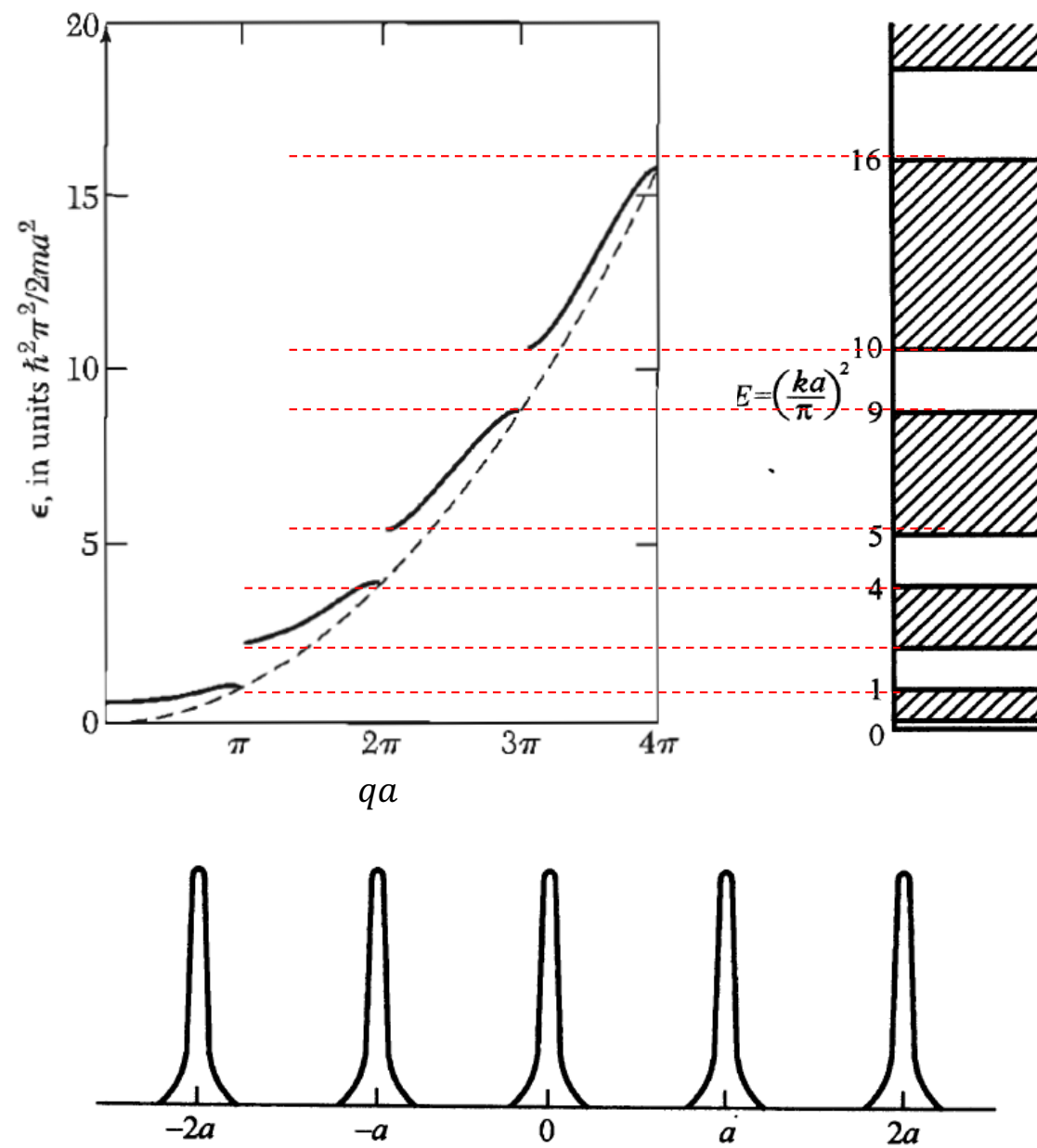
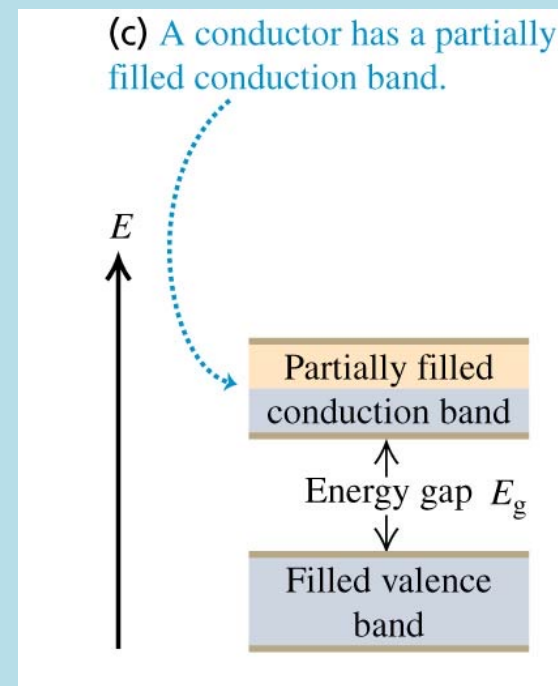
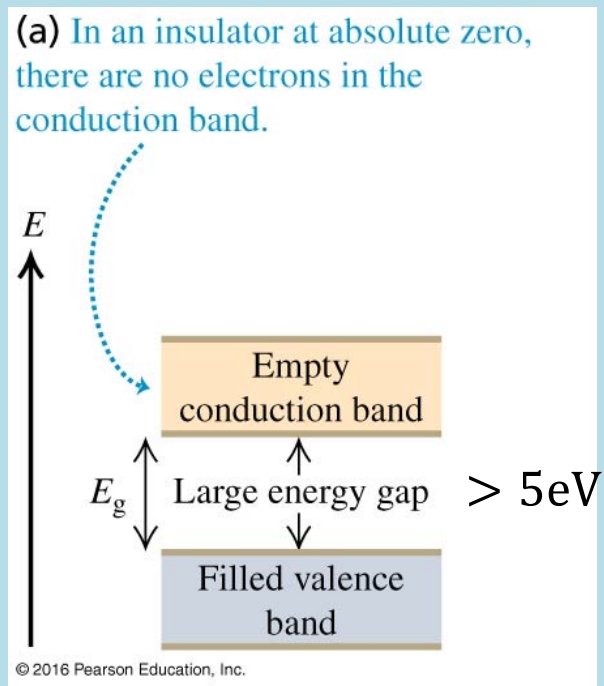
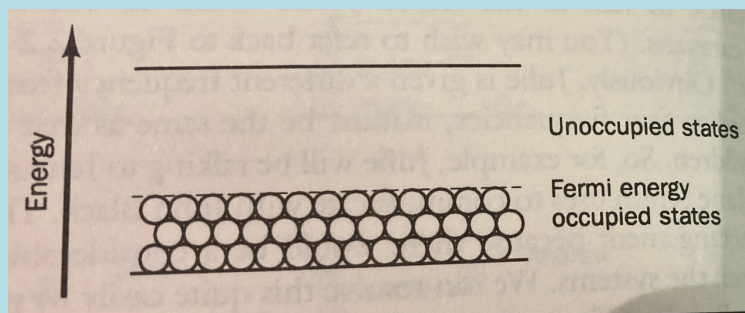


图 3.33 Dirac 梳

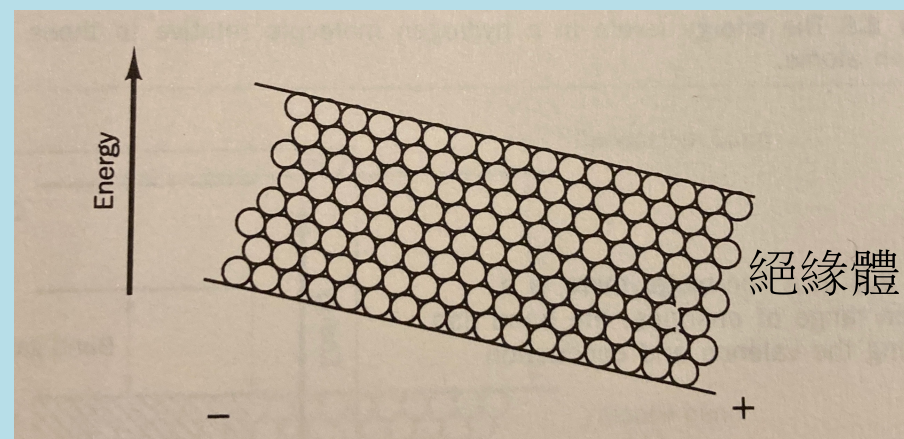
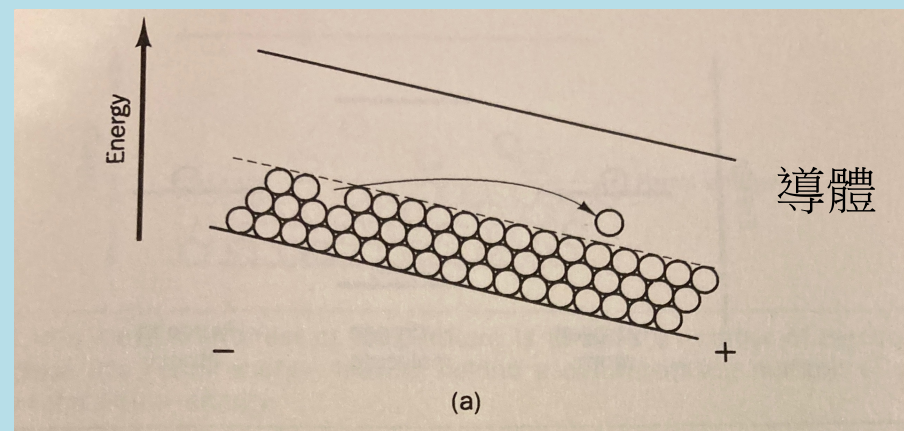
如果電子恰好填滿一個能帶（Valence），這些能帶中的電子無處可去！  
如同單一原子內的電子，需要很大能量才能克服間隙，改變狀態。  
如此電子即使不再被束縛於單一原子旁，但也不是機動的。  
這樣的固體無法導電，是絕緣體。



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。



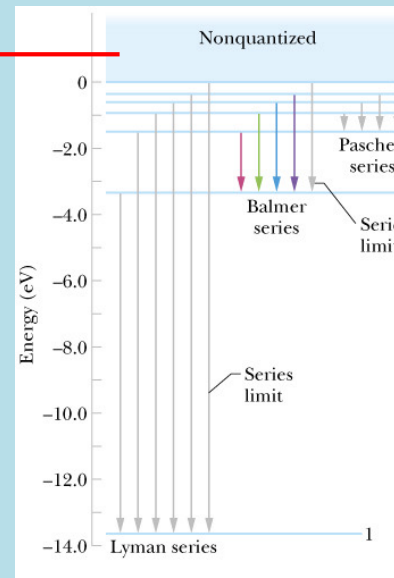
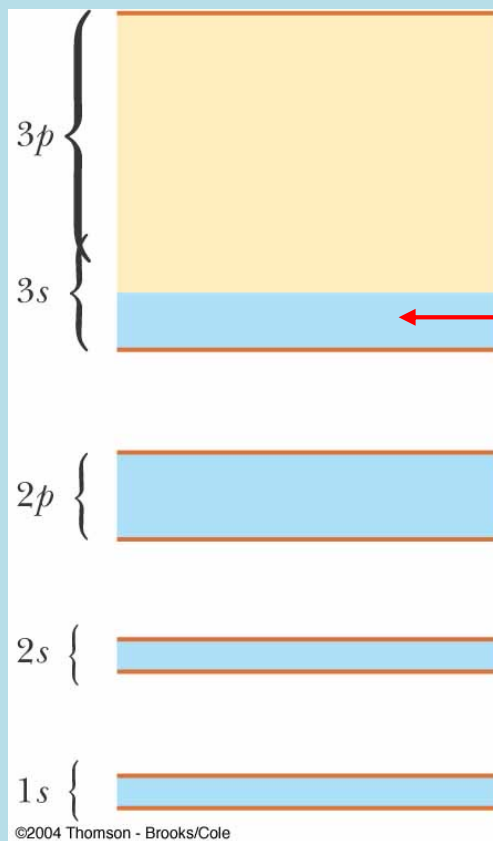
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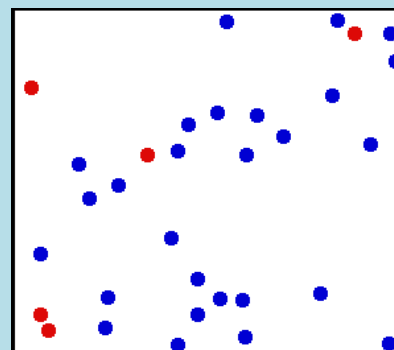
## 自由電子模型



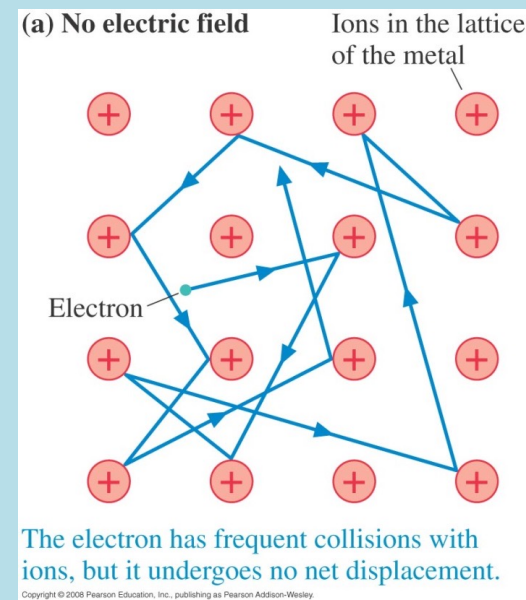
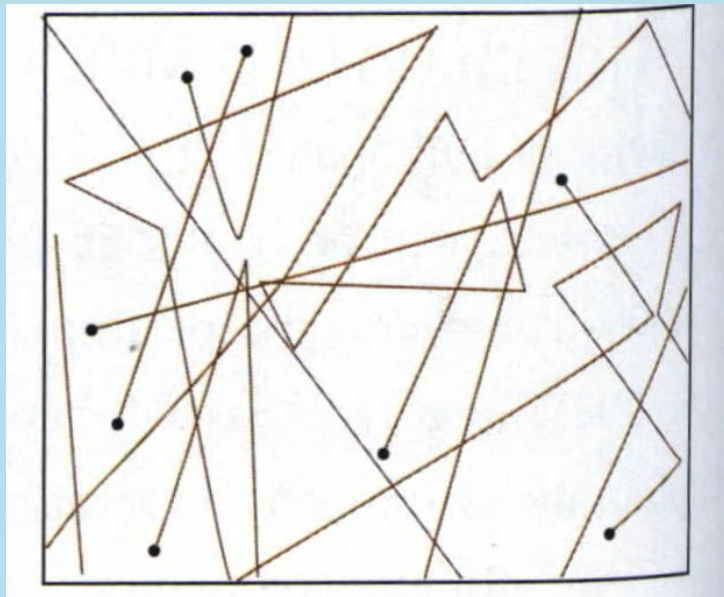
在未填滿的能帶內的電子能態，感覺就像原子能態中的連續能量自由態！

可以證明這些電子在固體內完全自由移動，等效於沒有原子核晶格存在一般。

就如同氣體中的分子一樣！



若是完美的晶格，這樣的電子不會被反彈，而且自由自在。



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！

有時又稱為無交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

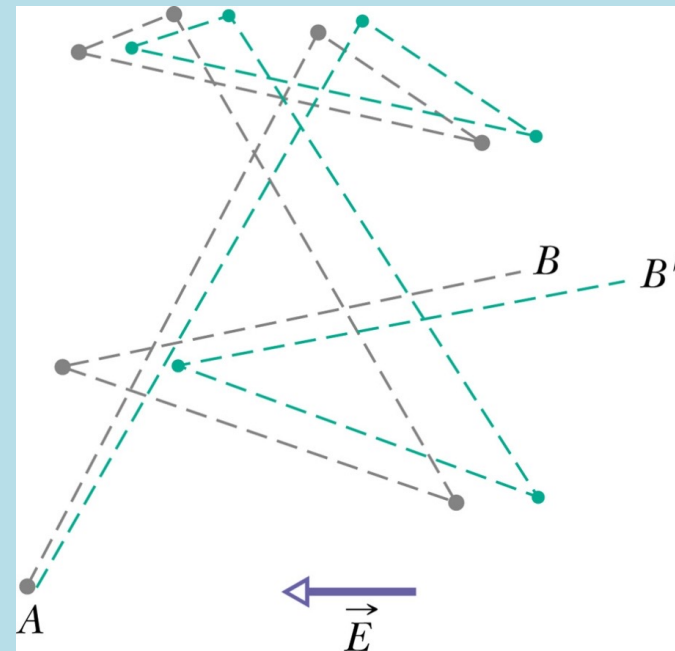
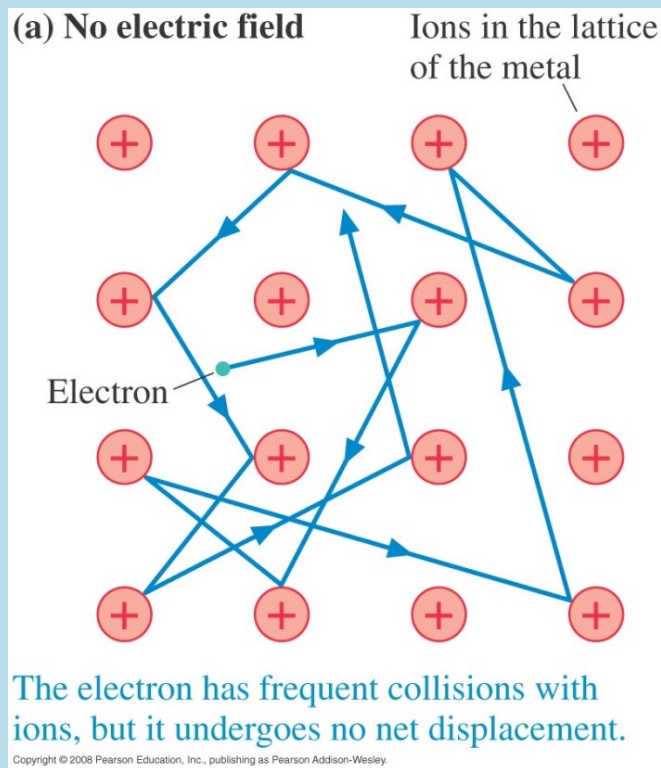
J.J. Thomson's 1896 discovery of the electron ("corpuscles of charge" that could be pulled out of metal) raised the question of how these charge carriers might move within the metal. In 1900 Paul Drude<sup>2</sup> realized that he could apply Boltzmann's kinetic theory of gases to understanding electron motion within metals. This theory was remarkably successful, providing a first understanding of metallic conduction.<sup>3</sup>

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 scattering<sup>4</sup> time  $\tau$ . The probability of scattering within a time interval  $dt$  is  $dt/\tau$ .
- (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.<sup>5</sup> 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！

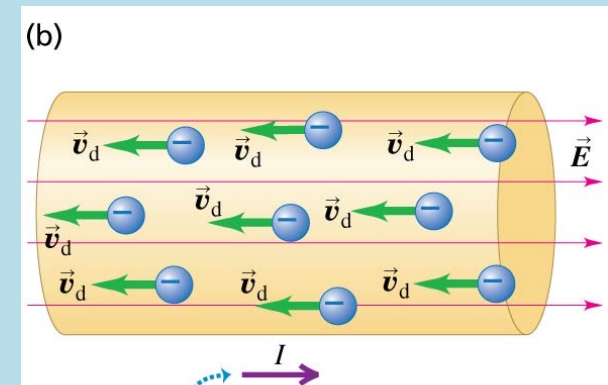
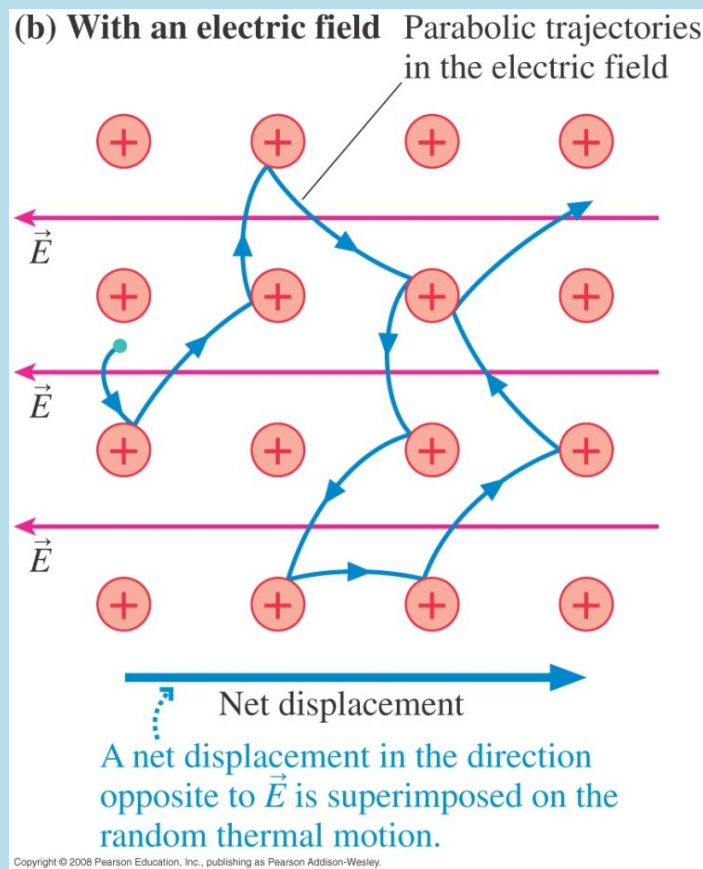
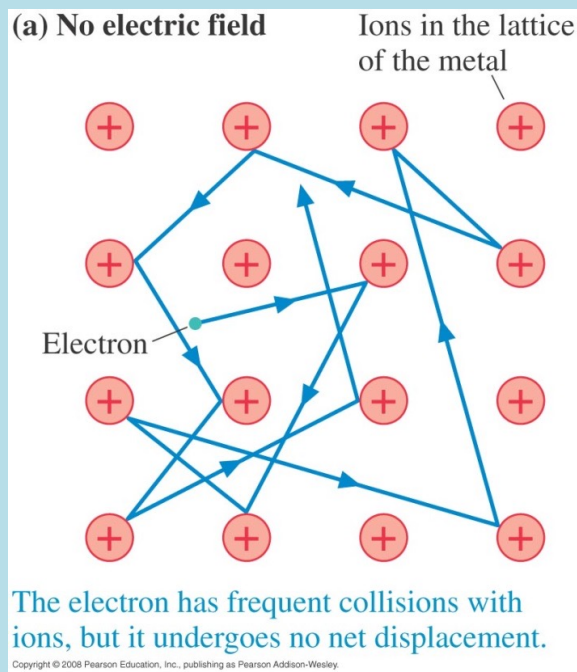


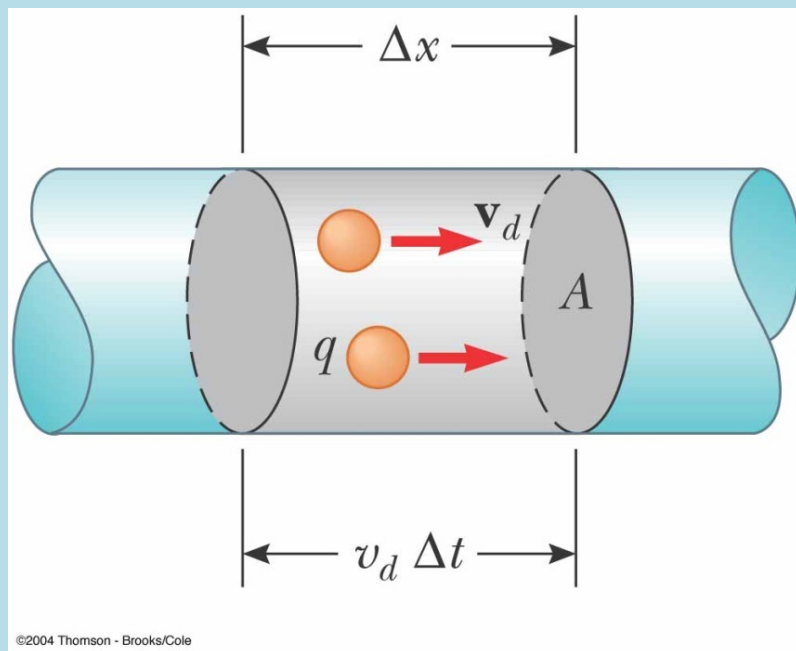
電場對電子產生一加速度：
$$a = \frac{F}{m} = \frac{eE}{m}$$

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  $v_d = a\tau = \frac{e\tau}{m} E$   $\tau$  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 $\Delta t$ ，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。



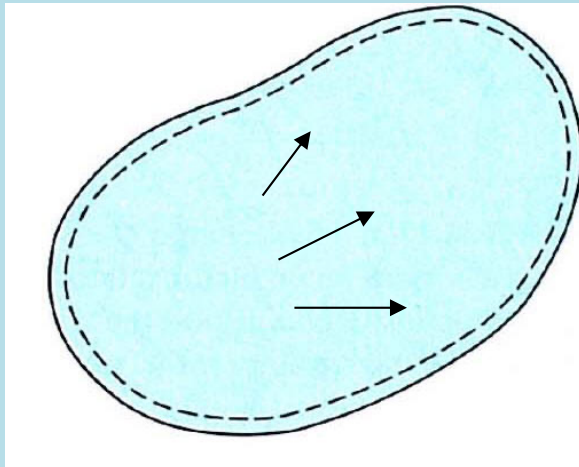
平均漂移速度與電場成正比。

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

電流密度與平均漂移速度成正比。

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

↓  $\tau$  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

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

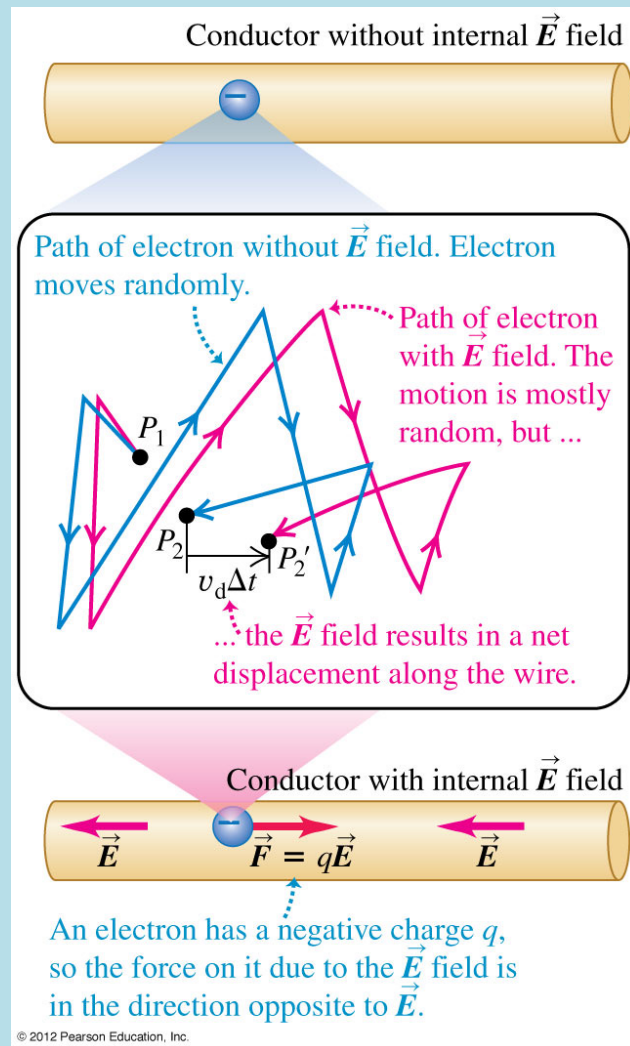
Georg Simon Ohm



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

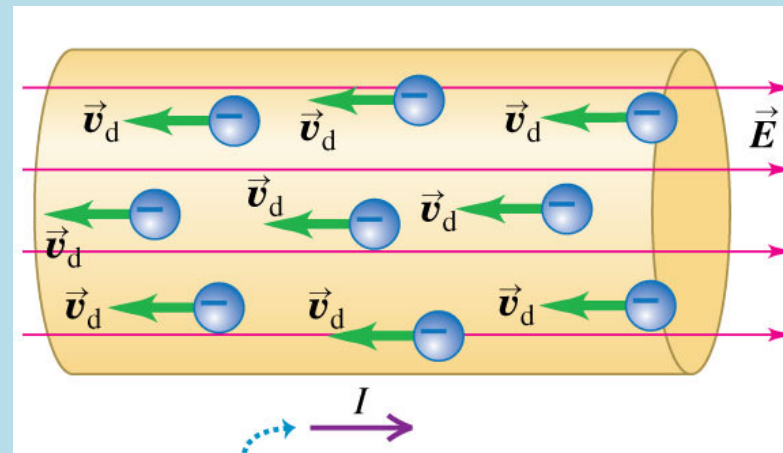
$$\rho = \frac{m}{e^2 n \tau}$$

$\rho$  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。



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

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

**TABLE 25.1** Resistivities at Room Temperature (20°C)

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

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

Material	$\frac{1}{-e R_H n_{atomic}}$	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!

Let us then calculate  $n = -1/(eR_H)$  for various metals and divide it by 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 it 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 atoms 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 these 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 analysis 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) have 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 the properties of metals.

If we believe the Hall effect measurement, we can then extract a scattering time from the expression for the conductivity. The Drude scattering time is found to be in the range of  $\tau \approx 10^{-14}$  seconds for most metals at room temperature.

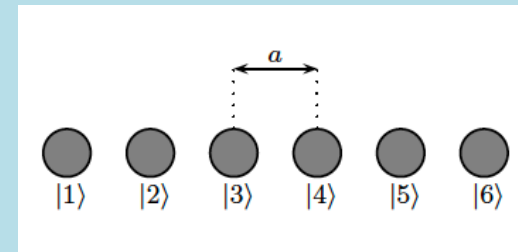
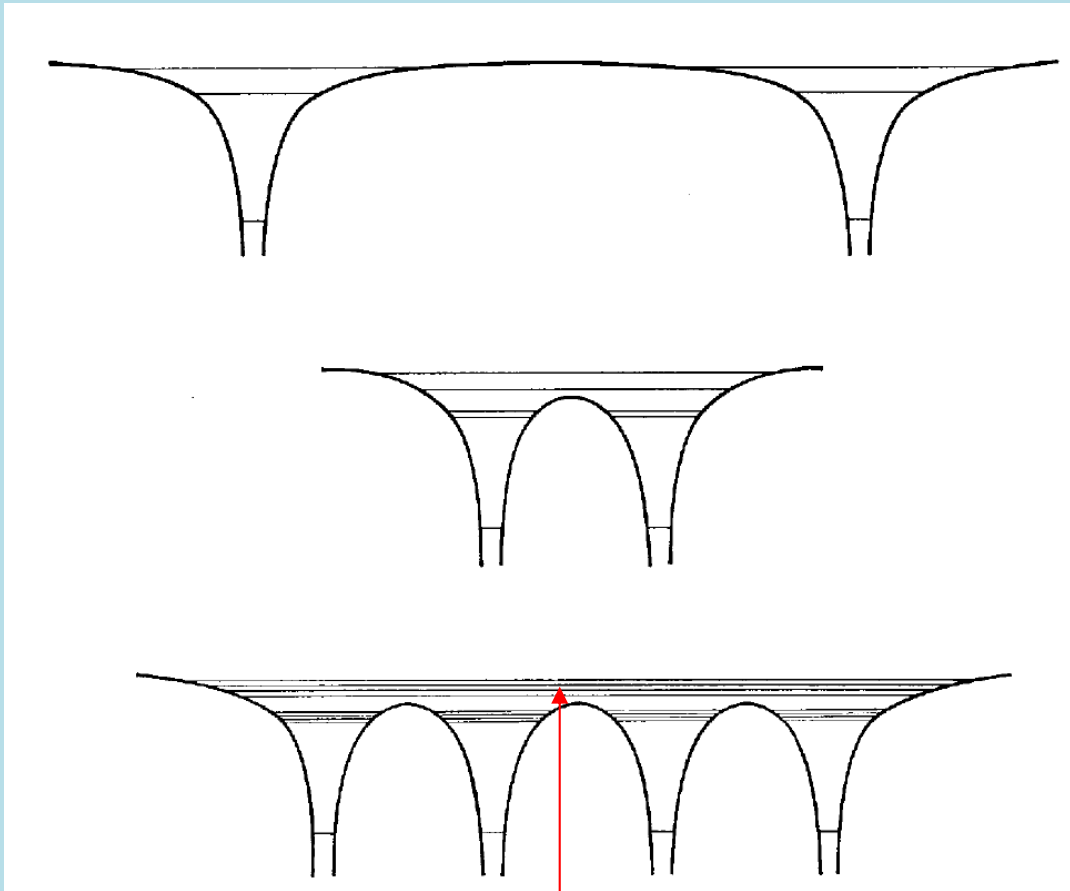
$$\tau \sim 10^{-14} \text{ s}$$

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

$$\text{自由徑} \sim 10^{-8} \text{ m}$$

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

## 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.



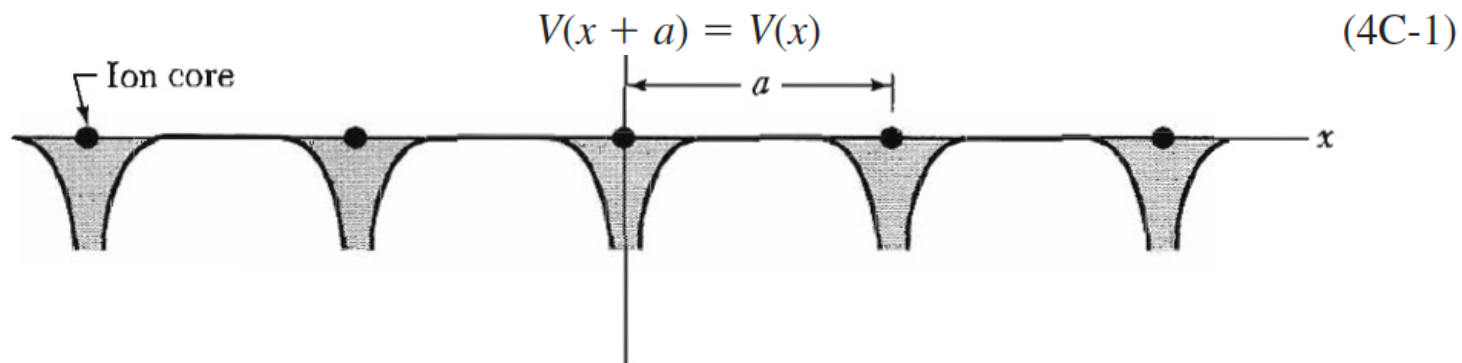
## Supplement 4-C

# 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, rectangular wells (representing ion cores) separated by flat regions. The distance between the centers of two adjacent wells is labeled  $a$ . The equation  $V(x + a) = V(x)$  is written above the diagram, indicating the periodicity of the potential. The  $x$ -axis is shown as a horizontal line with an arrow pointing to the right.

## Nearly free electron model

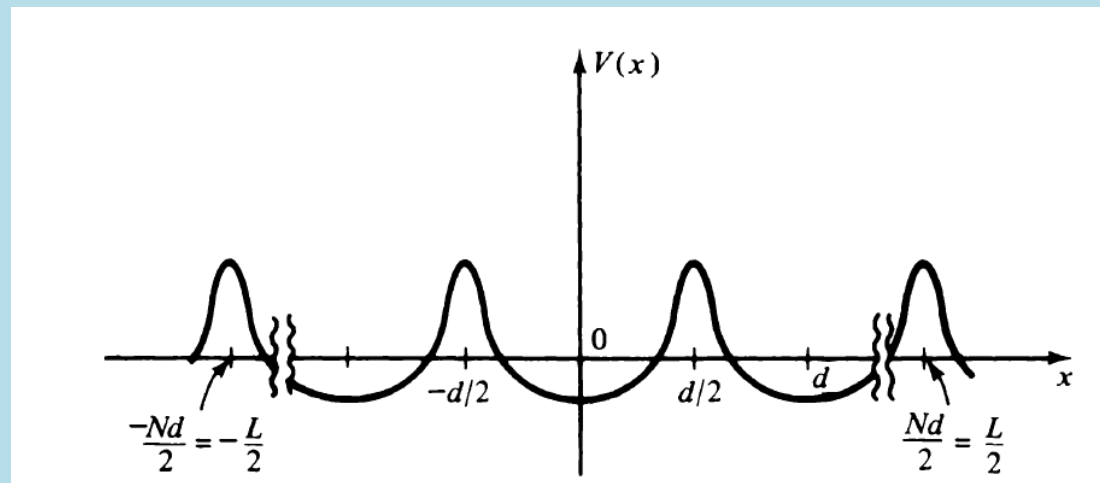
考慮一維空間，將自由電子視為未微擾模型，加入一週期性位能 $V(x)$ 作為微擾！

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

$$H_1 = V(x)$$

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

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，即是動量本徵態平面波 $|k\rangle$ ，設一維空間長度 $L$ ：

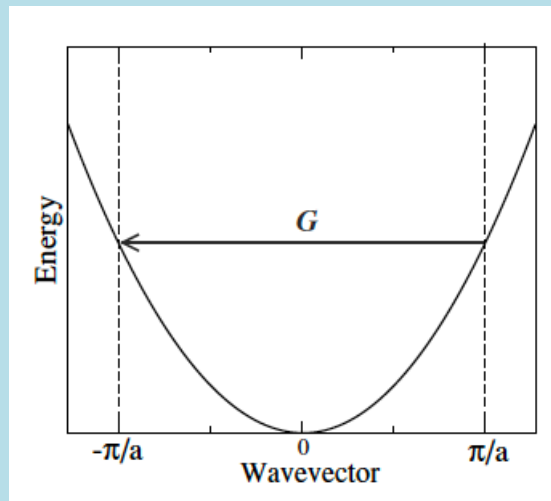
波函數以角波數 $k$ ，即動量標定：

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

對應的本徵值：

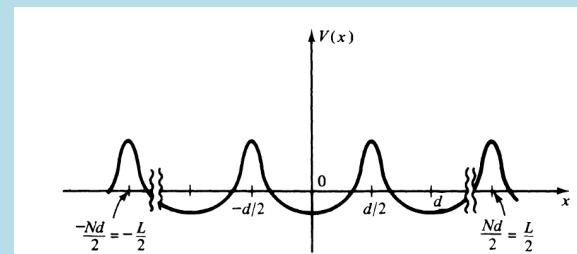
$$E^{(0)} = \frac{\hbar^2 k^2}{2m}$$

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 $\delta$ 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。

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

這個量會直接出現在我們計算中。

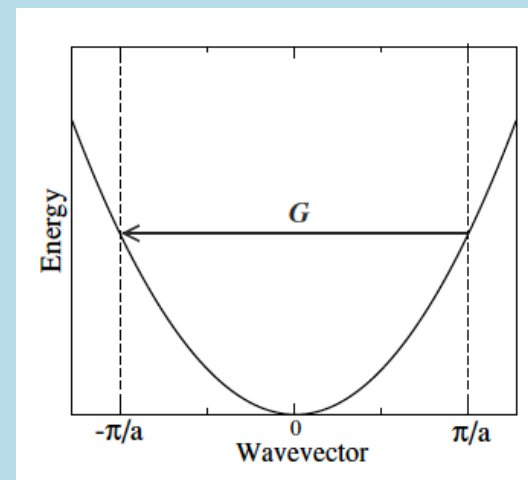
$$\langle q|V|k\rangle = V_1 \cdot \delta\left(k - q \pm \frac{2\pi}{a}\right) \quad \text{矩陣元只有在兩邊}k\text{相差}\pm\frac{2\pi}{a}\text{才不為零！}$$

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

$$E_n^{(1)} = \langle k|V|k\rangle = V_1 \cdot \delta\left(k - k \pm \frac{2\pi}{a}\right) = 0 \quad \text{能量的一階修正為零。}$$

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

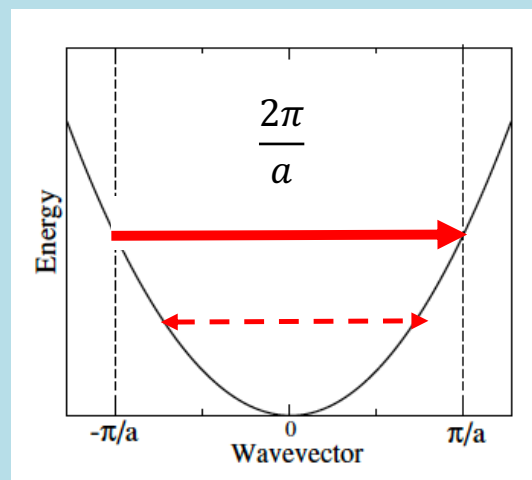
零階加一階本徵值能量 $E_k^{(0+1)}$ 對 $k$ 作圖



“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

自由電子能量有一個簡併，正負 $k$ 平面波的能量相等： $E_k^{(0)} = E_{-k}^{(0)}$

$|k\rangle \sim e^{-ikx}$ 與 $|-k\rangle \sim e^{ikx}$ 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： $\langle q|V|k\rangle = V_1 \cdot \delta\left(k - q \pm \frac{2\pi}{a}\right)$

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！

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

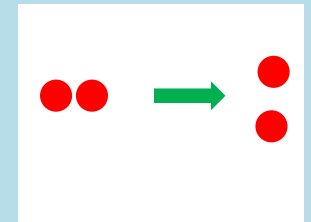
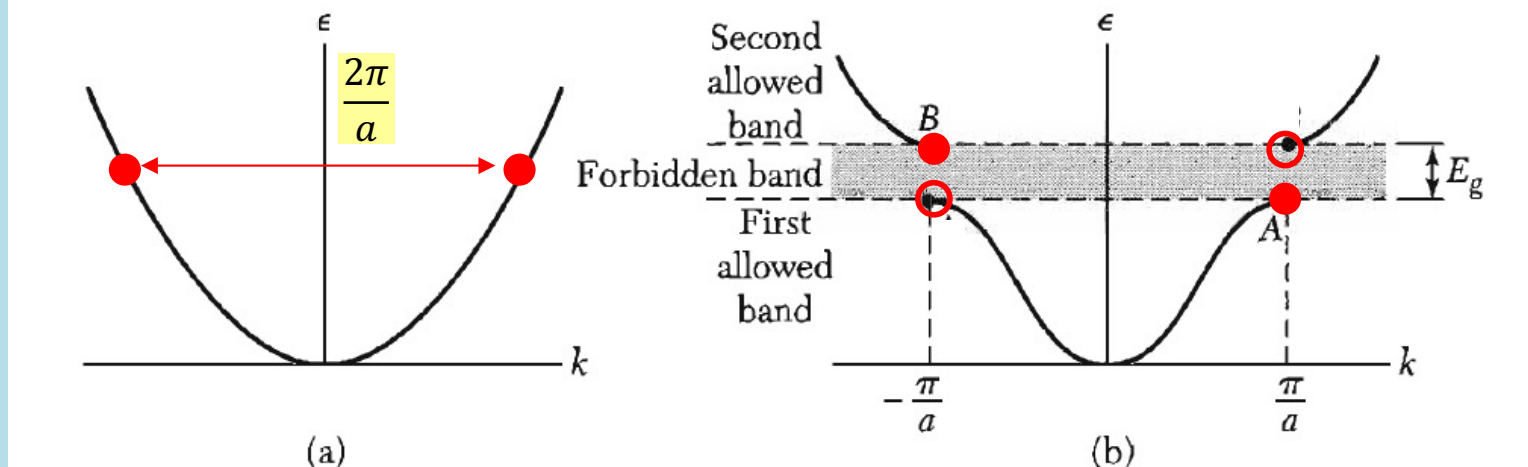
此時一般微擾公式的分母為零，混雜是無限大，就不能用了。

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。

因此能量在Band Edge處因微擾出現不連續的間隙Energy Gap。

Band Edge上的嚴格計算：

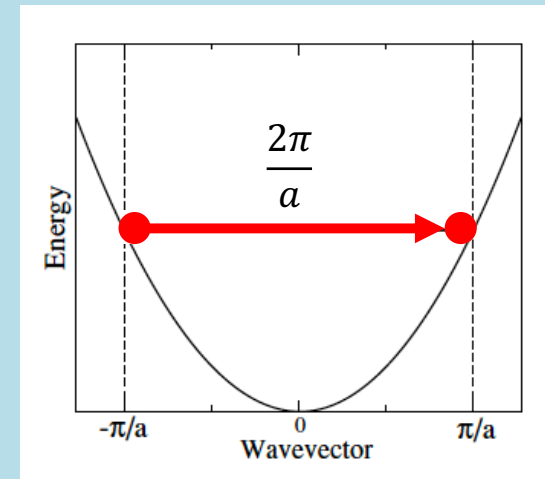
考慮  $|k = -\frac{\pi}{a}\rangle$  與  $|k + \frac{2\pi}{a} = \frac{\pi}{a}\rangle$  組成二維簡併空間，

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： $\sigma_x$ 的本徵態問題。

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

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

本徵值與本徵態如預期有兩組。

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

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

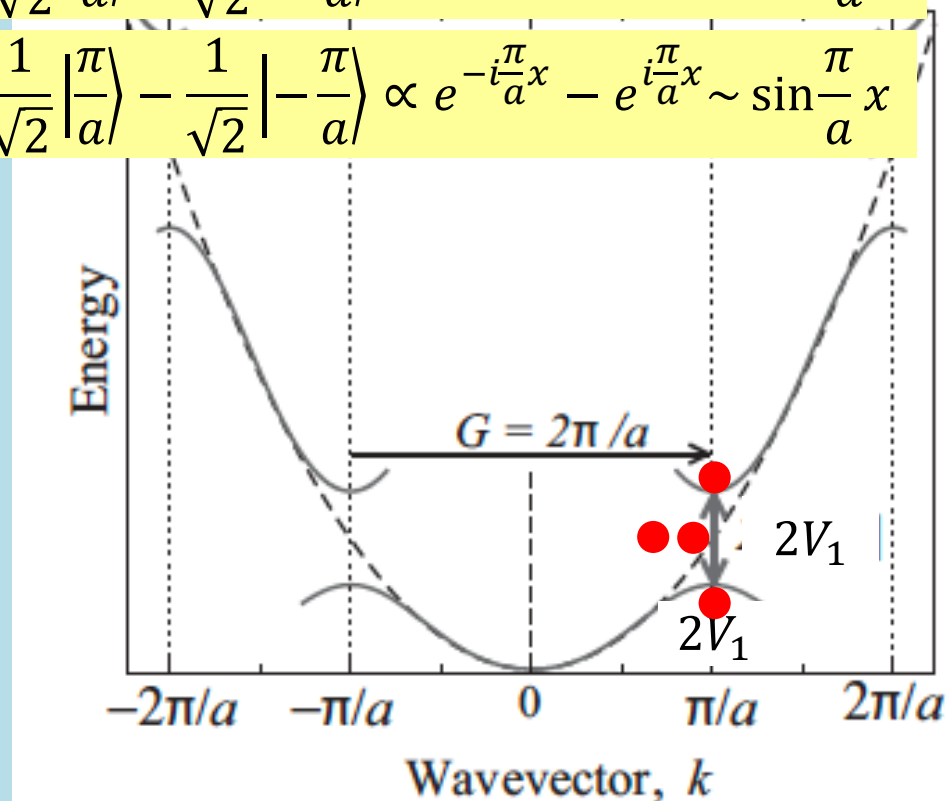
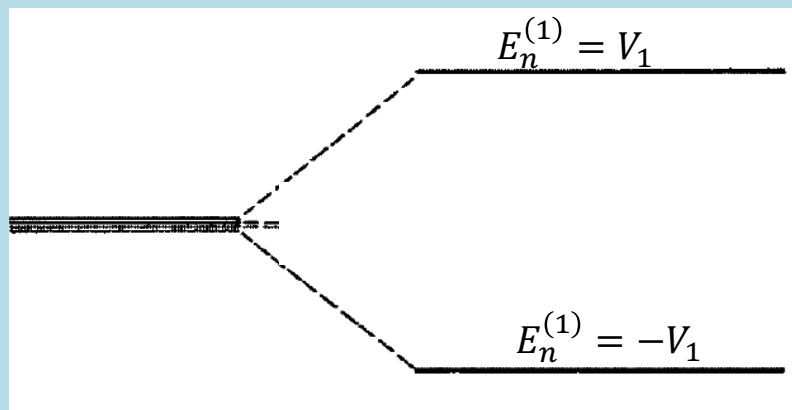
或者

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

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

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

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



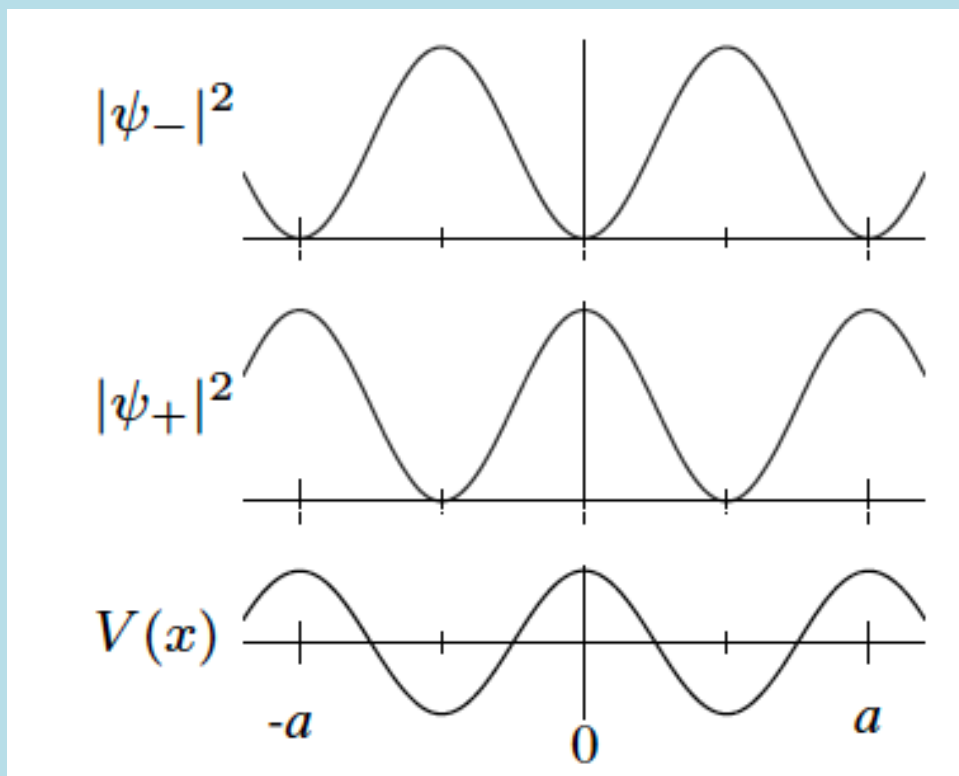
$k = \frac{\pi}{a}$  在  $k$  空間稱為 Band Edge。

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  $2V_1$ 。

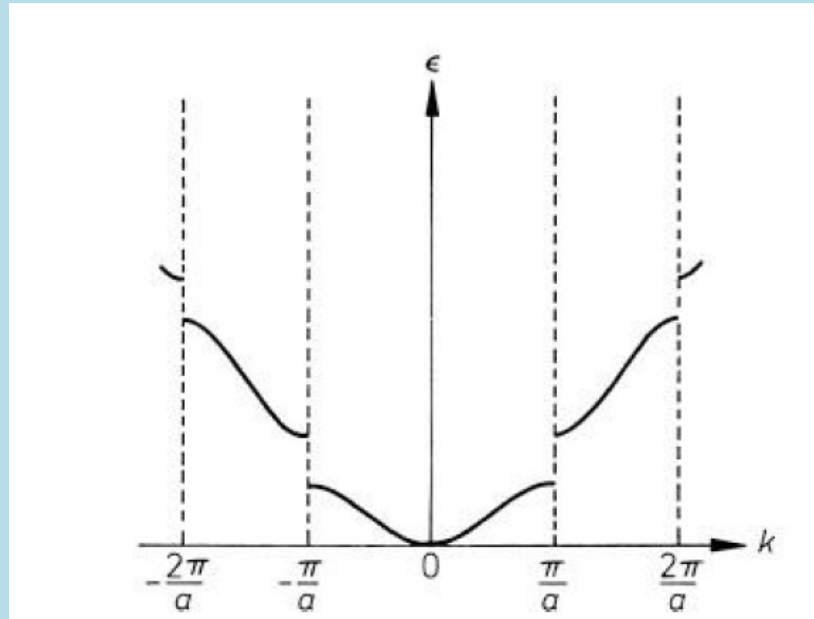
這兩個能量不等的態，是原本兩個簡併態 $e^{-i\frac{\pi}{a}x}$ 與 $e^{i\frac{\pi}{a}x}$ ，相加與相減形成的疊加態！

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。



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

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



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

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

兩者的 $k$ 正好相差，週期性位能 $V_1$ 會混雜的 $\frac{2\pi}{a}$ ！

此處稱為Band Edge，會發生簡併微擾，產生間隙Gap，大小為 $2V_1$ 。

若是考慮所有 $V_n$ ，每一個 $V_n$ 會對應一個Band Edge在  $k = \frac{n\pi}{a}$ 。

每一個Band Edge，都會出現大小為 $2V_n$ 的間隙Gap。。

這與真實可解的Dirac梳週期性位能非常類似！

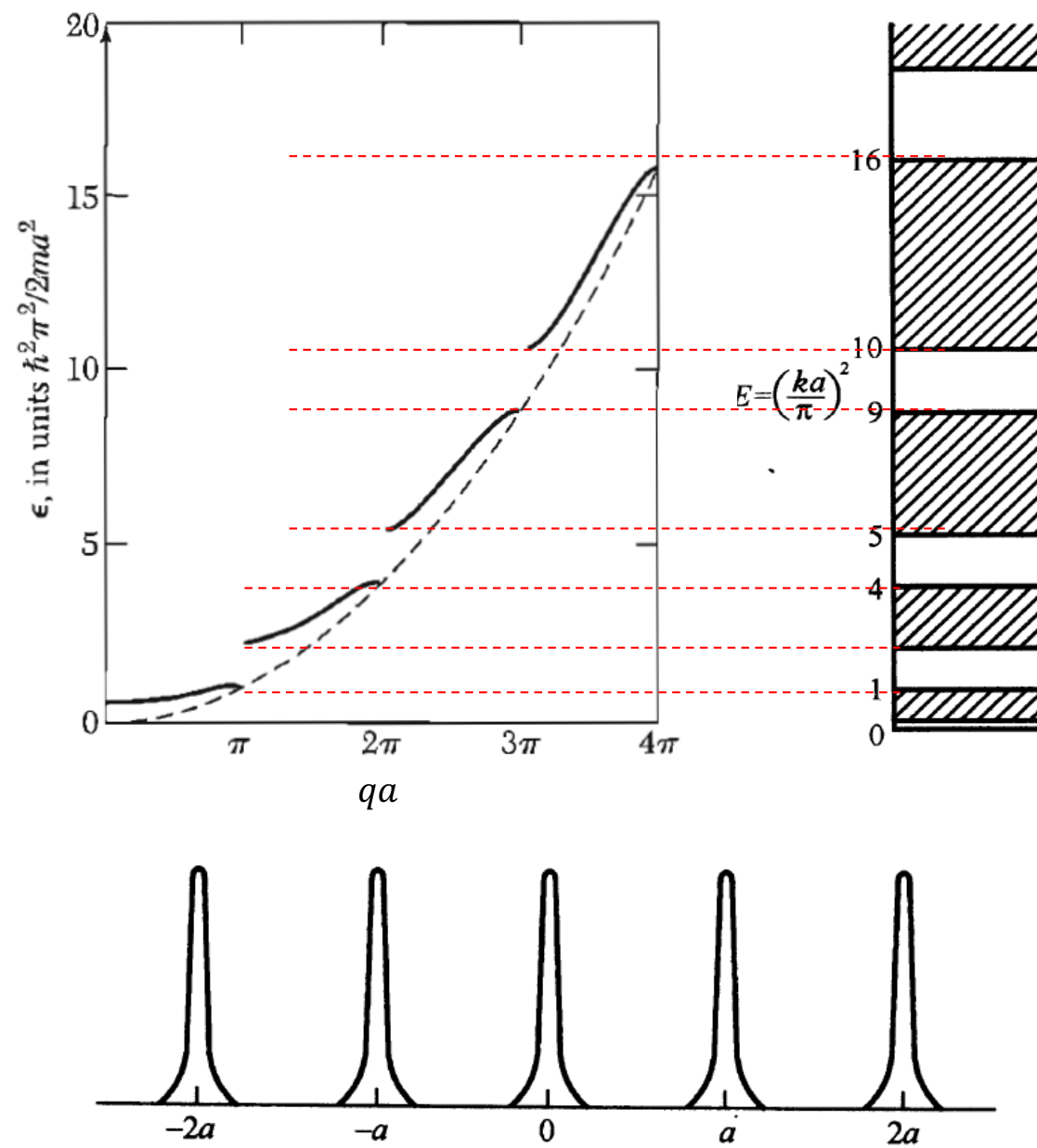
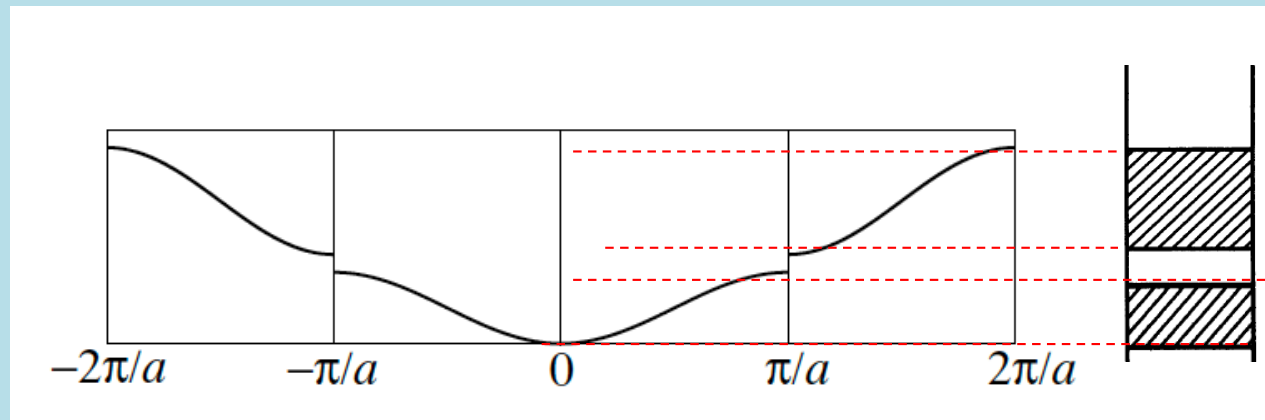
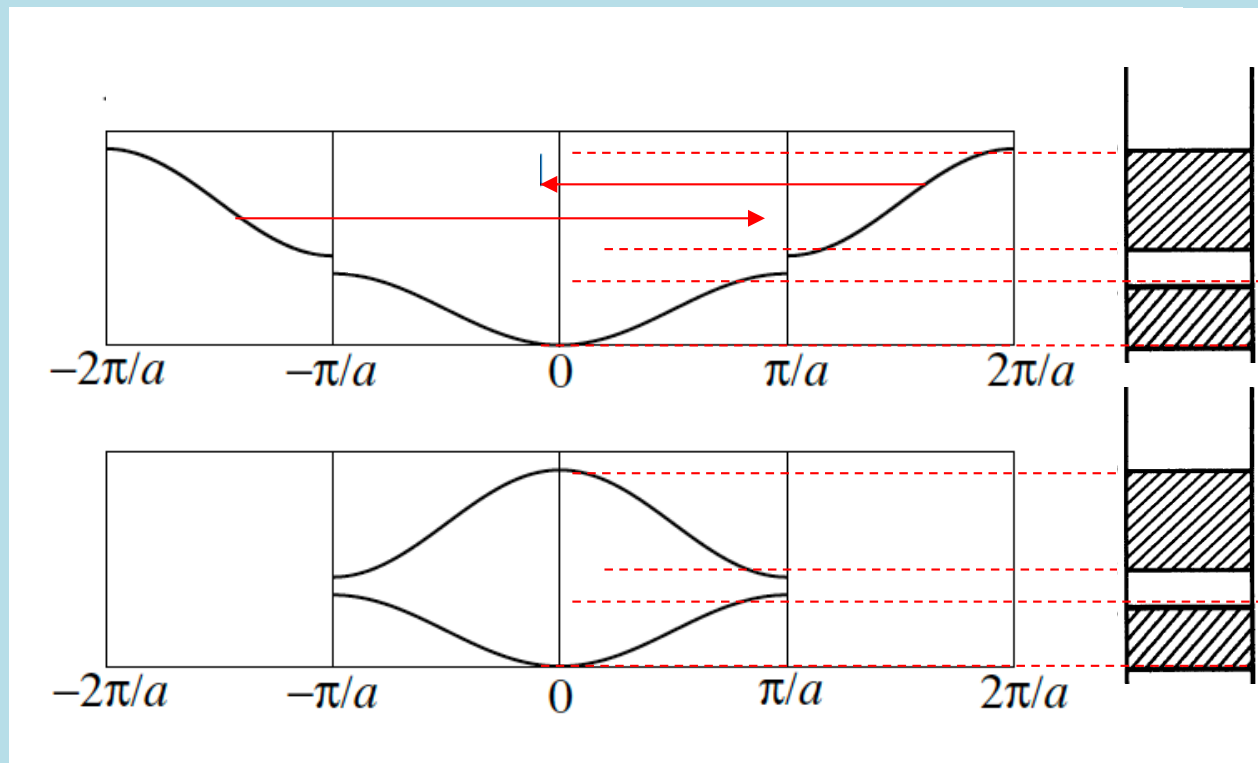


图 3.33 Dirac 梳



如果不標出 $k$ ，縱軸的能量有定態的區域就形成有間隙的能帶。





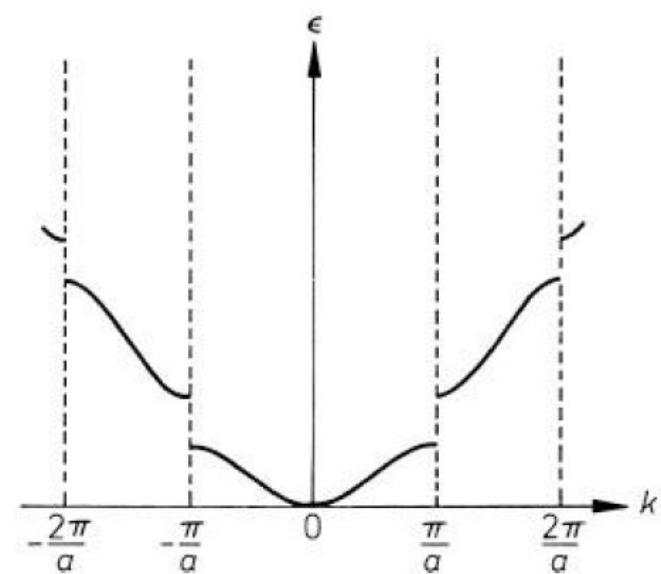
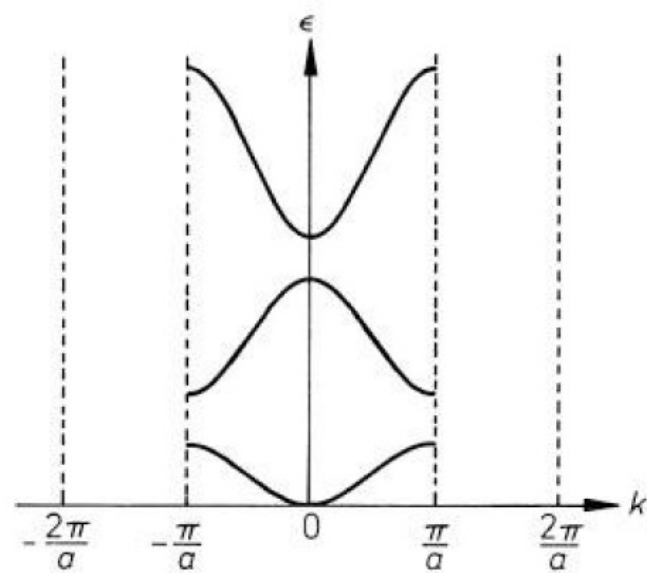
注意 $k$ 只是一個標籤，一般習慣將相差 $n \cdot 2\pi/a$ 的 $k$ 聚在一起。

$$k \sim k + n \cdot 2\pi/a$$

如此所有能態就會收集在  $-\pi/a < k < \pi/a$  之間。

每一個 $k$ ，由低而高對應一系列的能態。

而能態形成有間隙的連續能帶，這是最典型的能帶圖！



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

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 $\delta$ 很小， $\delta$ 的貢獻也構成微擾的一部分。

於是這兩個態的 $\delta$ 零階能量就相等，因此簡併！

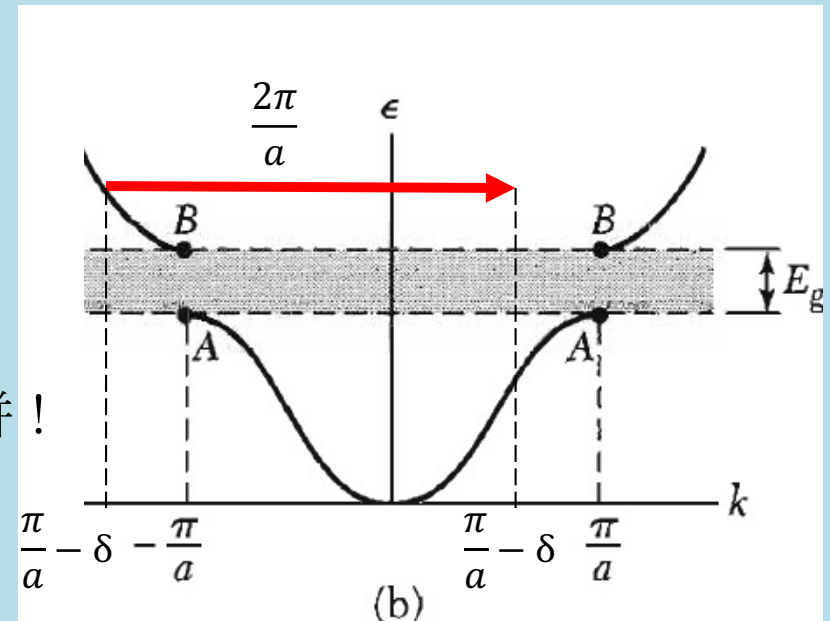
就應該把兩個態的混合也考慮進去。

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

兩個態與 $\delta$ 零階能量，即 $\left| \frac{\pi}{a} \right\rangle$ 的能量，能量差是 $\delta$ 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！

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



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

補充教材

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！

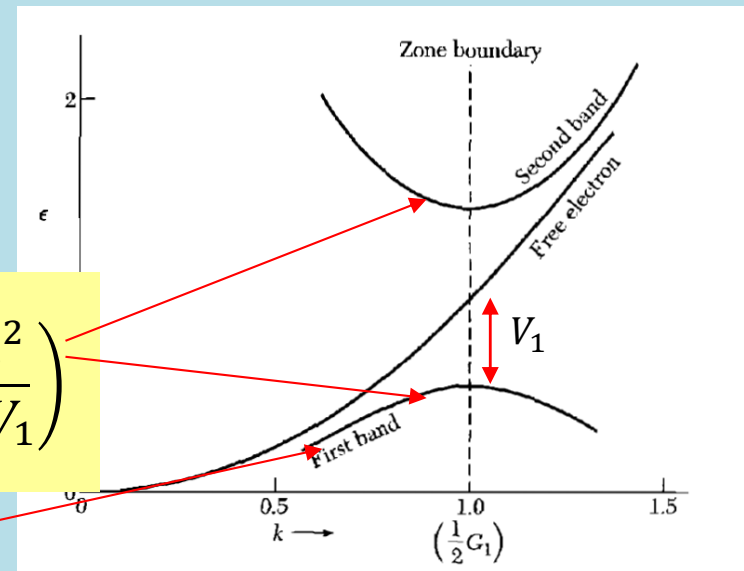
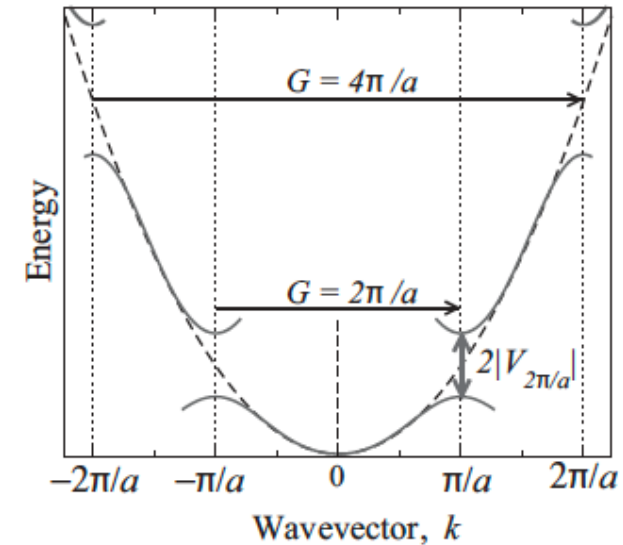
考慮 $\Delta \ll V_1$ ：

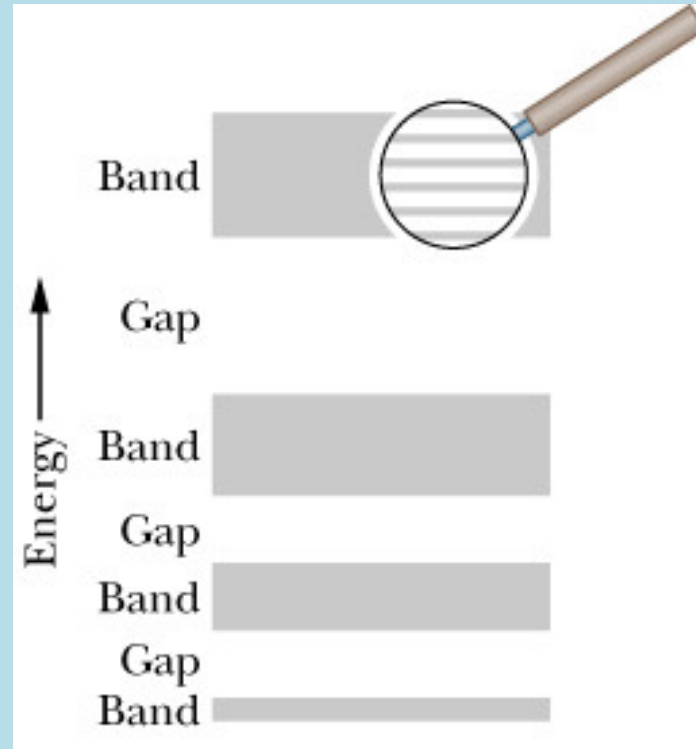
$$c = \pm \sqrt{\Delta^2 + V_1^2} = \pm \left( V_1 \sqrt{1 + \frac{\Delta^2}{V_1^2}} \right) = \pm \left( V_1 + \frac{\Delta^2}{2V_1} \right)$$

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！



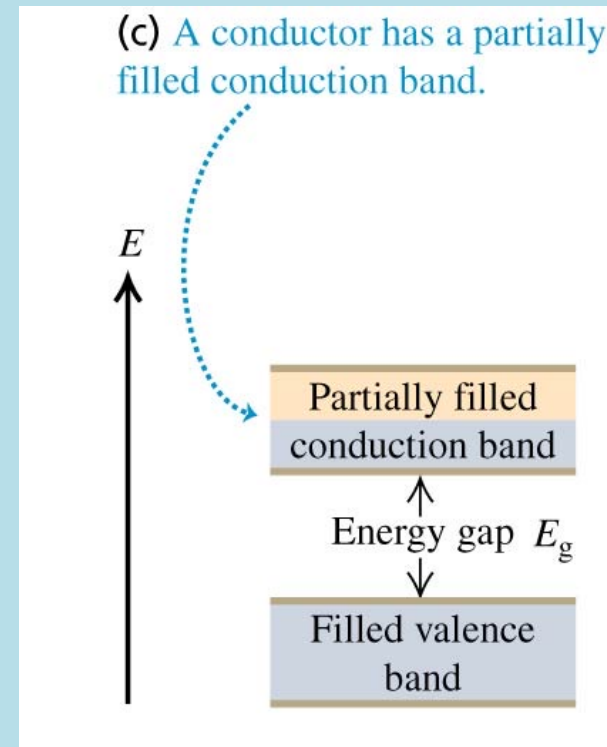
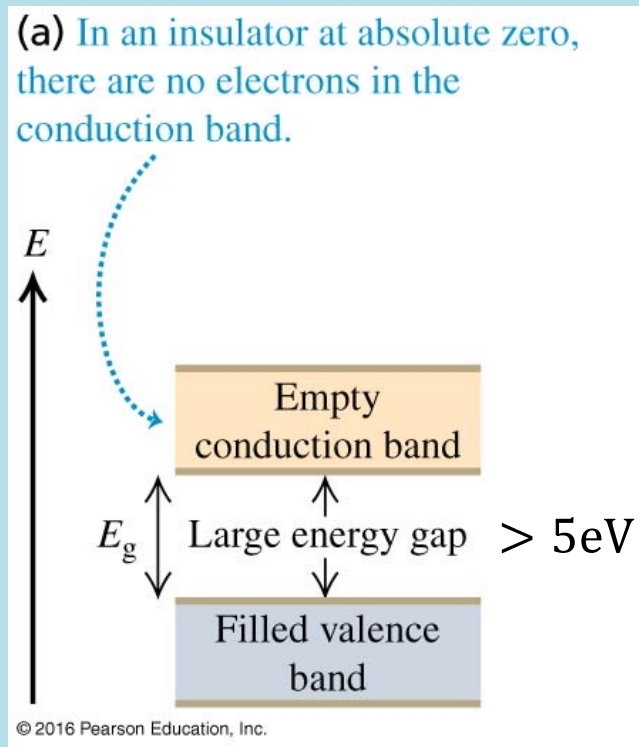
現在要幫電子往能態裡面填。

固態物理之父Bloch

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。

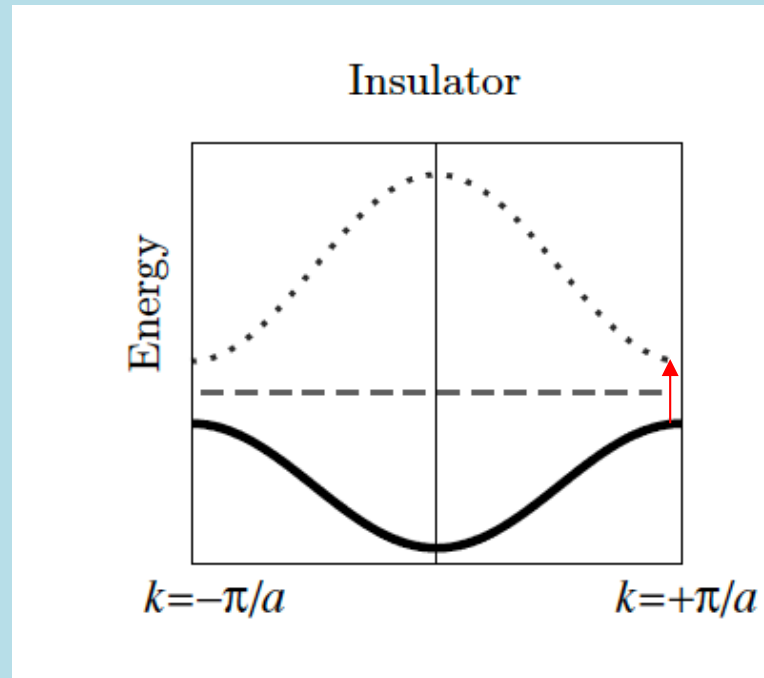
如此電子即使不再被束縛，但完全不能自由。這樣的固體無法導電，是絕緣體。



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。

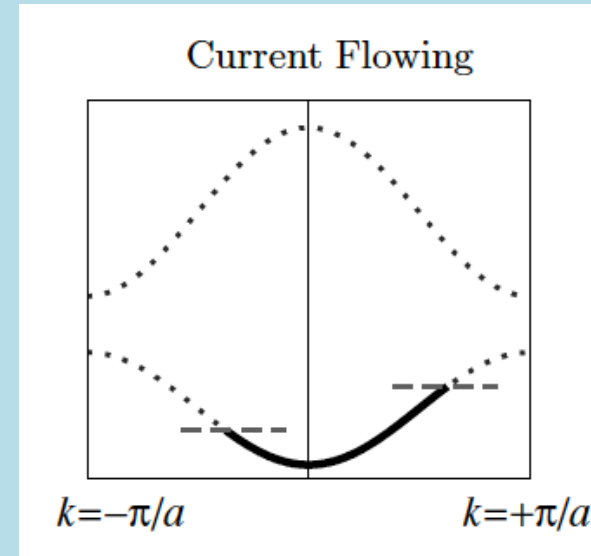
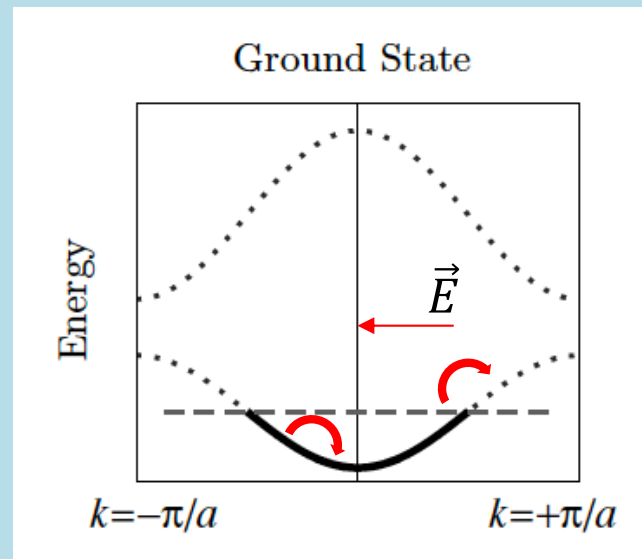
只要些許能量就能讓它激發到其他能態。

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。