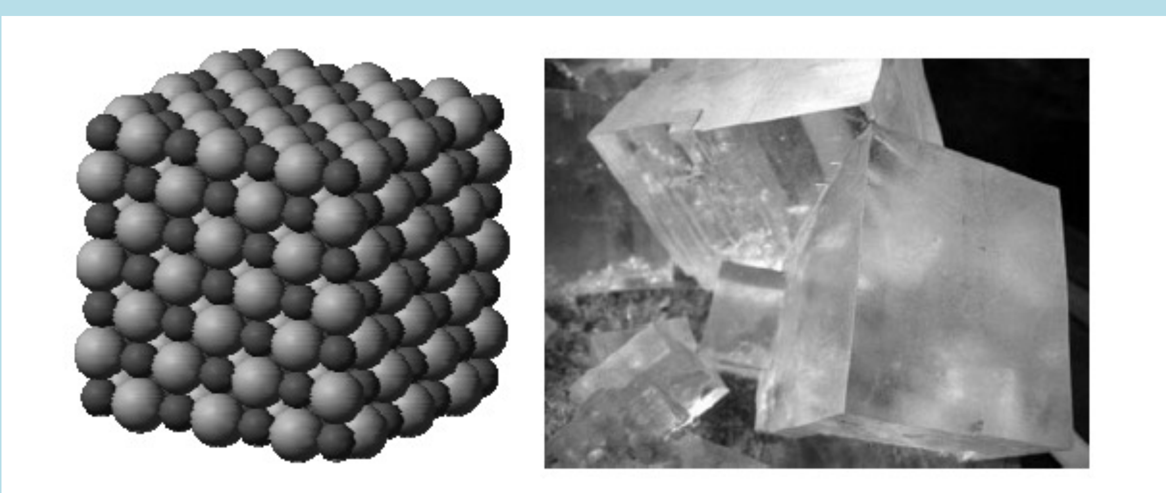
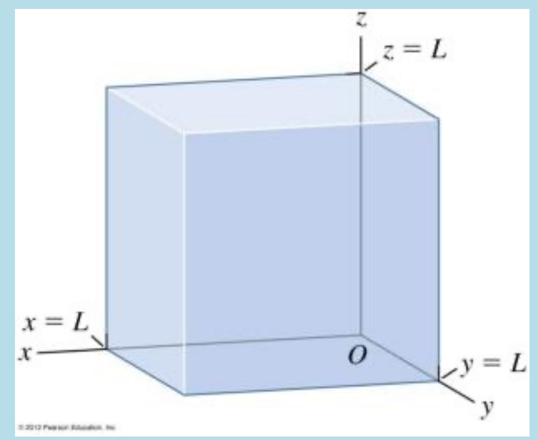
現在我們開始面對三維空間的固體。



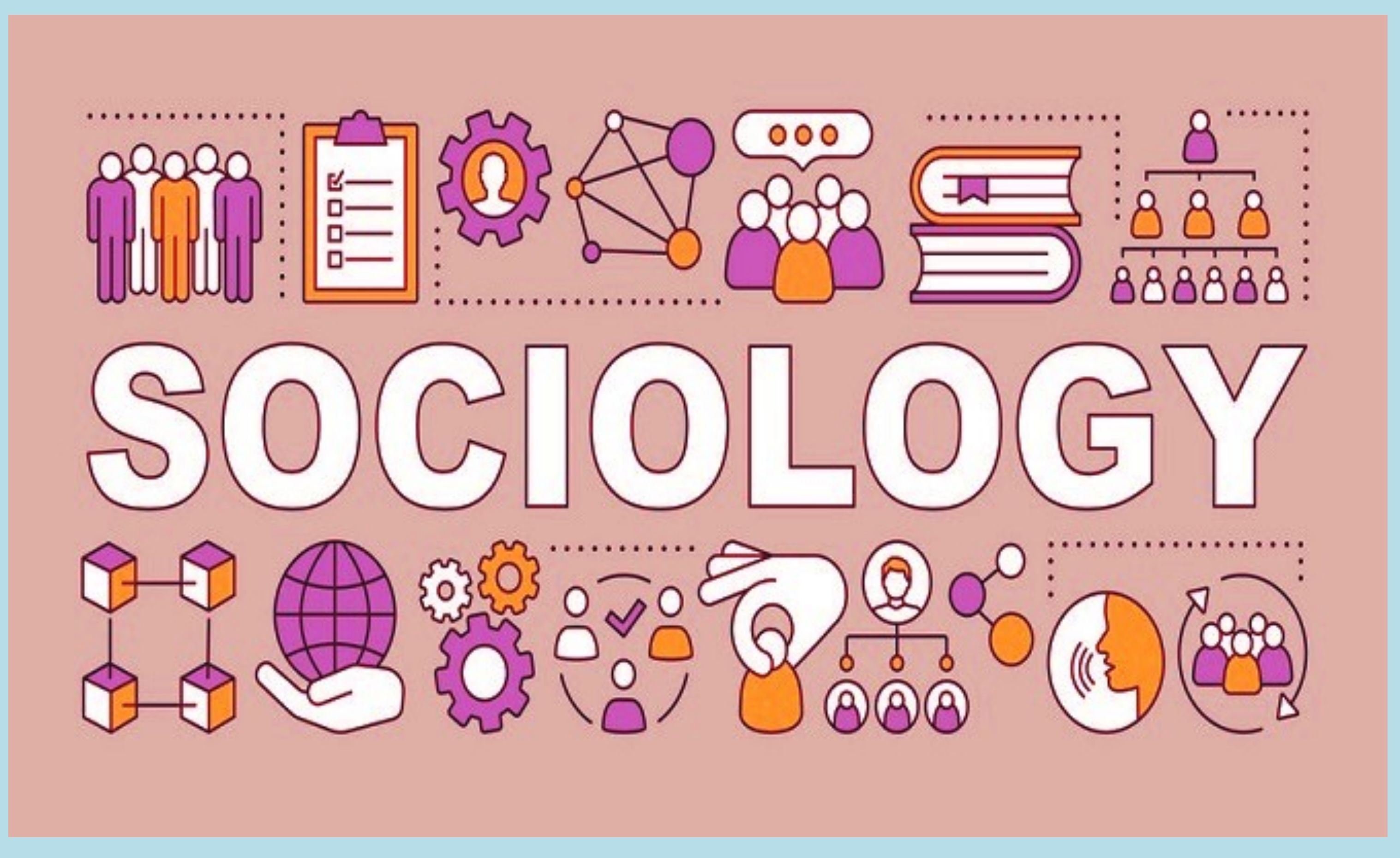
但避免同時面對兩個問題，我們將忽略晶格原子核的週期性位能。

因此將把固體看成自由空間，電子即自由電子。



電子的社會學

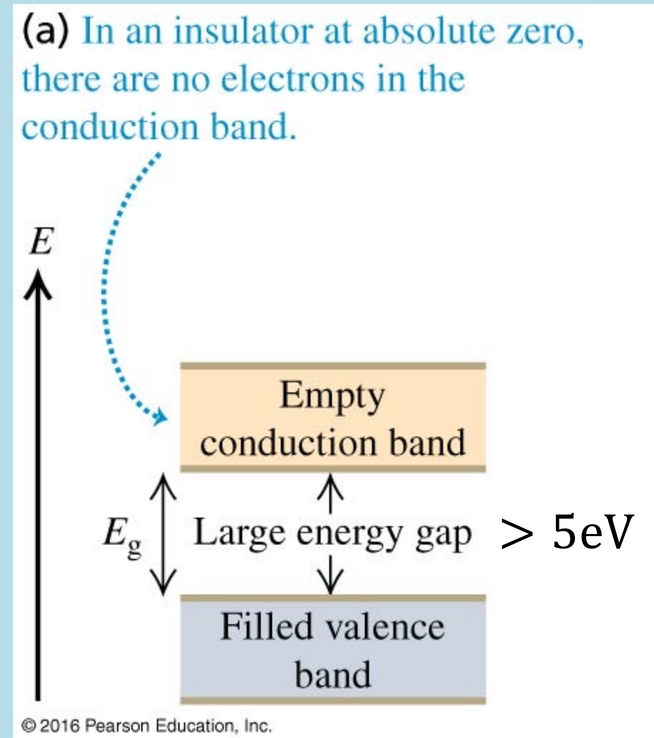
Identical Particles 全同粒子

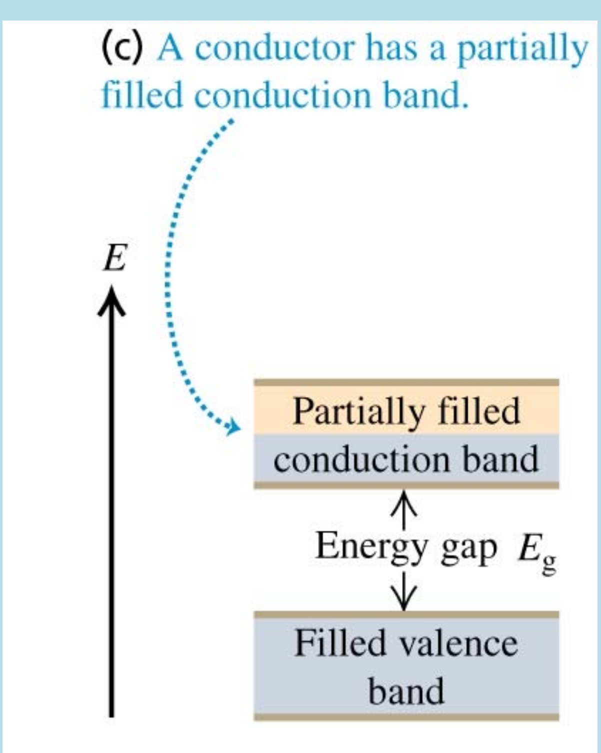


在三維的空間，電子的社會學更加戲劇化。

新的量子效應！彼此沒有作用的電子，其實會彼此影響。

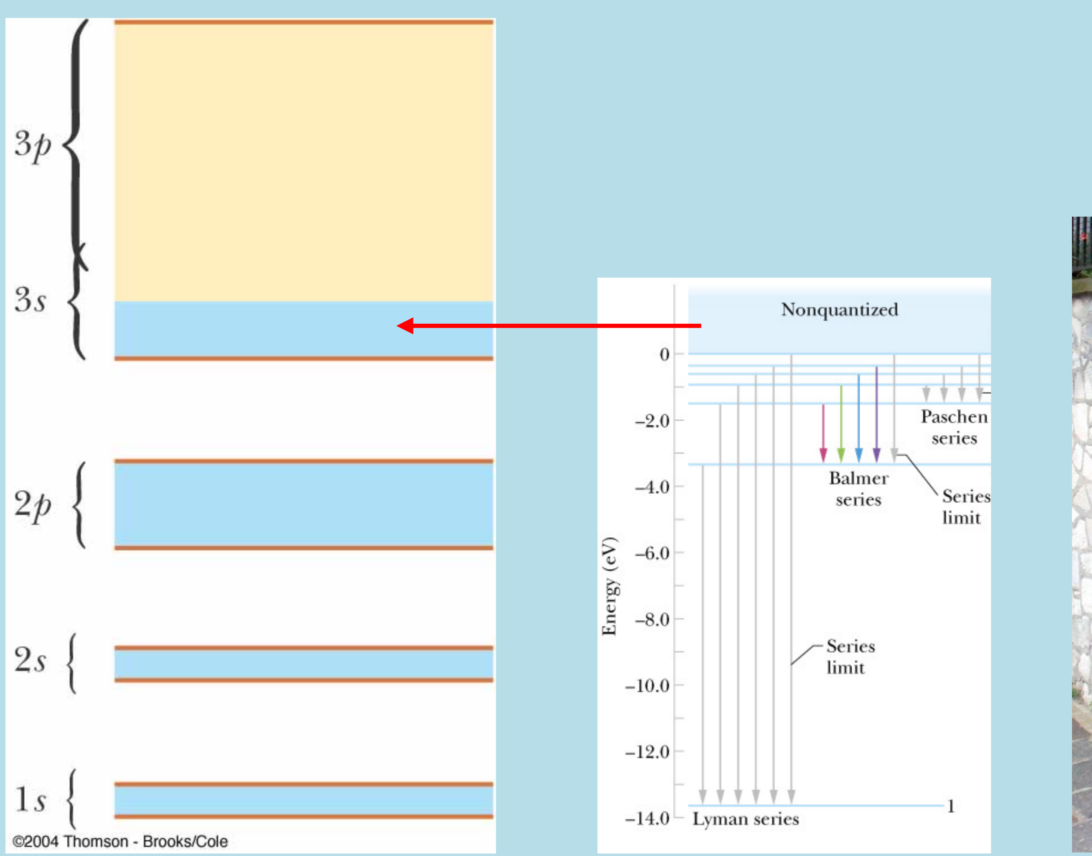
絕緣體與導體





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。

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！

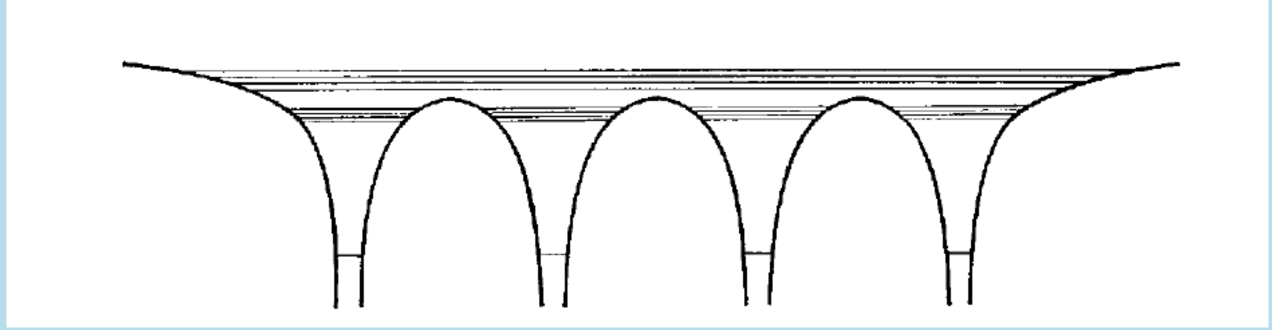
這些電子在固體內完全自由移動。彷彿沒有原子核存在一般。

這個模型有時就稱為無交互作用的理想電子氣體。電子因此作自由運動。

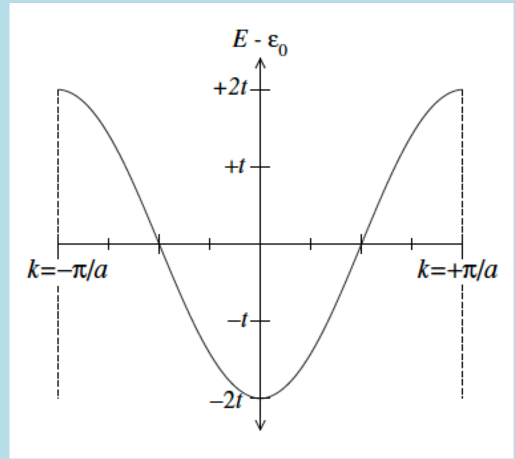
但彼此沒有作用的電子，其實會彼此影響。

Tight Binding Model

這些電子定態原來屬於私人，現在卻是公共財產！

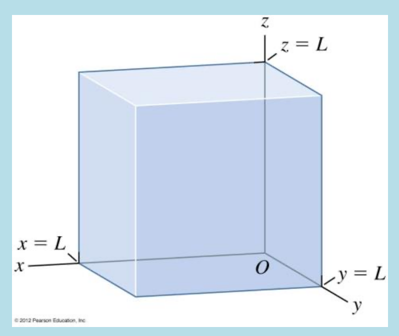


計算發現：每一角波數k對應一定態，能量本徵值與k的關係如下圖：



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

對於這些底部電子，原子核的位能似乎不存在。



描述導電固體，三度空間的Free Electron Model

Non-Interacting Electron Gas (Sommerfeld Model)

$$\hat{H}_0 = \frac{p^2}{2m}$$

3維空間能量本徵態的定態方程式：

$$H\psi_E(\vec{r}) = \frac{p^2}{2m}\psi_E(\vec{r}) = E\psi_E(\vec{r})$$

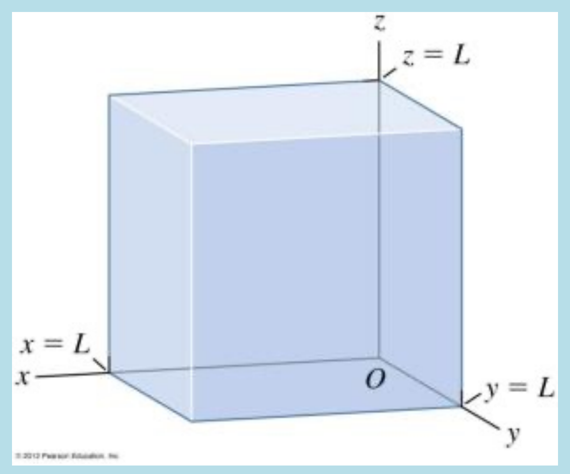
$$\vec{p} = (p_x, p_y, p_z) = \left(-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z}\right)$$

$$p^2 = -\hbar^2\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] = -\hbar^2\nabla^2$$

$$H\psi_E(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi_E(\vec{r}) = E\psi_E(\vec{r})$$

沒有位能。但的確有邊界。

將固體的邊界想像為無法透過的箱子。



3維箱子Box內自由空間的電子

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_E}{\partial x^2}+\frac{\partial^2\psi_E}{\partial y^2}+\frac{\partial^2\psi_E}{\partial z^2}\right)=-\frac{\hbar^2}{2m}\nabla^2\psi_E=E\psi_E$$

嘗試將波函數分解為三個變數個別函數的乘積：

$$\psi(x,y,z)=u(x)\cdot v(y)\cdot w(z)$$

代入定態方程式後，再除以ψ：

$$-\frac{\hbar^2}{2m}\left[\frac{1}{u}\frac{d^2u}{dx^2}(x)\right]-\frac{\hbar^2}{2m}\left[\frac{1}{v}\frac{d^2v}{dy^2}(y)\right]-\frac{\hbar^2}{2m}\left[\frac{1}{w}\frac{d^2w}{dz^2}(z)\right]=E$$

括號內分別只是x,y,z的函數，相加後為常數的唯一可能：

括號內都是常數，訂為E_1,E_2,E_3。

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2}=E_1u$$

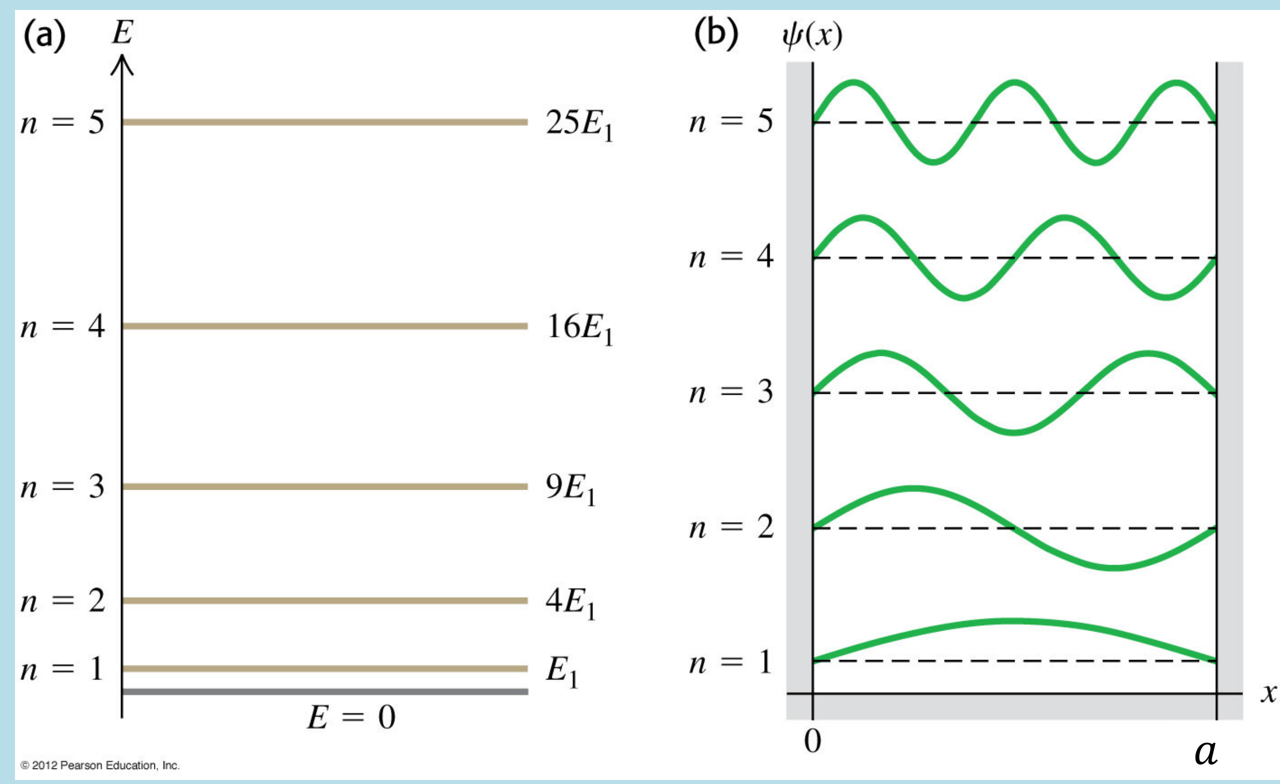
$$-\frac{\hbar^2}{2m}\frac{d^2v}{dy^2}=E_2v$$

$$-\frac{\hbar^2}{2m}\frac{d^2w}{dz^2}=E_3w$$

$$E_1+E_2+E_3=E$$

三維Box簡化為三個一維Box！

角波數 Angular Wave Number $k_n = \frac{n\pi}{a}$



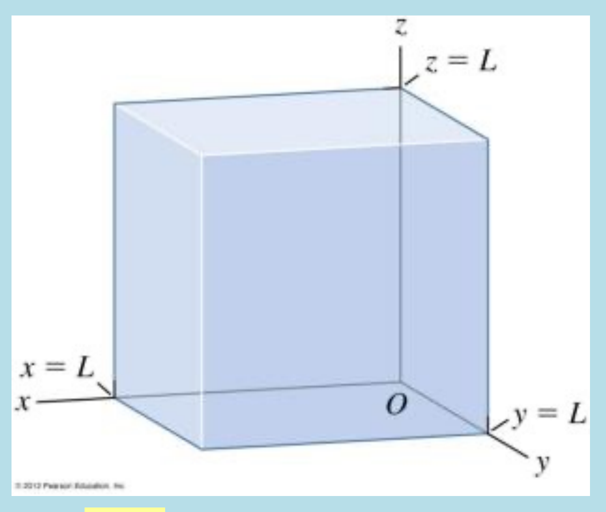
$u_n = C \sin\left(\frac{n\pi}{a}x\right)$ 代入 $-\frac{\hbar^2}{2m}\frac{d^2\psi_E(x)}{dx^2} = E\psi_E(x)$

能量等於：

$$E_n = \left(\frac{\hbar^2}{2m}\right)\frac{\pi^2}{a^2}n^2 = \left(\frac{h^2}{8ma^2}\right)n^2$$

電子組成波包，群速度為：

$$v_g = \frac{\partial\omega}{\partial k} = \frac{1}{\hbar}\frac{\partial E}{\partial k} = \hbar\frac{k}{m}$$



三維Box簡化為三個一維Box！

別忘了：自由電子氣的電子還是比較像波！

注意箱壁上波函數必須是零！

每一個方向有一個量子數，

一組(n_x, n_y, n_z)對應一個態！

k_x

$$u = \sqrt{\frac{2}{L}} \sin\left(\frac{n_x \pi}{L} x\right)$$

$$v = \sqrt{\frac{2}{L}} \sin\left(\frac{n_y \pi}{L} y\right)$$

$$w = \sqrt{\frac{2}{L}} \sin\left(\frac{n_z \pi}{L} z\right)$$

$$E_1 = \left(\frac{\hbar^2}{2m}\right)\frac{\pi^2}{L^2} n_x^2$$

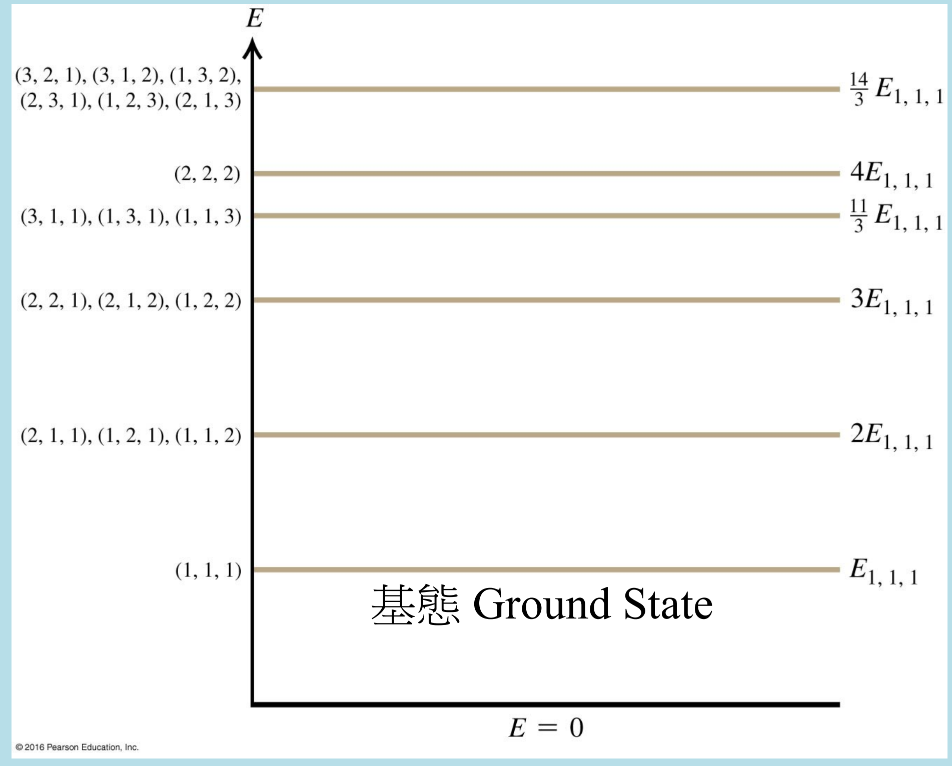
$$E_2 = \left(\frac{\hbar^2}{2m}\right)\frac{\pi^2}{L^2} n_y^2$$

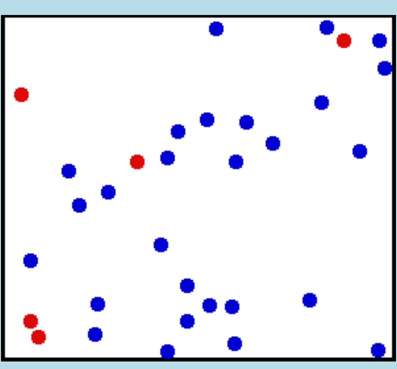
$$E_3 = \left(\frac{\hbar^2}{2m}\right)\frac{\pi^2}{L^2} n_z^2$$

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

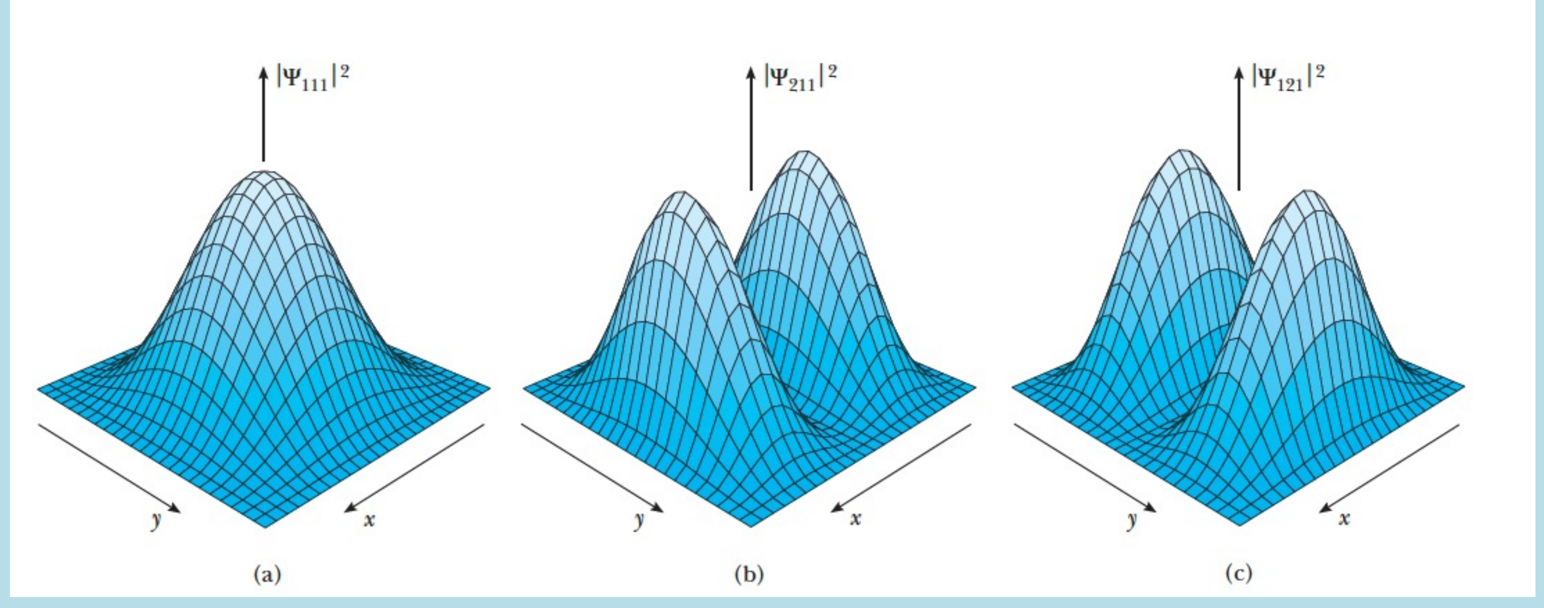
$$\psi(x, y, z) = \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right)$$

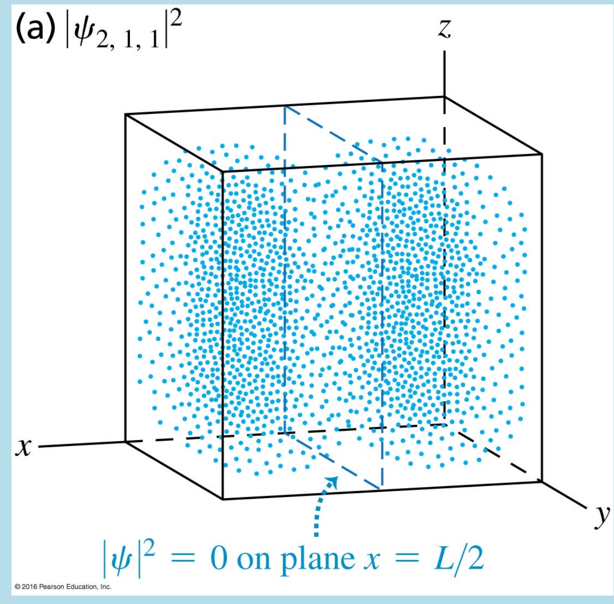
這是三維箱子內單一電子的定態能階與波函數。

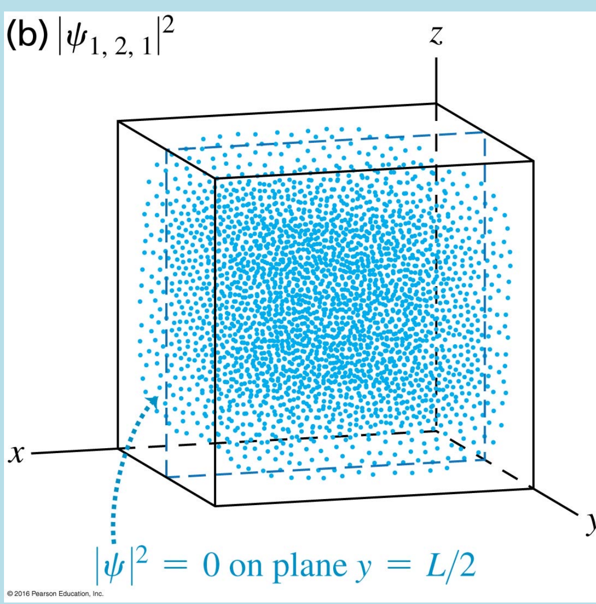


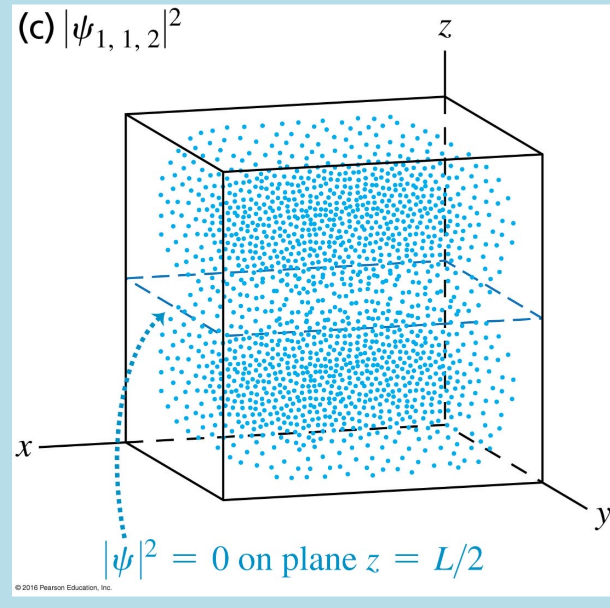


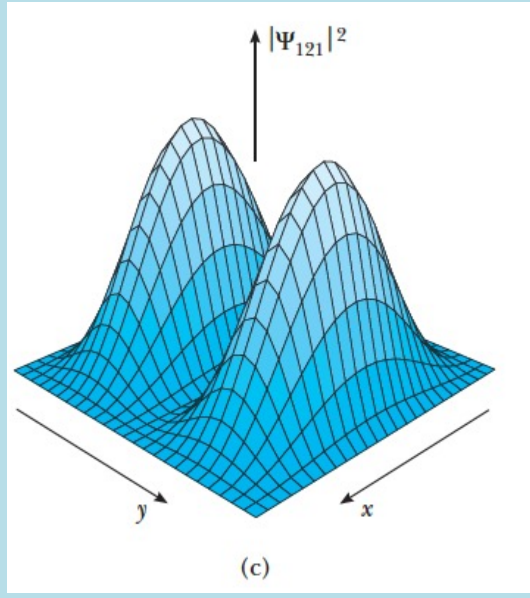
其實比較像空腔輻射！



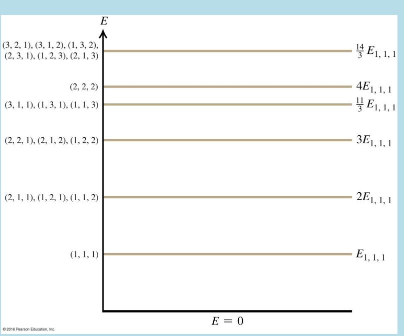








(c)

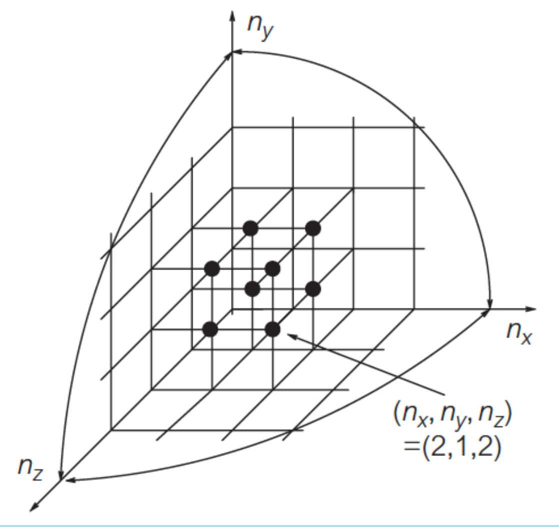


能態的分布還可以用另一個圖像來表示，當量子數大時使用更加方便：

$$\sin\left(\frac{n_x\pi}{L}x\right)\sin\left(\frac{n_y\pi}{L}y\right)\sin\left(\frac{n_z\pi}{L}z\right)$$

一組(n_x, n_y, n_z)對應一個態！

以(n_x, n_y, n_z)畫一空間，一個態即是一個點，在此空間內狀態分佈的密度是1！



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

這圖除了狀態的分佈，其實也標示出了狀態的能量E。

$n_x^2 + n_y^2 + n_z^2$是在(n_x, n_y, n_z)空間中，與原點的距離平方。恰等於$\frac{2mL^2}{\hbar^2\pi^2}E$。

代表態的點距離原點越遠，能量越大！

電子氣是把N個彼此無作用的自由電子放入箱中。

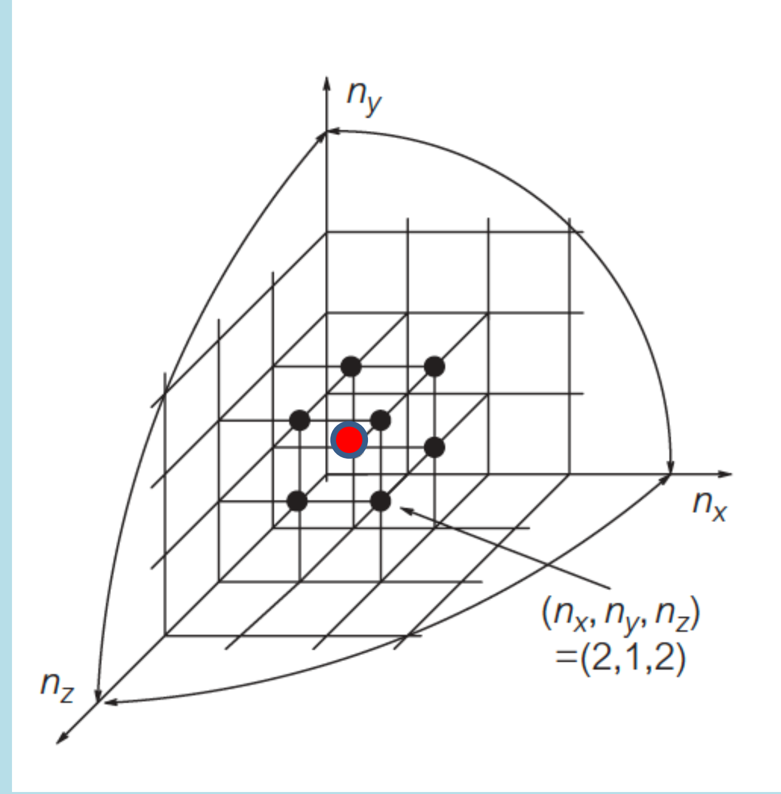
電子彼此無作用，所以電子就會選擇進入以上所得到的單一電子定態。

現在問：如果溫度為零，電子的狀態會是如何？

根據波茲曼分佈，

彼此不干擾的電子個自都會選擇進入能量最低的狀態。

$n_x = n_y = n_z = 1$ 基態 Ground State



電子等費米子卻有奇特的社交規則：

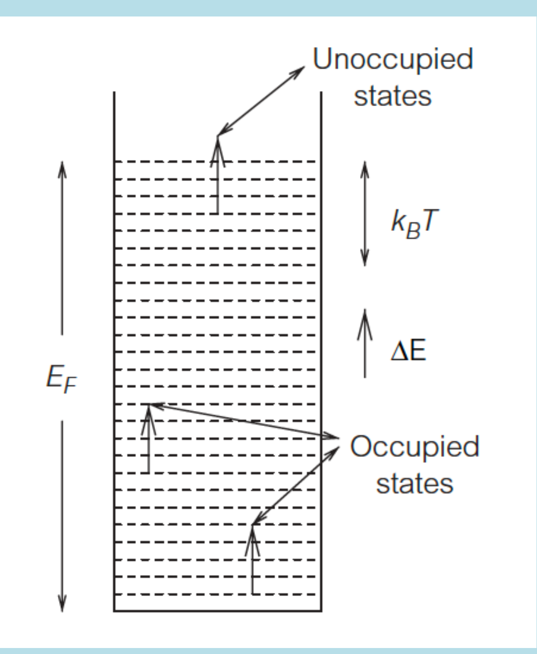
電子滿足不形容原理：兩個電子不能占據同一個量子態。

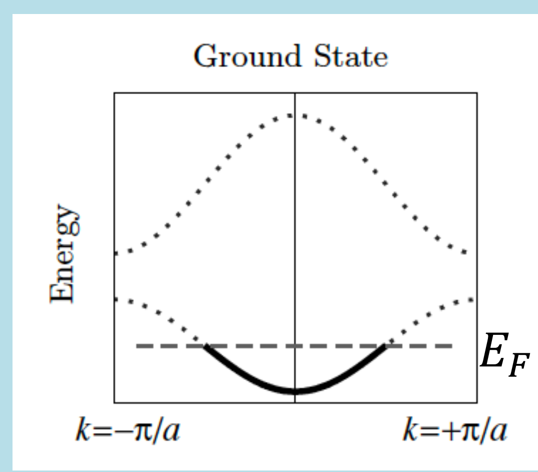
電子會一個一個由下往上填，就是由最低的能階向上一一配置！

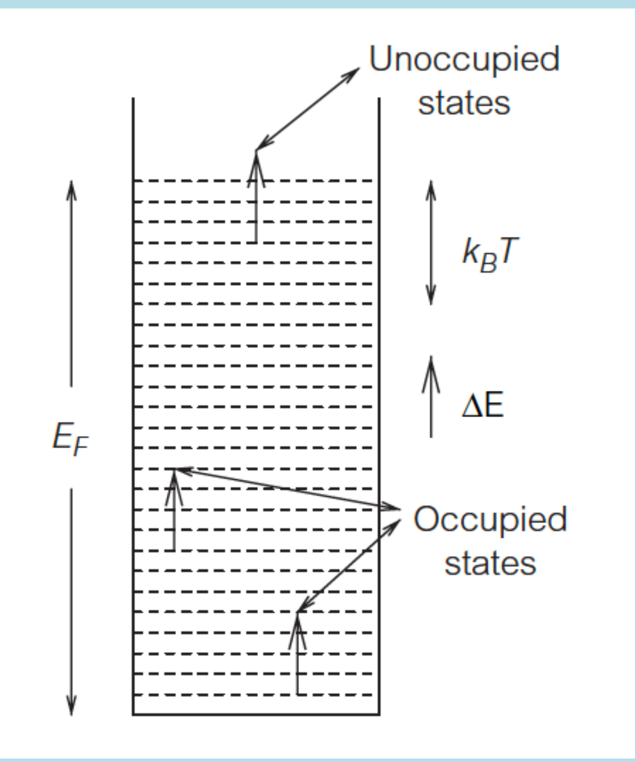
一個量子狀態，只能放置一個電子。

所以彼此不作用的自由電子，彼此卻好像有一個不能忽略的排斥作用。

電子能填到的最高能量，就稱為費米能量Fermi Energy：E_F。







而且只有能量略低於E_F的電子才有機會透過加熱或加電場改變狀態！

其餘的電子，改變的機會都已被其他電子佔據。

可見固體的性質，常是由電子在能量接近E_F時的行為所決定！

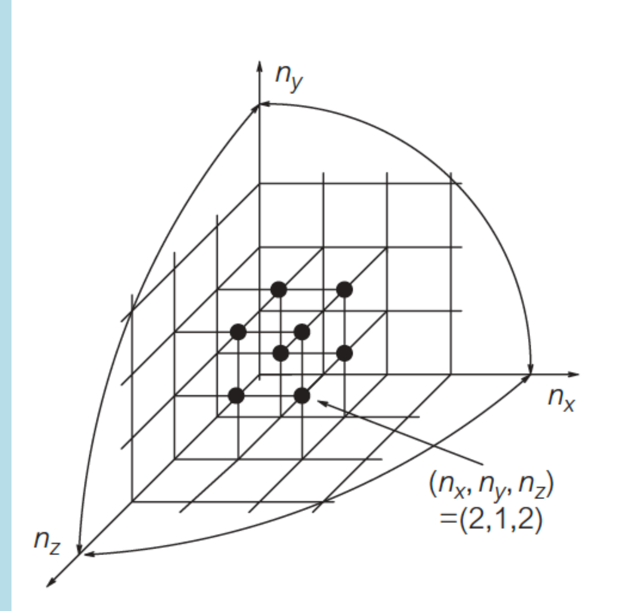
費米能量E_F顯然由自由電子個數N決定，

如何由電子個數N計算費米能量E_F？

因為一個量子態只能容納一個電子，

可見：能量低於費米能量E_F的能態的數目就是電子個數N。計算能態數目即可。

在(n_x, n_y, n_z)空間，一個態即是一個點，狀態分佈的密度是1！



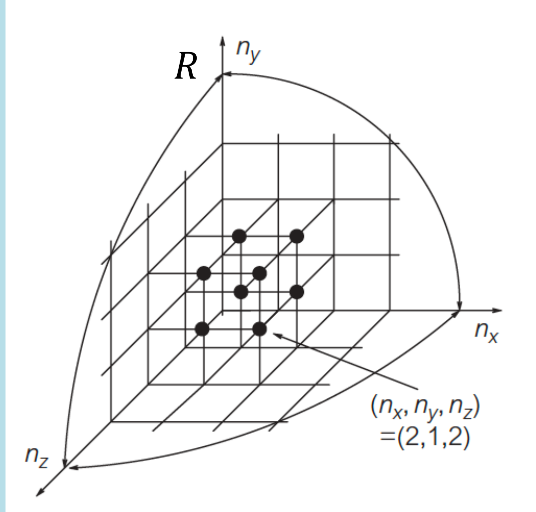
$$E = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

定義與原點距離：$n = \sqrt{n_x^2 + n_y^2 + n_z^2}$ $\quad E = \frac{\hbar^2\pi^2}{2mL^2} n^2$

因此能量小於E_F的態， 距離平方n^2就小於$\frac{2mL^2}{\hbar^2\pi^2} E_F$。將此值記為$R^2$ 。

對應的點就在一半徑為R的球內，因狀態分佈密度是1，球體積就是狀態數目。

有電子佔據的態，對應的點就在一半徑R的八分之一球內，
因狀態分佈的密度是1，八分之一球的體積就是狀態數目。



$$\frac{1}{8}\int_{n^2<R^2} d^3\vec{n} = \frac{1}{8}\frac{4}{3}\pi R^3$$

$$\frac{2mL^2}{\hbar^2\pi^2}E_F \equiv R^2$$

能量低於費米能量E_F的能態的數目乘2就是電子個數N。

$$N = 2\cdot\frac{1}{6}\pi R^3 = 2\cdot\frac{1}{6}\pi\left(\frac{2mL^2}{\hbar^2\pi^2}E_F\right)^{\frac{3}{2}} = \frac{1}{3}\pi L^3\left(\frac{2m}{\hbar^2\pi^2}E_F\right)^{\frac{3}{2}}$$

$$E_F = \frac{\hbar^2\pi^2}{2m}\left(\frac{3}{\pi}\frac{N}{L^3}\right)^{\frac{2}{3}} = \frac{\hbar^2\pi^2}{2m}\left(\frac{3}{\pi}n_e\right)^{\frac{2}{3}}$$

E_F由單位體積電子數決定： $n_e = \frac{N}{V}$

以銅為例，代入n_e， $E_F \sim 7\ \text{eV} \sim k\cdot 80000\ \text{K}$ 費米能量高達80000度的熱能。
電子速度高達$0.1c$。

這表示電子氣在溫度為零，能量最低時，電子必然是充滿動能！
民主的活力？☺ 量子驚奇！

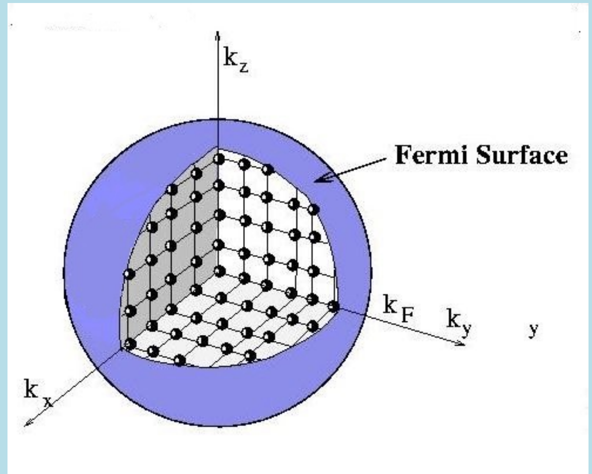
Fermi Surface

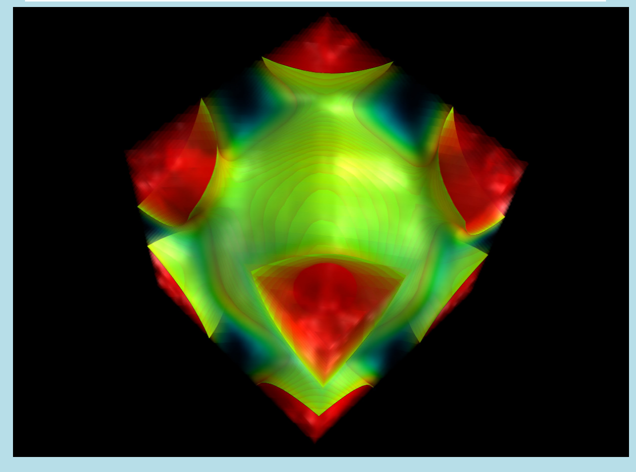
$$\psi(x,y,z) \sim \sin\left(\frac{n_x\pi}{L}x\right)\sin\left(\frac{n_y\pi}{L}y\right)\sin\left(\frac{n_z\pi}{L}z\right) \sim \sin(k_x x)\sin(k_y y)\sin(k_z z)$$

$$k_x = \frac{\pi}{L}n_x \quad k_y = \frac{\pi}{L}n_y \quad k_z = \frac{\pi}{L}n_z$$

角波數$\vec{k}$是一個向量，標記電子的狀態：

有電子佔據的態就在一個球內！此球面是能量最高的邊界，就稱為費米面！





有了這個圖像，N個電子總能量也能計算。已知定態的能量為：$E = \frac{\hbar^2\pi^2}{2mL^2}n^2$

能量接近在E與$E + dE$之間的態，代表的點就位於半徑n、厚度dn的球殼內。

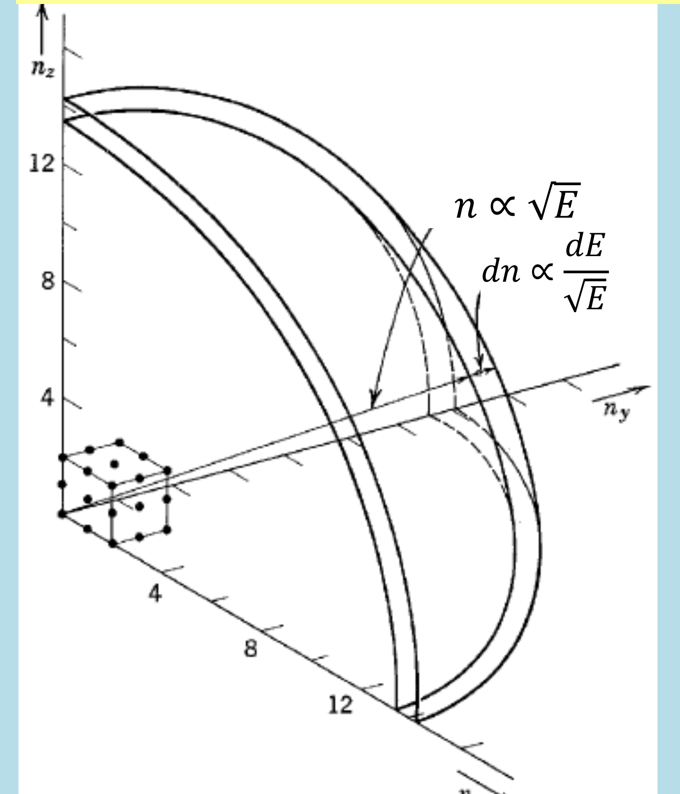
球殼內狀態數目就是球殼體積：$4\pi n^2 \cdot dn$

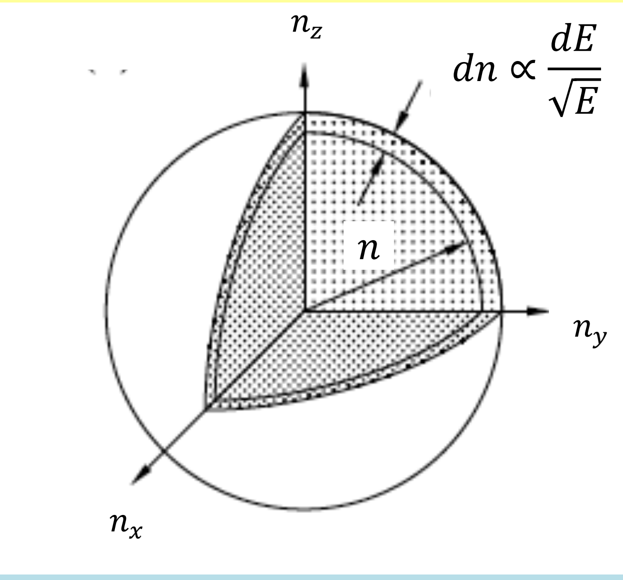
若以E表示，這個量記為$g(E)$，稱狀態數密度density of states.

球殼內總能量即是狀態的能量乘狀態數，接著再加總至費米能量對應的半徑R：

$$E_{\text{Total}} = \int_0^R dn \cdot \frac{2}{8} 4\pi n^2 \cdot \frac{\hbar^2\pi^2}{2mL^2} n^2 = \frac{\hbar^2\pi^2}{2mL^2}\frac{\pi}{5}R^5 = \frac{\hbar^2\pi^3}{10m}\left(\frac{3}{\pi}N\right)^{\frac{5}{3}} V^{-\frac{2}{3}}$$

$$N = \frac{1}{3}\pi R^3$$





Degeneracy Pressure

If the electron gas is compressed, the electrons are pushed closer to each other, and this decreases the de Broglie wavelength and, equivalently, increases the kinetic energy. Thus the compression is resisted, and the pressure resisting the compression is called the *degeneracy pressure*. It is given by

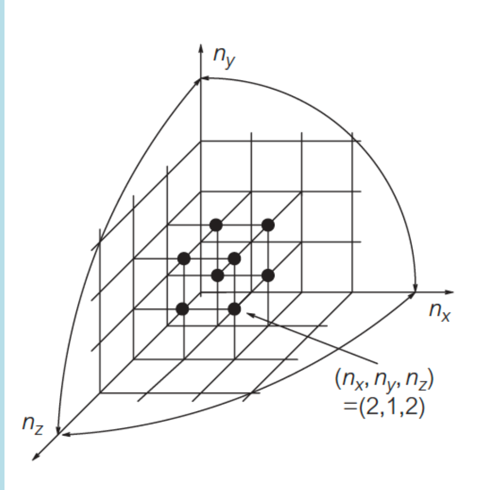
$$E_{\text{Total}} \propto V^{-\frac{2}{3}}$$

能量隨體積減少而變大，壓縮電子氣會增加其內能。

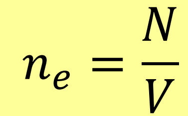
可見電子氣如理想氣體一般，有一個對外的壓力！

$$E_{\text{Total}} = \frac{\hbar^2\pi^3}{10m}\left(\frac{3}{\pi}N\right)^{\frac{5}{3}} V^{-\frac{2}{3}}$$

$$P = -\frac{\partial E_{\text{Total}}}{\partial V} = \frac{\hbar^2\pi^3}{15m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{\frac{5}{3}}$$



壓力由單位體積電子數決定：



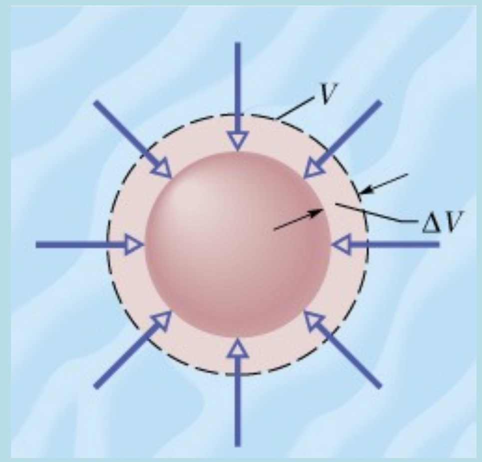
壓力與體積滿足特定關係：

$$PV^{\frac{5}{3}} = \frac{\hbar^2\pi^3}{15m}\left(\frac{3}{\pi}N\right)^{\frac{5}{3}}$$

右邊是常數，這就是電子氣溫度為零時的狀態方程式！

這是可以測量驗證的。

物質的體積變化比例與壓力變化成正比！



$$\Delta P = -B \cdot \frac{\Delta V}{V}$$

B是體積彈性係數Bulk Modulus

$$P = nRT \cdot V^{-1}$$

等溫理想氣體

$$B = -\frac{dP}{dV} \cdot V = nRTV^{-1} = P$$

$$P = c \cdot V^{-\gamma}$$

絕熱理想氣體

$$B = -\frac{dP}{dV} \cdot V = \gamma c V^{-\gamma} = \gamma P = 1.4P$$

$$B = 1.4P$$

$$PV^{\frac{5}{3}} = c$$

電子氣的狀態方程式！

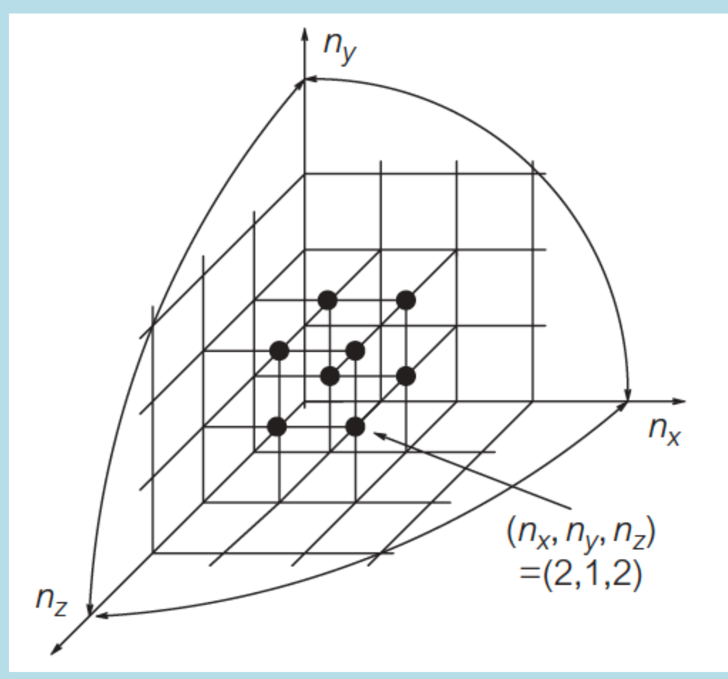
$$B = -\frac{dP}{dV} \cdot V = -\frac{d}{dV} cV^{-\frac{5}{3}} \cdot V = c\frac{5}{3}V^{-\frac{5}{3}} = \frac{5}{3}P$$

$$B = \frac{5}{3}P = \frac{\hbar^2\pi^3}{9m}\left(\frac{3}{\pi}n\right)^{\frac{5}{3}}$$

體積彈性係數也由單位體積電子數決定。

The use of a degenerate electron gas model for a metal gives the correct order of magnitude for the bulk modulus B. For example, for copper we have $n_e = 8.47 \times 10^{28}$ electrons/m^3, so that $B = 6.4 \times 10^{10}$ N/m^2. The experimental value is 14×10^{10} N/m^2.

接著可以為電子氣加上電場，增加溫度。



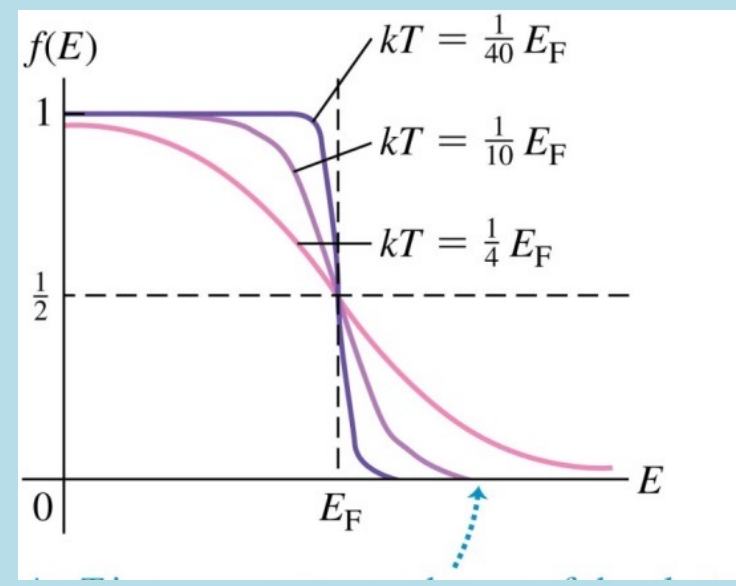
在溫度為T時，氣體分子處於能量E的機率等於：

$$f(E) \propto e^{-\frac{E}{kT}} = e^{-\frac{mv^2}{2kT}}$$ Boltzmann Factor

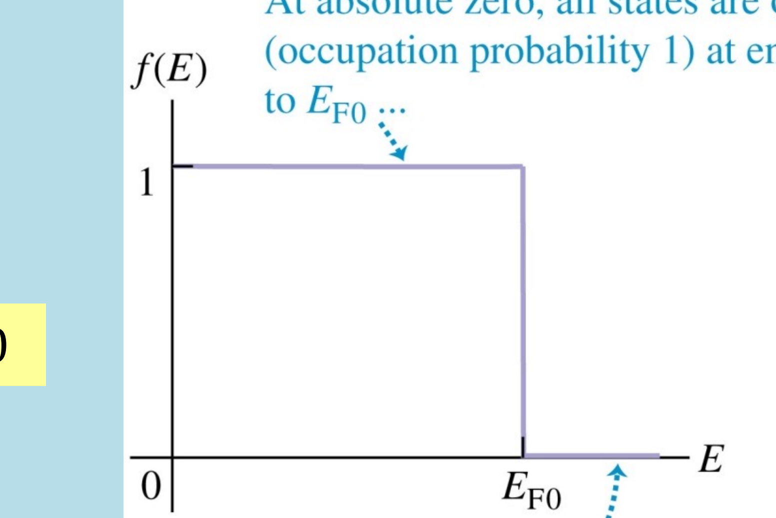
在理想電子氣體，此式必須以Fermi-Dirac Factor取代，稱費米統計：

$$f(E) = \frac{1}{e^{\frac{(E-E_F)}{kT}} + 1}$$

$$f(E) \to e^{-\frac{E}{kT}}, T \gg 0$$



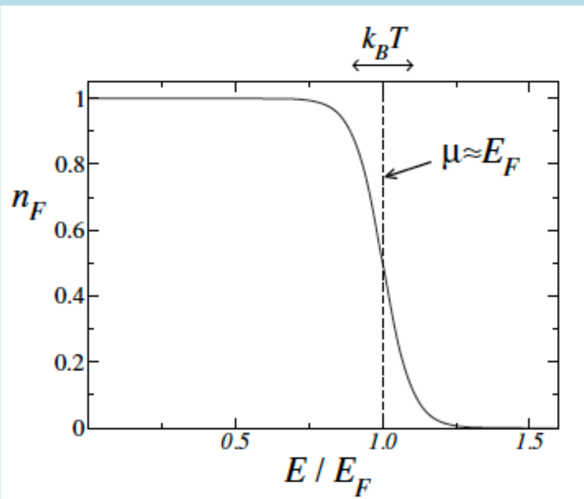
$T = 0$



總能量E_{Total}即是狀態的能量、乘狀態數密度，乘費米統計，再加總至無限大：

$$E_{\text{Total}} = \int_0^{\infty} dE \cdot E \cdot g(E) \cdot f(E)$$

$$E_{\text{Total}} = \int_0^\infty dE \cdot E \cdot g(E) \cdot f(E)$$



導體熱性質例如比熱c_V就可以推導出來！

但別忘了$kT \ll E_F$：室溫時，電子費米機率變化很小！

out as in Fig. 4.1. We see in the figure that only electrons within an energy range of roughly $k_B T$ of the Fermi surface can be excited—in general they are excited above the Fermi surface by an energy of about $k_B T$. Thus we can approximately write

We can then derive the heat capacity

$$C = \partial E / \partial T = \tilde{\gamma} k_B g(E_F) k_B T V$$

which then using Eq. 4.11 we can rewrite as

$$C = \tilde{\gamma} \left(\frac{3 N k_B}{2} \right) \left(\frac{T}{T_F} \right) \quad (4.12)$$

The first term in brackets is just the classical result for the heat capacity of a gas, but the final factor T/T_F is tiny (0.01 or smaller!). This is the above promised linear T term in the heat capacity of electrons (see Fig. 2.5), which is far smaller than one would get for a classical gas.

More Electrons in Metals: Sommerfeld (Free Electron) Theory

4

In 1925 Pauli discovered the exclusion principle, that no two electrons may be in the exact same state. In 1926, Fermi and Dirac separately derived what we now call Fermi–Dirac statistics.[1] Upon learning about these developments, Sommerfeld[2] realized that Drude's theory of metals could easily be generalized to incorporate Fermi statistics, which is what we shall presently do.

[1]Fermi–Dirac statistics were actually derived first by Pascual Jordan in 1925. Unfortunately, the referee of the manuscript, Max Born, misplaced it and it never got published. Many people believe that were it not for the fact that Jordan later joined the Nazi party, he might have won the Nobel Prize along with Born and Walther Bothe.

[2]Sommerfeld never won a Nobel Prize, although he was nominated for it 81 times—more than any other physicist. He was also a research advisor for more Nobel laureates than anyone else in history, including Heisenberg, Pauli, Debye, Bethe, Pauling, and Rabi.

4.1 Basic Fermi–Dirac Statistics

Given a system of free[3] electrons with chemical potential[4] μ the probability of an eigenstate of energy E being occupied[5] is given by the Fermi factor (See Fig. 4.1)

$$n_F(\beta(E-\mu)) = \frac{1}{e^{\beta(E-\mu)}+1}. \quad (4.1)$$

[3]Here "free" means that they do not interact with each other, with the background crystal lattice, with impurities, or with anything else for that matter.

At low temperature the Fermi function becomes a step function (states below the chemical potential are filled, those above the chemical potential are empty), whereas at higher temperatures the step function becomes more smeared out.

We will consider the electrons to be in a box of size $V = L^3$ and, as with our discussion in Section 2.2.1, it is easiest to imagine that

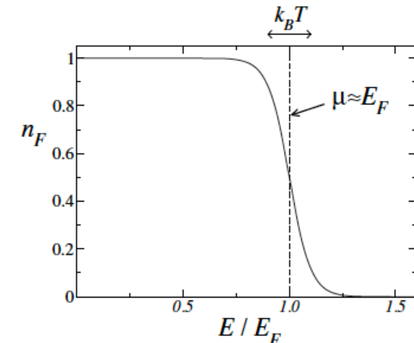


Fig. 4.1 The Fermi distribution for $k_BT \ll E_F$. The dashed line marks the chemical potential μ, which is approximately E_F. At $T = 0$ the distribution is a step, but for finite T it gets smeared over a range of energies of width a few times k_BT.

[4]In case you did not properly learn about chemical potential in your statistical physics course, it can be *defined* via Eq. 4.1, by saying that μ is whatever constant needs to be inserted into this equation to make it true. It can also be defined as an appropriate thermodynamical derivative such as $\mu = \partial U/\partial N|_{V,S}$ with U the total energy and N the number of particles or $\mu = \partial G/\partial N|_{T,P}$, with G the Gibbs potential. However, such a definition can be tricky if one worries about the discreteness of the particle number—since N must be an integer, the derivative may not be well defined. As a result the definition in terms of Eq. 4.1 is frequently best (i.e., we are treating μ as a Lagrange multiplier).

[5]When we say that there are a particular set of N orbitals occupied by electrons, we really mean that the overall wavefunction of the system is an antisymmetric function which can be expressed as a Slater determinant of N single electron wavefunctions. We will never need to actually write out such Slater determinant wavefunctions except in Section 23.3, which is somewhat more advanced material.

the box has periodic boundary conditions.[6] The plane wavefunctions are of the form $e^{i\mathbf{k}\cdot\mathbf{r}}$ where due to the boundary conditions $\mathbf{k}$ must take value $(2\pi/L)(n_1, n_2, n_3)$ with n_i integers. These plane waves have corresponding energies

$$\epsilon(\mathbf{k}) = \frac{\hbar^2|\mathbf{k}|^2}{2m} \tag{4.2}$$

with m the electron mass. Thus the total number of electrons in the system is given by

$$N = 2\sum_{\mathbf{k}} n_F(\beta(\epsilon(\mathbf{k}) - \mu)) = 2\frac{V}{(2\pi)^3}\int \mathbf{dk}\; n_F(\beta(\epsilon(\mathbf{k}) - \mu)) \tag{4.3}$$

where the prefactor of 2 accounts for the two possible spin states for each possible wavevector $\mathbf{k}$. In fact, in a metal, N will usually be given to us, and this equation will define the chemical potential as a function of temperature.

We now define a useful concept:

Definition 4.1 *The* ***Fermi energy****, E_F is the chemical potential at temperature $T = 0$.*

This is also sometimes called the *Fermi level*. The states that are filled at $T = 0$ are sometimes called the *Fermi sea*. Frequently one also defines a *Fermi temperature* $T_F = E_F/k_B$, and also the *Fermi wavevector* k_F defined via

$$E_F = \frac{\hbar^2 k_F^2}{2m} \tag{4.4}$$

and correspondingly a *Fermi momentum* $p_F = \hbar k_F$ and a *Fermi velocity*[7]

$$v_F = \hbar k_F/m. \tag{4.5}$$

[6] As mentioned in Section 2.2.1, any properties of the bulk of the solid should be independent of the type of boundary conditions we choose. If you have doubts, you can try repeating all the calculations using hard wall boundary conditions, and you will find all the same results (It is more messy, but not too much harder!).

[7] Yes, Fermi got his name attached to many things. To help spread the credit around I've called this section "Basic Fermi–Dirac Statistics" instead of just "Basic Fermi Statistics".

Aside: Frequently people think of the Fermi energy as the energy of the most energetic occupied electron state in system. While this is correct in the case where you are filling a continuum of states, it can also lead you to errors in cases where the energy eigenstates are discrete (see the related footnote 4 of this chapter), or more specifically when there is a gap between the most energetic occupied electron state in the system, and the least energetic unoccupied electron state. More correctly the Fermi energy, i.e., the chemical potential at $T = 0$, will be half-way between the most energetic occupied electron state, and the least energetic unoccupied electron state (see Exercise 4.6).

Let us now calculate the Fermi energy in a (three-dimensional) metal with N electrons in it. At $T = 0$ the Fermi function (Eq. 4.1) becomes a step function (which we write as Θ. I.e., $\Theta(x) = 1$ for $x \geqslant 0$ and $\Theta(x) = 0$ for $x < 0$), so that Eq. 4.3 becomes

$$N = 2\frac{V}{(2\pi)^3}\int \mathbf{dk}\; \Theta(E_F - \epsilon(\mathbf{k})) = 2\frac{V}{(2\pi)^3}\int^{|k|<k_F} \mathbf{dk}.$$

The final integral here is just an integral over a ball of radius k_F. Thus the integral gives us the volume of this ball ($4\pi/3$ times the cube of the radius) yielding

$$N = 2\frac{V}{(2\pi)^3}\left(\frac{4}{3}\pi k_F^3\right). \tag{4.6}$$

In other words, at $T = 0$ the electrons simply fill a ball in k-space of radius k_F. The surface of this ball, a sphere (the "Fermi sphere") of radius k_F is known as the *Fermi surface*—a term more generally defined as the surface dividing filled from unfilled states at zero temperature.

Using the fact that the density is defined as $n = N/V$ we can rearrange Eq. 4.6 to give

$$k_F = (3\pi^2 n)^{1/3}$$

and correspondingly

$$E_F = \frac{\hbar^2(3\pi^2 n)^{2/3}}{2m}. \tag{4.7}$$

Since we know roughly how many free electrons there are in a metal (say, one per atom for monovalent metals such as sodium or copper), we can estimate the Fermi energy, which, say for copper, turns out to be on the order of 7 eV, corresponding to a Fermi temperature of about 80,000 K(!). This amazingly high energy scale is a result of Fermi statistics and the very high density of electrons in metals. It is crucial to remember that for all metals, $T_F \gg T$ for any temperature anywhere near room temperature. In fact metals melt (and even vaporize!) at temperatures far far below their Fermi temperatures.

Similarly, one can calculate the Fermi velocity, which, for a typical metal such as copper, may be as large as 1% the speed of light! Again, this enormous velocity stems from the Pauli exclusion principle—all the lower momentum states are simply filled, so if the density of electrons is very high, the velocities will be very high as well.

With a Fermi energy that is so large, and therefore a Fermi sea that is very deep, any (not insanely large) temperature can only make excitations of electrons that are already very close to the Fermi surface (i.e., they can jump from just below the Fermi surface to just above with only a small energy increase). The electrons deep within the Fermi sea, near $\mathbf{k} = \mathbf{0}$, cannot be moved by any reasonably low-energy perturbation simply because there are no available unfilled states for them to move into unless they absorb a very large amount of energy.

4.2 Electronic Heat Capacity

We now turn to examine the heat capacity of electrons in a metal. Analogous to Eq. 4.3, the total energy of our system of electrons is given now by

$$\begin{aligned} E_{total} &= \frac{2V}{(2\pi)^3}\int \mathbf{dk}\, \epsilon(\mathbf{k})\, n_F(\beta(\epsilon(\mathbf{k}) - \mu)) \\ &= \frac{2V}{(2\pi)^3}\int_0^\infty 4\pi k^2 dk\, \epsilon(\mathbf{k})\, n_F(\beta(\epsilon(\mathbf{k}) - \mu)) \end{aligned}$$

where the chemical potential is defined as above by

$$N = \frac{2V}{(2\pi)^3}\int \mathbf{dk}\, n_F(\beta(\epsilon(\mathbf{k})-\mu)) = \frac{2V}{(2\pi)^3}\int_0^\infty 4\pi k^2 dk\; n_F(\beta(\epsilon(\mathbf{k})-\mu)).$$

(In both equations we have changed to spherical coordinates to obtain a one-dimensional integral and a factor of $4\pi k^2$ out front.)

It is convenient to replace k in this equation by the energy ϵ by using Eq. 4.2 or equivalently

$$k = \sqrt{\frac{2\epsilon m}{\hbar^2}}$$

so that

$$dk = \sqrt{\frac{m}{2\epsilon\hbar^2}}\; d\epsilon.$$

We can then rewrite these expressions as

$$E_{total} = V\int_0^\infty d\epsilon\;\epsilon\; g(\epsilon)\; n_F(\beta(\epsilon-\mu)) \tag{4.8}$$

$$N = V\int_0^\infty d\epsilon\; g(\epsilon)\; n_F(\beta(\epsilon-\mu)) \tag{4.9}$$

where

$$\begin{aligned} g(\epsilon)d\epsilon &= \frac{2}{(2\pi)^3}4\pi k^2 dk = \frac{2}{(2\pi)^3}4\pi\left(\frac{2\epsilon m}{\hbar^2}\right)\sqrt{\frac{m}{2\epsilon\hbar^2}}\; d\epsilon \\ &= \frac{(2m)^{3/2}}{2\pi^2\hbar^3}\epsilon^{1/2}d\epsilon \end{aligned} \tag{4.10}$$

is the *density of states per unit volume*. The definition[8] of this quantity is such that $g(\epsilon)d\epsilon$ is the total number of eigenstates (including both spin states) with energies between ϵ and $\epsilon + d\epsilon$.

From Eq. 4.7 we can simply derive $(2m)^{3/2}/\hbar^3 = 3\pi^2 n/E_F^{3/2}$, thus we can simplify the density of states expression to

$$g(\epsilon) = \frac{3n}{2E_F}\left(\frac{\epsilon}{E_F}\right)^{1/2} \tag{4.11}$$

which is a fair bit simpler. Note that the density of states has dimensions of a density (an inverse volume) divided by an energy. It is clear that this is the dimensions it must have, given Eq. 4.9 for example.

Note that the expression Eq. 4.9 should be thought of as defining the chemical potential given the number of electrons in the system and the temperature. Once the chemical potential is fixed, then Eq. 4.8 gives us the total kinetic energy of the system. Differentiating that quantity would give us the heat capacity. Unfortunately there is no way to do this analytically in all generality. However, we can use to our advantage that $T \ll T_F$ for any reasonable temperature, so that the Fermi factors n_F are close to a step function. Such an expansion was first used by Sommerfeld, but it is algebraically rather complicated[9] (see Ashcroft and Mermin Chapter 2 to see how it is done in detail). However, it is

not hard to make an estimate of what such a calculation must give—which we shall now do.

When $T = 0$ the Fermi function is a step function and the chemical potential is (by definition) the Fermi energy. For small T, the step function is smeared out as we see in Fig. 4.1. Note, however, that in this smearing, the number of states that are removed from below the chemical potential is almost exactly the same as the number of states that are added above the chemical potential.[10] Thus, for small T, one does not have to move the chemical potential much from the Fermi energy in order to keep the number of particles fixed in Eq. 4.9. We conclude that $\mu \approx E_F$ for any low temperature. (In more detail we find that $\mu(T) = E_F + \mathcal{O}(T/T_F)^2$, see Ashcroft and Mermin Chapter 2.)

Thus we can focus on Eq. 4.8 with the assumption that $\mu = E_F$. At $T = 0$ let us call the kinetic energy[11] of the system $E(T = 0)$. At finite temperature, instead of a step function in Eq. 4.8 the step is smeared out as in Fig. 4.1. We see in the figure that only electrons within an energy range of roughly $k_B T$ of the Fermi surface can be excited—in general they are excited above the Fermi surface by an energy of about $k_B T$. Thus we can approximately write

$$E(T) = E(T = 0) + (\tilde{\gamma}/2)[V g(E_F)(k_B T)](k_B T) + \ldots.$$

Here $V g(E_F)$ is the density of states near the Fermi surface (recall g is the density of states per unit volume), so the number of particles close enough to the Fermi surface to be excited is $V g(E_F)(k_B T)$, and the final factor of $(k_B T)$ is roughly the amount of energy that each one gets excited by. Here $\tilde{\gamma}$ is some constant which we cannot get right by such an approximate argument (but it can be derived more carefully, and it turns out that $\tilde{\gamma} = \pi^2/3$, see Ashcroft and Mermin).

We can then derive the heat capacity

$$C = \partial E/\partial T = \tilde{\gamma} k_B g(E_F) k_B T V$$

which then using Eq. 4.11 we can rewrite as

$$C = \tilde{\gamma} \left(\frac{3Nk_B}{2}\right)\left(\frac{T}{T_F}\right). \qquad (4.12)$$

The first term in brackets is just the classical result for the heat capacity of a gas, but the final factor T/T_F is tiny (0.01 or smaller!). This is the above promised linear T term in the heat capacity of electrons (see Fig. 2.5), which is far smaller than one would get for a classical gas.

This Sommerfeld prediction for the electronic (linear T) contribution to the heat capacity of a metal is typically not too far from being correct (see Table 4.1). A few metals, however, have specific heats that deviate from this prediction by a factor of 10 or more. Note that there are other measurements that indicate that these errors are associated with the electron mass being somehow changed in the metal. We will discover the reason for these deviations later when we study band theory (mainly in Chapter 17).

[10] Since the Fermi function has a precise symmetry around μ given by $n_F(\beta(E-\mu)) = 1 - n_F(\beta(\mu - E))$, this equivalence of states removed from below the chemical potential and states inserted above would be an exact statement if the density of states in Eq. 4.9 were independent of energy.

[11] In fact $E(T = 0) = (3/5)NE_F$, which is not too hard to show. See Exercise 4.1.

Table 4.1 Low-temperature heat capacity coefficient for some metals. All of these metals have heat capacities of the form $C = \gamma T + \alpha T^3$ at low temperature. This table gives the measured experimental (exp) value and the Sommerfeld theoretical (th) predictions for the coefficient γ in units of 10^{-4} J/(mol-K).

Material	γ_{exp}	γ_{th}
Lithium (Li)	18	7.4
Sodium (Na)	15	11
Potassium (K)	20	17
Copper (Cu)	7	5.0
Silver (Ag)	7	6.4
Beryllium (Be)	2	2.5
Bismuth (Bi)	1	5.0
Manganese (Mn)	170	5.2

The theoretical value is obtained by setting the electron density equal to the atomic density times the valence (number of free electrons per atom), then calculating the Fermi temperature from the density and using Eq. 4.12. Note that Mn has multiple possible valence states. In the theoretical calculation we assume valence of one which gives the largest possible predicted value of γ_{th}.

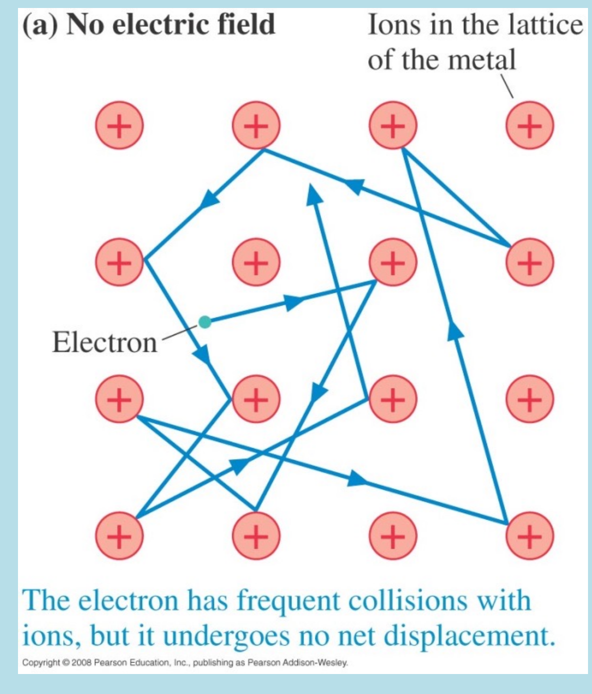
電場對電子產生一加速度： $a = \frac{F}{m} = \frac{eE}{m}$

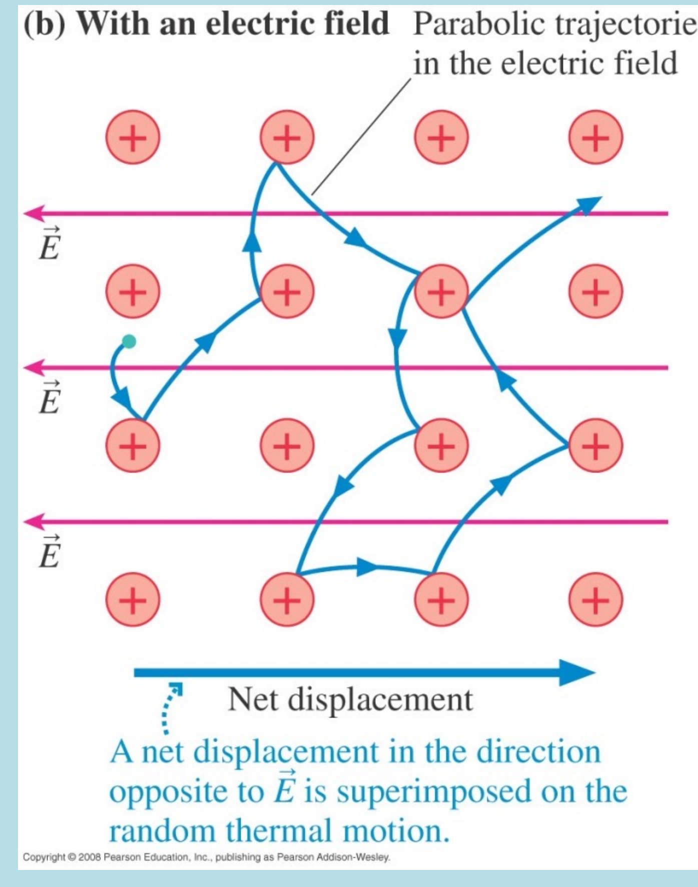
這是等加速度運動，電子速度一直增加，直到與離子碰撞後大致歸零。

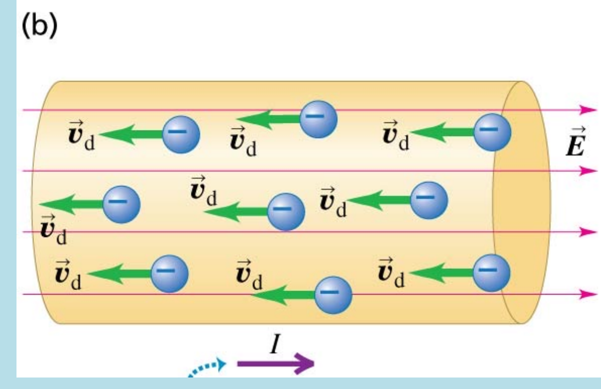
我們可以兩次碰撞間，電子的平均速度，來估計電子漂移的平均速度。

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。







比較進化的推導：

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

We consider an electron with momentum $\mathbf{p}$ at time t and ask what momentum it will have at time $t+dt$. There are two terms in the answer. There is a probability dt/τ that it will scatter to momentum zero. If it does not scatter to momentum zero (with probability $1-dt/\tau$) it simply accelerates as dictated by its usual equations of motion $d\mathbf{p}/dt = \mathbf{F}$. Putting the two terms together we have

$$\langle \mathbf{p}(t+dt)\rangle = \left(1 - \frac{dt}{\tau}\right)(\mathbf{p}(t) + \mathbf{F}dt) + \mathbf{0}\,dt/\tau$$

or keeping terms only to linear order in dt then rearranging,[6]

$$\frac{d\mathbf{p}}{dt} = \mathbf{F} - \frac{\mathbf{p}}{\tau} \tag{3.1}$$

where here the force $\mathbf{F}$ on the electron is just the Lorentz force

$$\mathbf{F} = -e(\mathbf{E} + \mathbf{v}\times\mathbf{B}).$$

One can think of the scattering term $-\mathbf{p}/\tau$ as just a drag force on the electron. Note that in the absence of any externally applied field the solution to this differential equation is just an exponentially decaying momentum

$$\mathbf{p}(t) = \mathbf{p}_{initial}\; e^{-t/\tau}$$

which is what we should expect for particles that lose momentum by scattering.

[6]Here we really mean the thermal average $\langle \mathbf{p}\rangle$ when we write $\mathbf{p}$. Since our scattering is probabilistic, we should view all quantities (such as the momentum) as being an expectation over these random events. A more detailed theory would keep track of the entire distribution of momenta rather than just the average momentum. Keeping track of distributions in this way leads one to the Boltzmann Transport Equation, which we will not discuss.

3.1 Electrons in Fields

3.1.1 Electrons in an Electric Field

Let us start by considering the case where the electric field is non-zero but the magnetic field is zero. Our equation of motion is then

$$\frac{d\mathbf{p}}{dt} = -e\mathbf{E} - \frac{\mathbf{p}}{\tau}.$$

In steady state, $d\mathbf{p}/dt = 0$ so we have

$$m\mathbf{v} = \mathbf{p} = -e\tau\mathbf{E}$$

with m the mass of the electron and $\mathbf{v}$ its velocity.

Now, if there is a density n of electrons in the metal each with charge $-e$, and they are all moving at velocity $\mathbf{v}$, then the electrical current is given by

$$\mathbf{j} = -en\mathbf{v} = \frac{e^2\tau n}{m}\mathbf{E}$$

or in other words, the conductivity of the metal, defined via $\mathbf{j} = \sigma\mathbf{E}$ is given by[7]

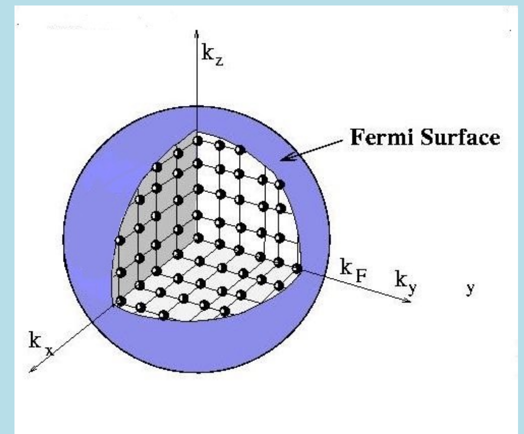
$$\sigma = \frac{e^2\tau n}{m}. \tag{3.2}$$

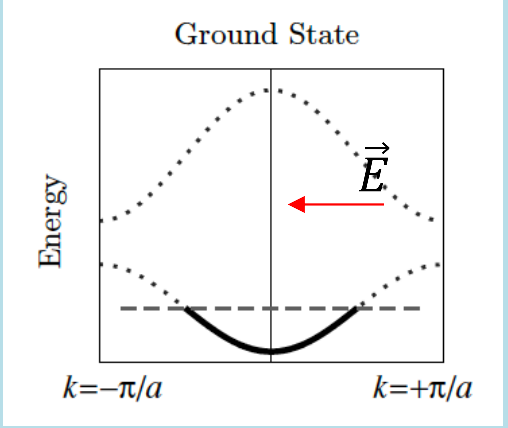
By measuring the conductivity of the metal (assuming we know both the charge and mass of the electron) we can determine the product of the electron density and scattering time of the electron.

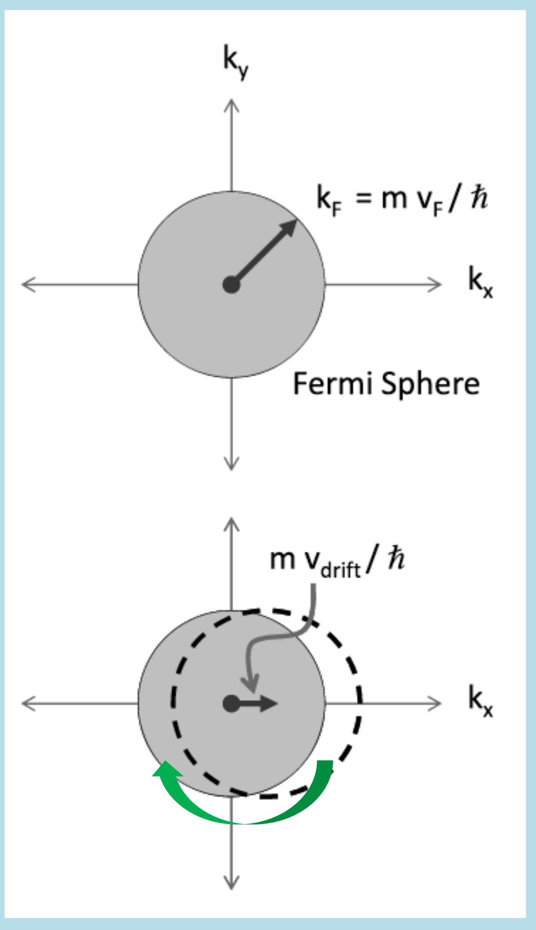
[7]A related quantity is the *mobility*, defined by $\mathbf{v} = \mu\mathbf{E}$, which is given in Drude theory by $\mu = e\tau/m$. We will discuss mobility further in Section 17.1.1.

有電子佔據的態就在一個球內！此球面是能量最高的邊界，就稱為費米面！

費米面在常數電場下會沿電場反方向定速移動。



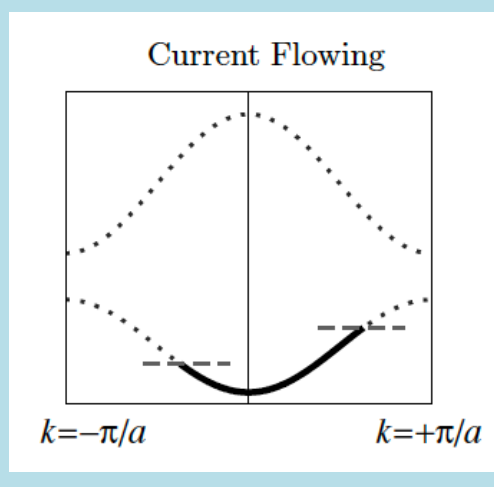




$$\hbar \frac{dk}{dt} = eE - \frac{\hbar k}{\tau}$$

$\hbar k_d = eE\tau$ 達到穩定的飄移

$$v_d = \frac{\hbar k_d}{m} = \frac{e\tau}{m} E$$

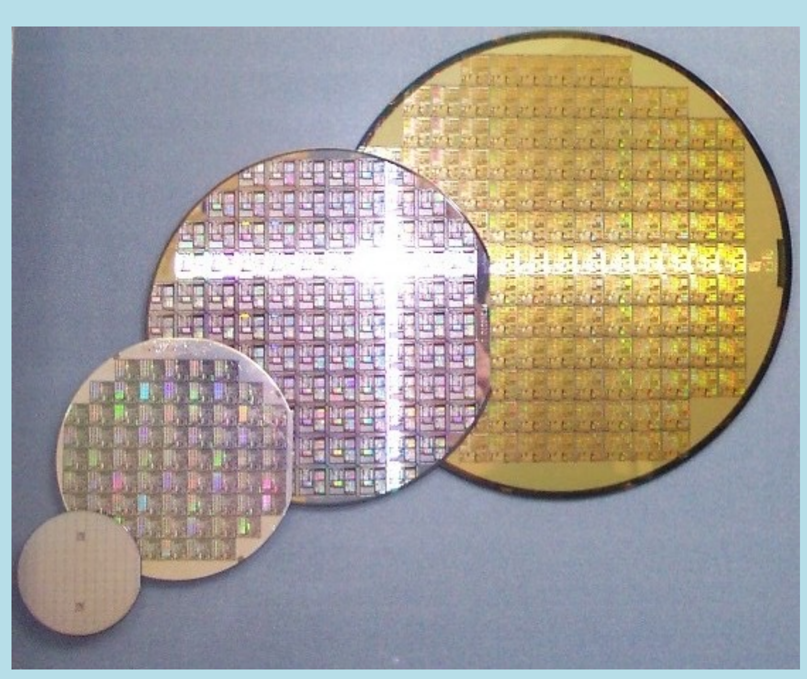


同時，右邊能量超越原本費米面的電子，可以與離子散射，回到能量較低的狀態。

兩個過程彼此抵消時，高斯面就會停在該處，此時的平均$\hbar k_d = eE\tau$。

平均速度v_d就維持向右大概不變，

半導體 Semiconductor



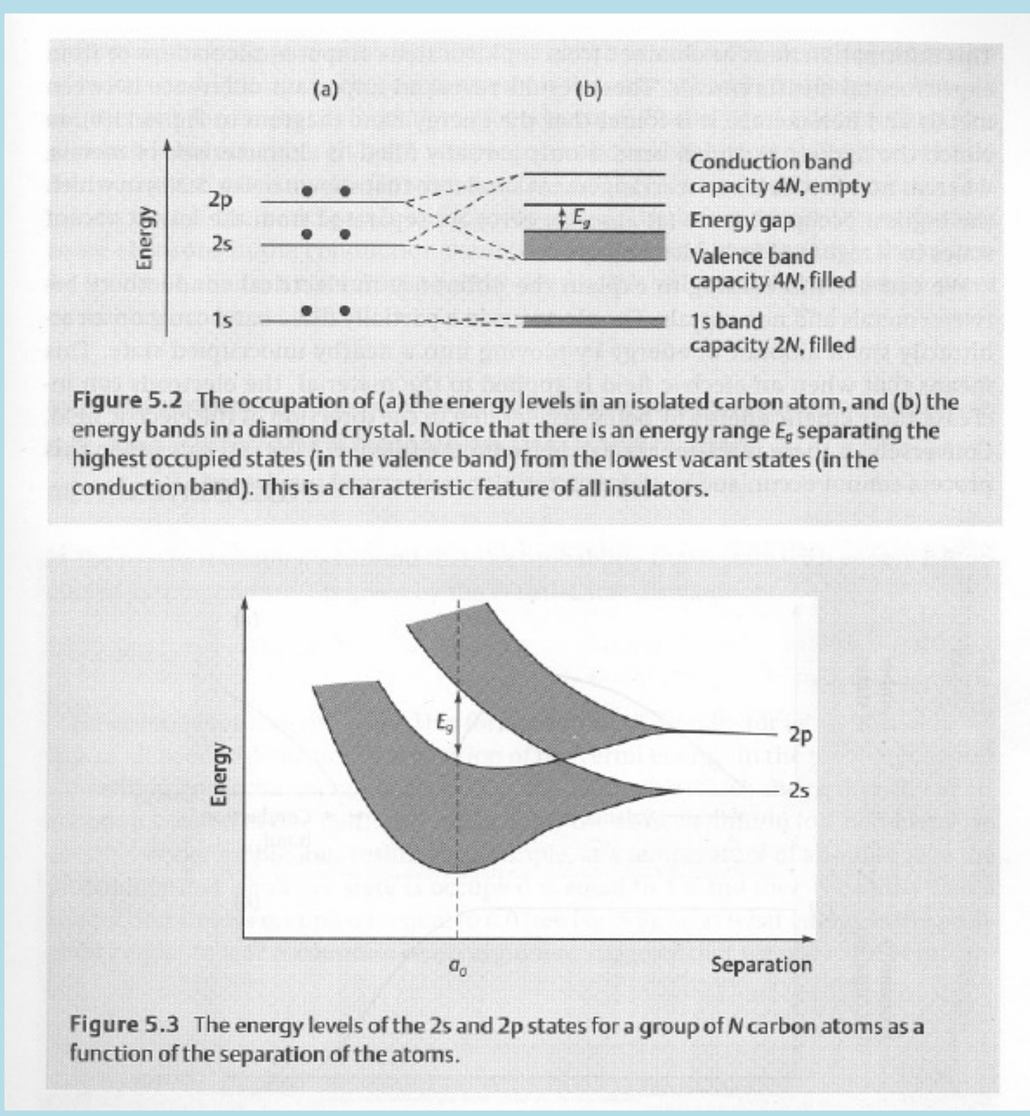
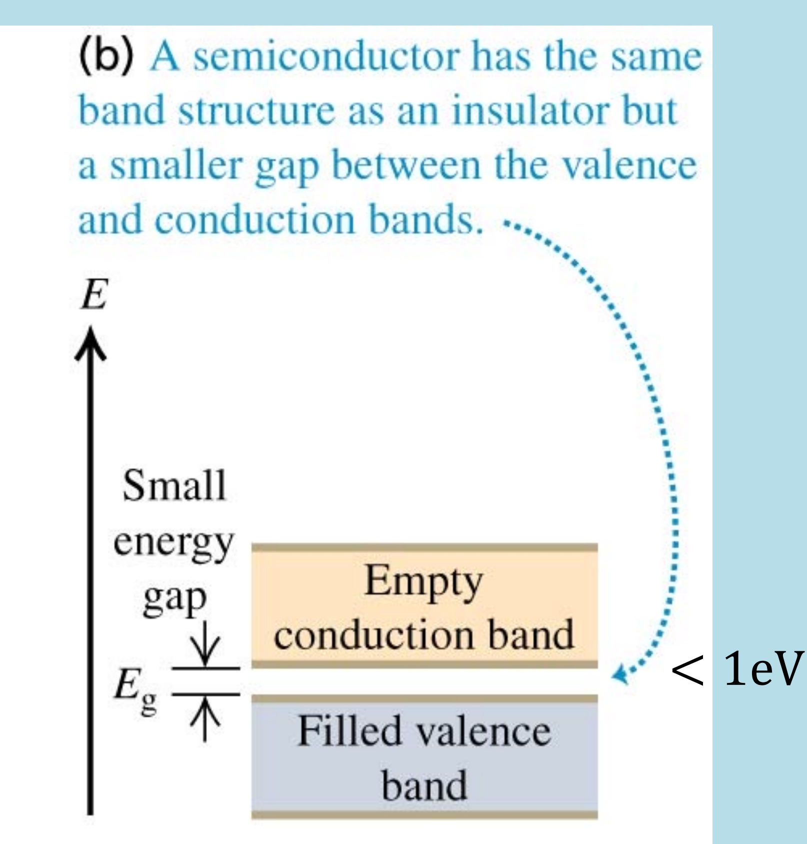


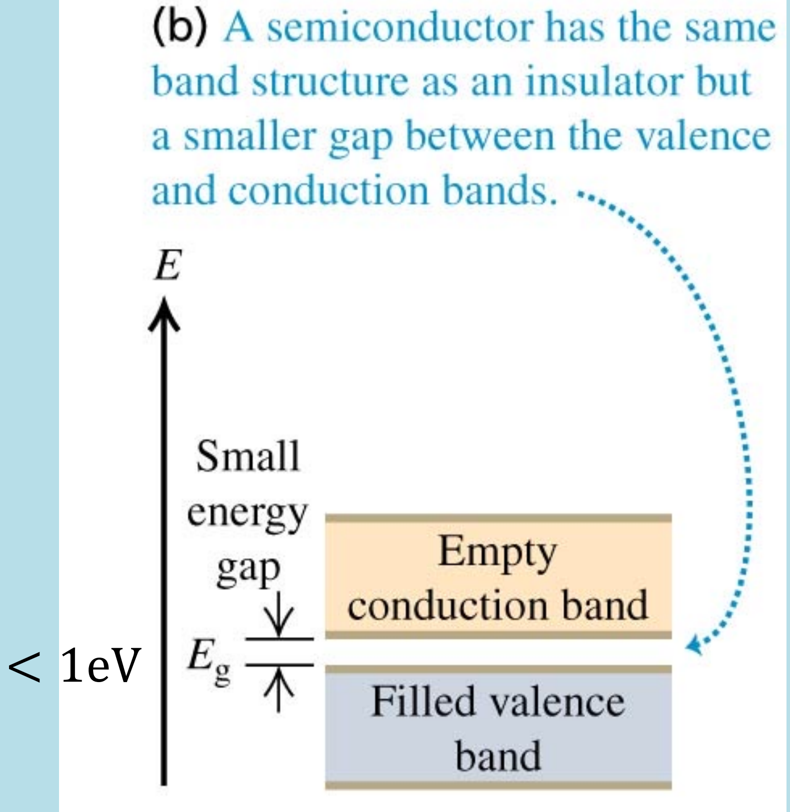
Figure 5.2 The occupation of (a) the energy levels in an isolated carbon atom, and (b) the energy bands in a diamond crystal. Notice that there is an energy range E_g separating the highest occupied states (in the valence band) from the lowest vacant states (in the conduction band). This is a characteristic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

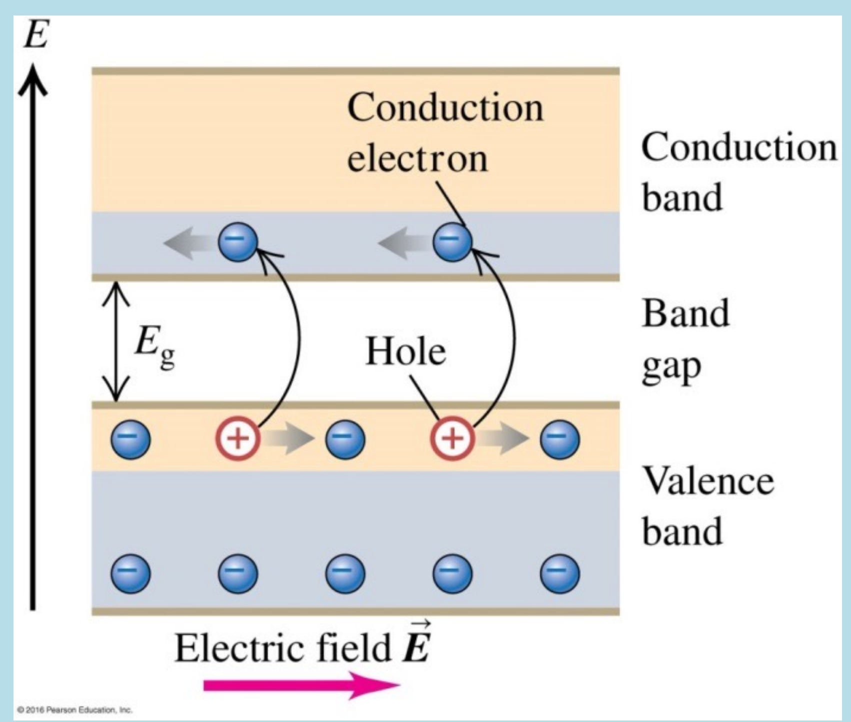
Figure 5.3 The energy levels of the 2s and 2p states for a group of N carbon atoms as a function of the separation of the atoms.



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！

半導體 Semiconductor





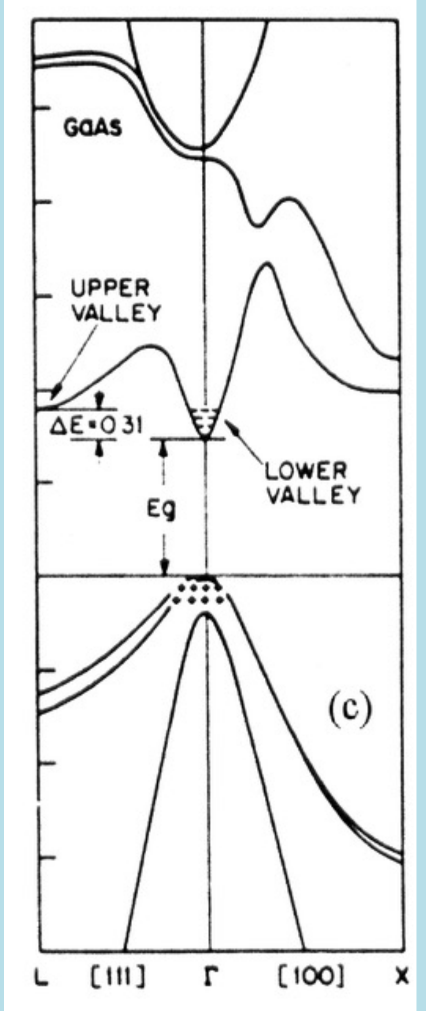
半導體的能帶間隙小，在室溫時即可以有電子由Valence跳上Conduction。

Conduction帶內的電子及Valence帶內的電洞形成導電的載體carrier。

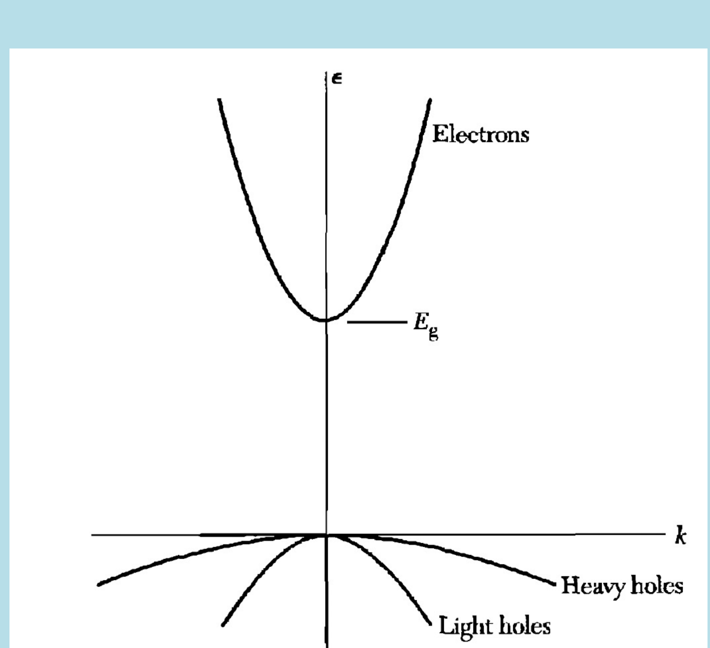
砷化鎵

Gallium arsenide

						2 He
	5 B	6 C	7 N	8 O	9 F	10 Ne
	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
112						

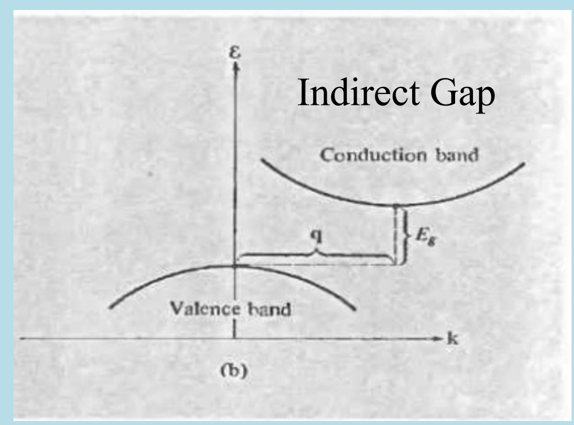


這是一個典型的能帶圖：

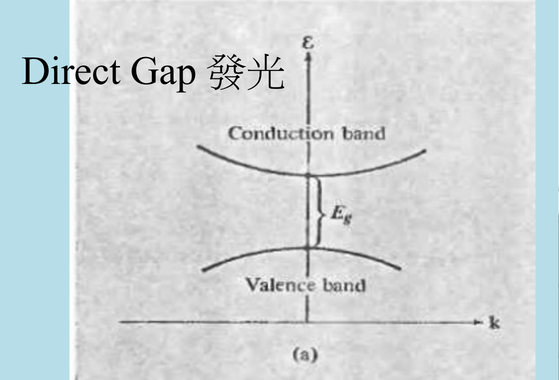


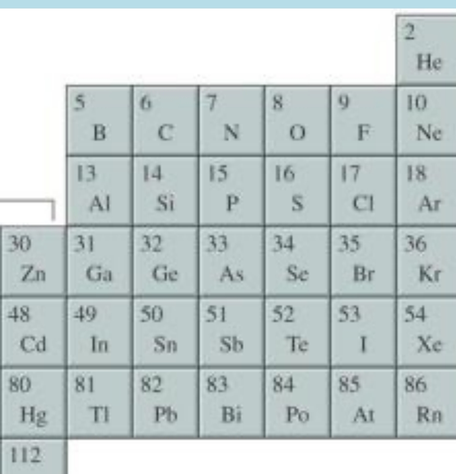
橫軸是能態波函數的晶體動量k。

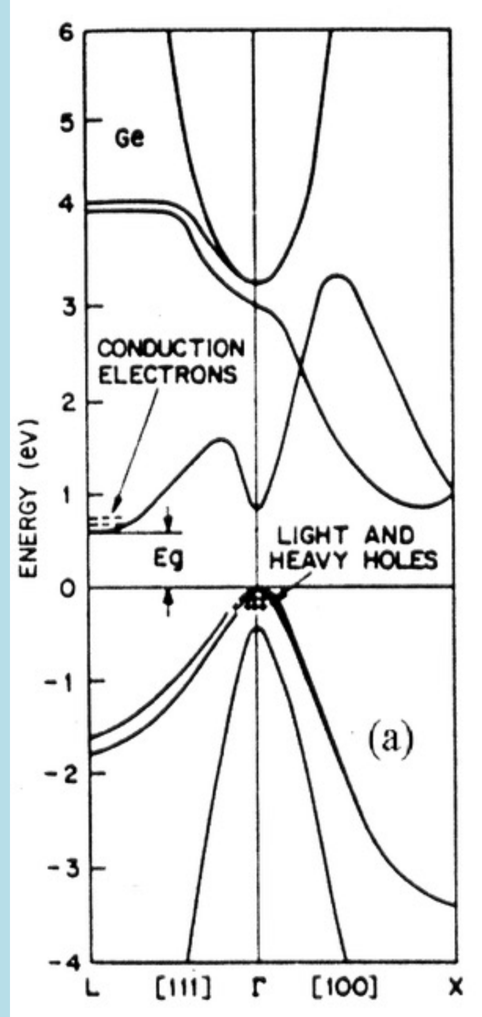
Indirect Gap

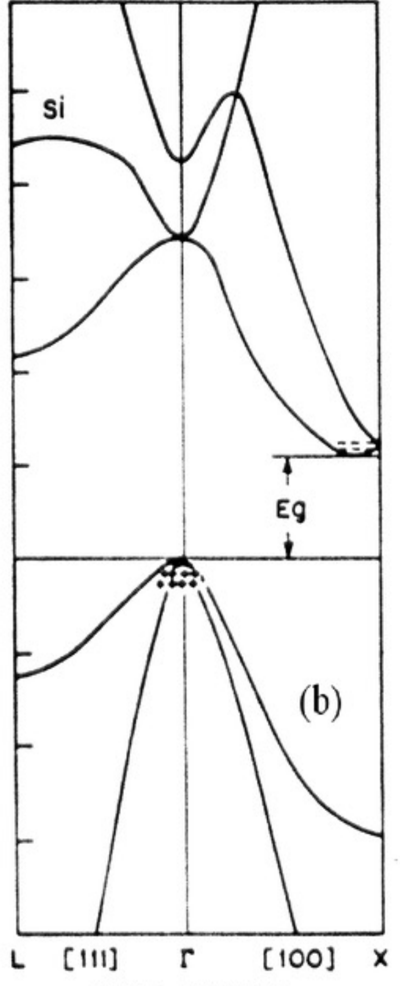


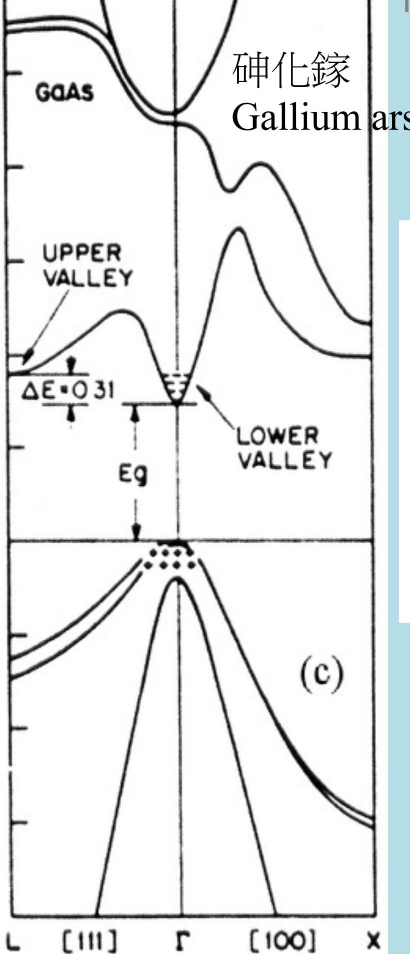
Direct Gap 發光



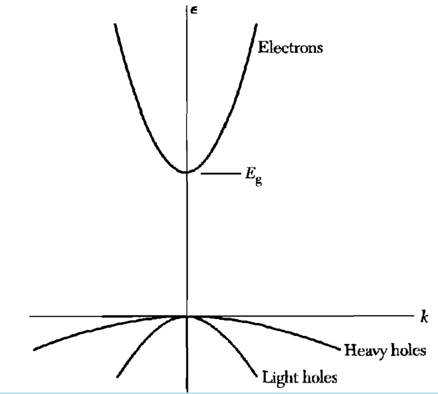


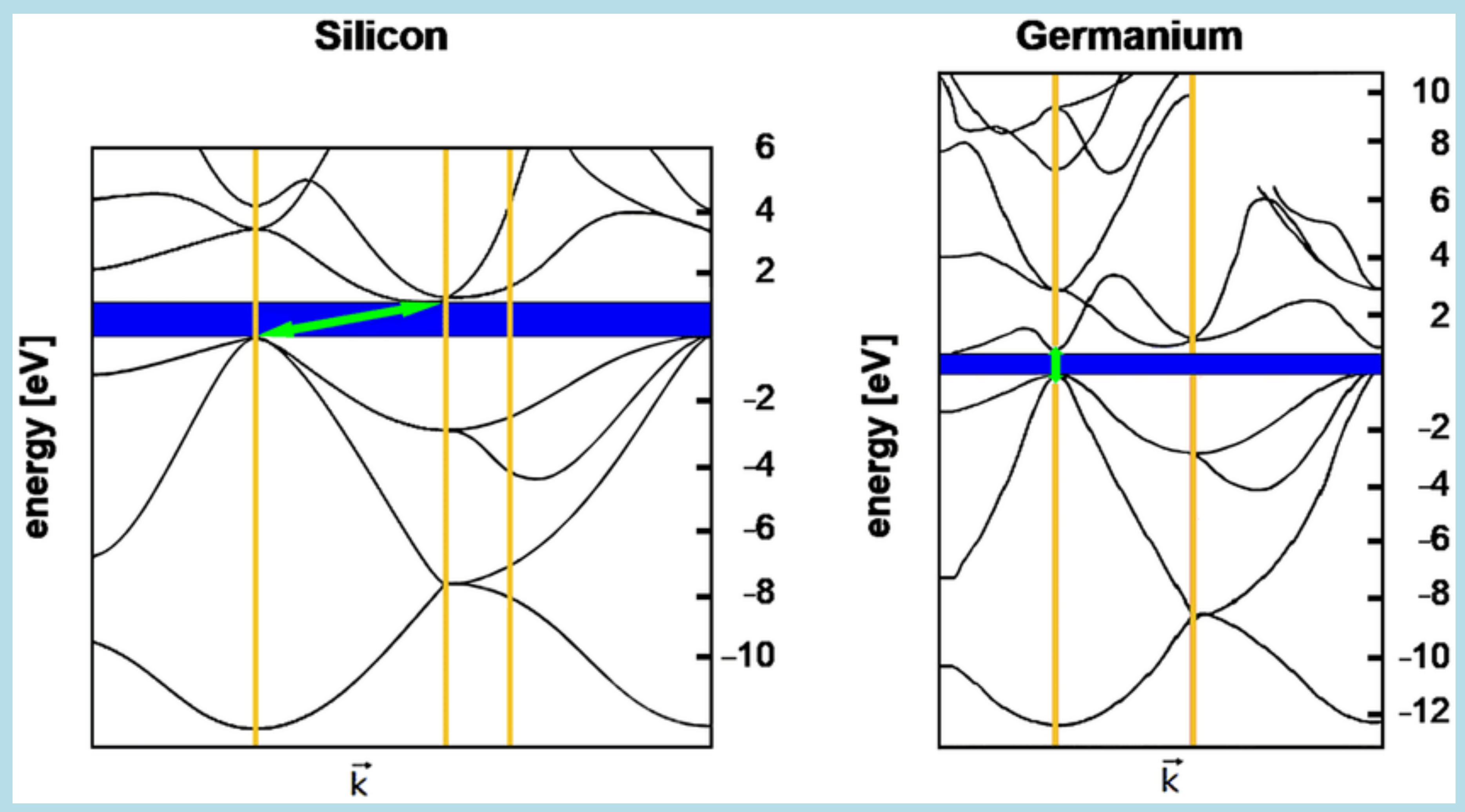




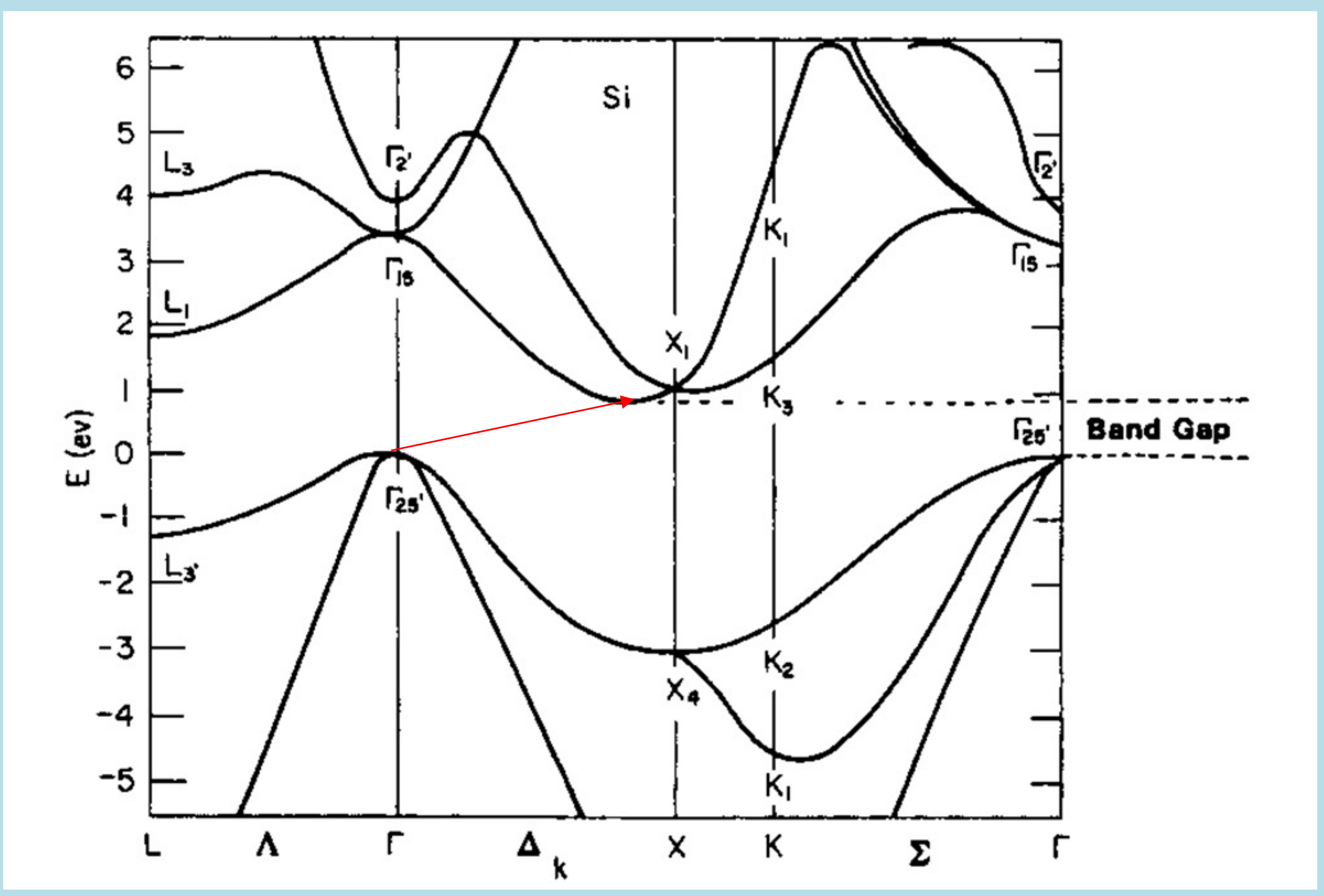


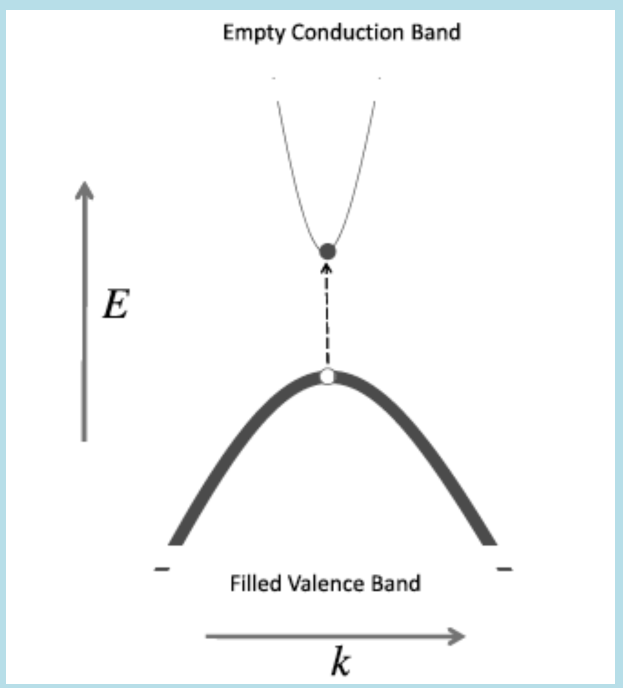
砷化鎵
Gallium arsenide

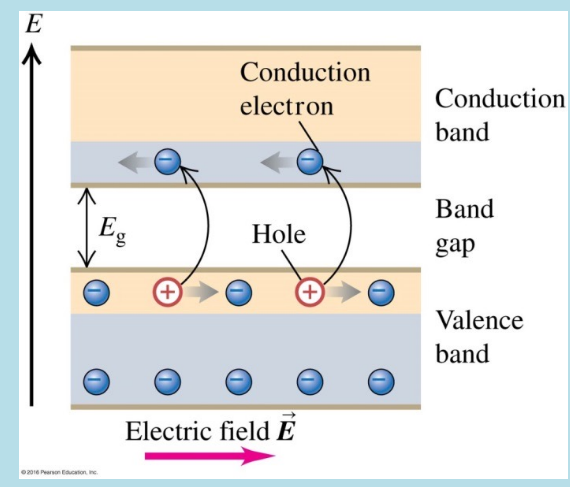




Silicon
Germanium
6
4
2
-2
-4
-6
-8
-10
energy [eV]
$\vec{k}$
10
8
6
4
2
-2
-4
-6
-8
-10
-12
energy [eV]
$\vec{k}$


Si
E (ev)
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
L₃
L₁
L₃'
Γ₂'
Γ₁₅
Γ₂₅'
X₁
X₄
K₁
K₃
K₂
K₁
Γ₂'
Γ₁₅
Γ₂₅'
Band Gap
L
Λ
Γ
Δ
k
X
K
Σ
Γ





由價能帶跳上導能帶的傳導電子，在能量最低點的$k_{\min}$附近，能量可寫成：

$$E \sim E_{\min} + \alpha |k - k_{\min}|^2 = E_{\min} + \frac{\hbar^2}{2m_e^*} |k - k_{\min}|^2$$

m_e^*稱為電子有效質量。就是若將m_e^*代入動能公式就得到電子在導帶的能量。

電子組成的波包，群速度為動量為$\hbar(k - k_{\min})$的電子波包的群速度：

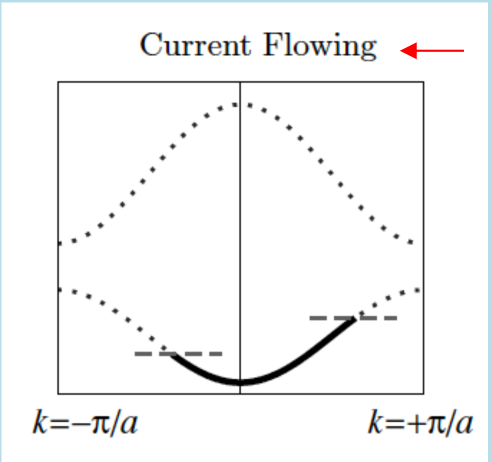
$$v_g = \frac{\partial \omega}{\partial k} = \frac{1}{\hbar} \frac{\partial E}{\partial k} = \hbar \frac{k - k_{\min}}{m_e^*}$$

能量最低點附近，傳導電子完全像質量為m_e^*、動量$\hbar(k - k_{\min})$的自由電子！

在外加均勻電場下，所有電子態的k會以均勻變化率變化：

$$\hbar \frac{dk}{dt} = -eE$$

而傳導電子的性質就如帶負電，質量為m_e^*電子有效質量的自由粒子！



At any rate, in the semiclassical picture, we can write a simple Drude transport equation (really Newton's equations!) for electrons in the conduction band

$$m_e^* \, d\mathbf{v}/dt = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - m_e^* \, \mathbf{v}/\tau$$

with m_e^* the electron effective mass. Here the first term on the right-hand side is the Lorentz force on the electron, and the second term is a drag force with an appropriate scattering time τ. The scattering time

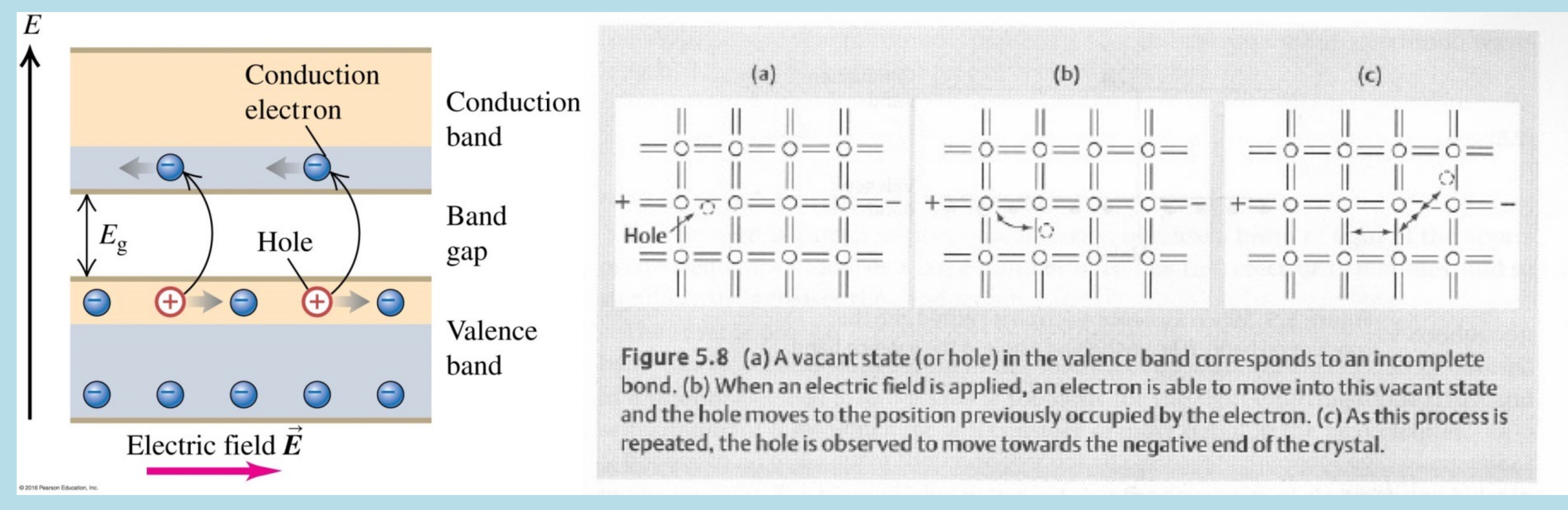
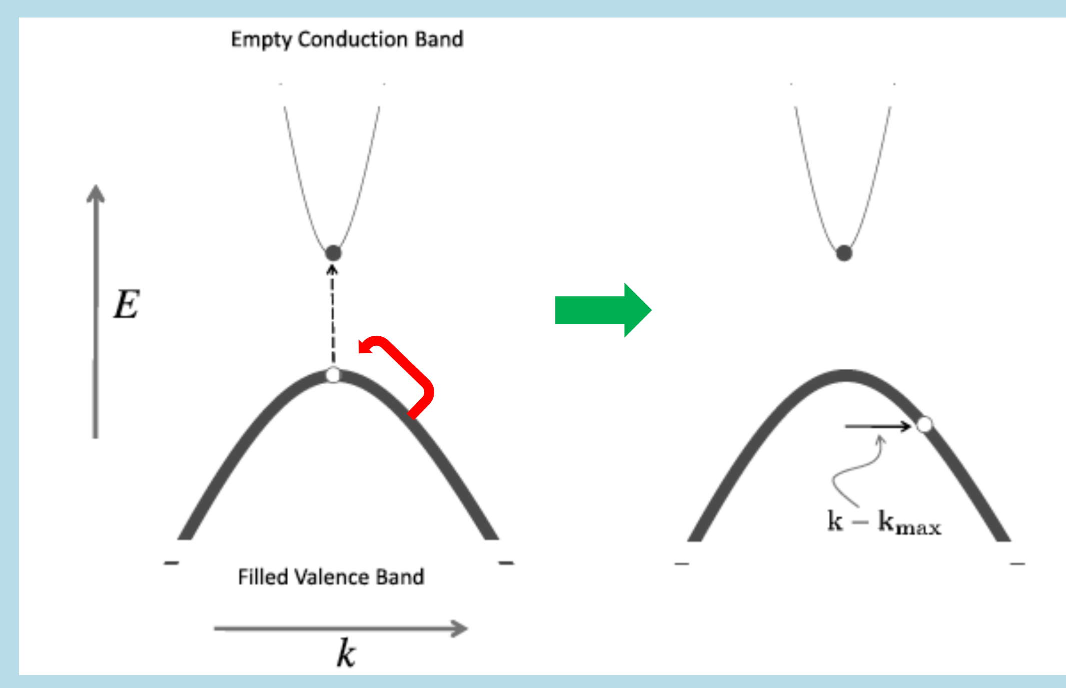


Figure 5.8 (a) A vacant state (or hole) in the valence band corresponds to an incomplete bond. (b) When an electric field is applied, an electron is able to move into this vacant state and the hole moves to the position previously occupied by the electron. (c) As this process is repeated, the hole is observed to move towards the negative end of the crystal.

電洞也能導電！



價能帶的能量：設$k_{max} = 0$

$E \sim E_{max} - \alpha k^2$

$$= E_{max} - \frac{\hbar^2}{2m^*_{hole}} k^2$$

m^*_{hole}稱為電洞的有效質量

考慮右圖$k \neq 0$態缺電子的電洞，此狀態是在左圖將$k \neq 0$態電子移入頂點電洞。

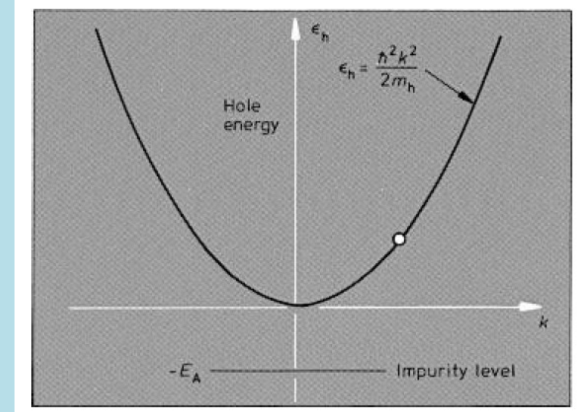
右圖狀態相對於左圖狀態，動量為移走電子動量的負號：$p_{hole} = -\hbar k$

左圖狀態動量為零，因此上式即為右圖狀態的動量！

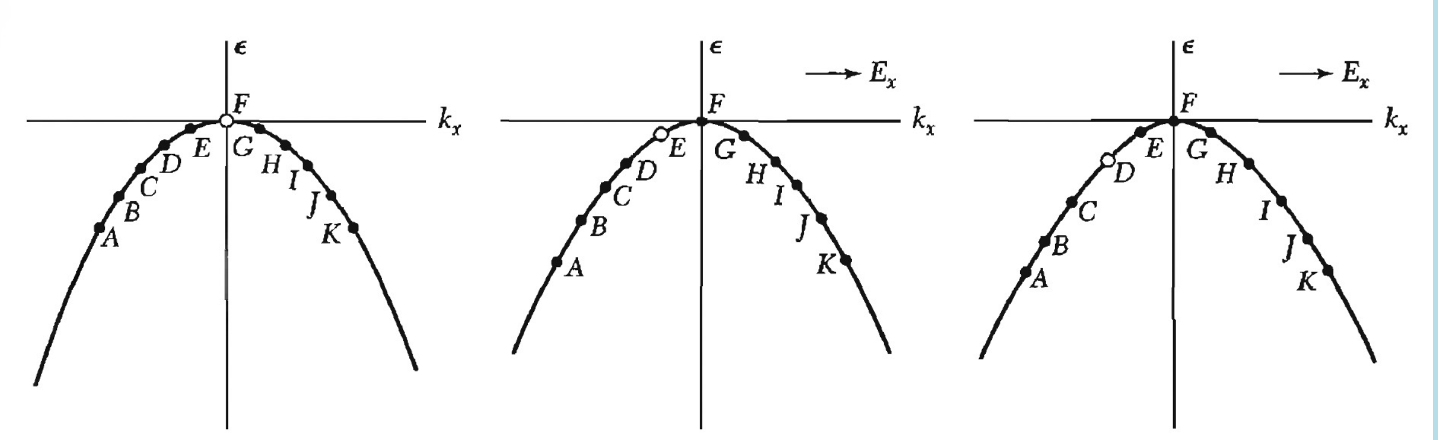
而右圖狀態相對於左圖狀態，實體電子能量是增加的。

因此若以左圖能量為零點，右圖狀態的能量即為：

$$E_{hole} \sim \frac{\hbar^2}{2m^*_{hole}} k^2$$



電洞的行為完全像質量為m^*_{hole}、動量為$p_{hole} = -\hbar k$的自由粒子！



在外加均勻電場下，電子態的k會均勻變化率變化：

$$\hbar\frac{dk}{dt} = -eE$$

在軸上電洞位置，也跟著電子如一條chain移動，若以$p_{\mathrm{hole}} = -\hbar k$表示：

$$\hbar\frac{dp_{\mathrm{hole}}}{dt} = +eE$$

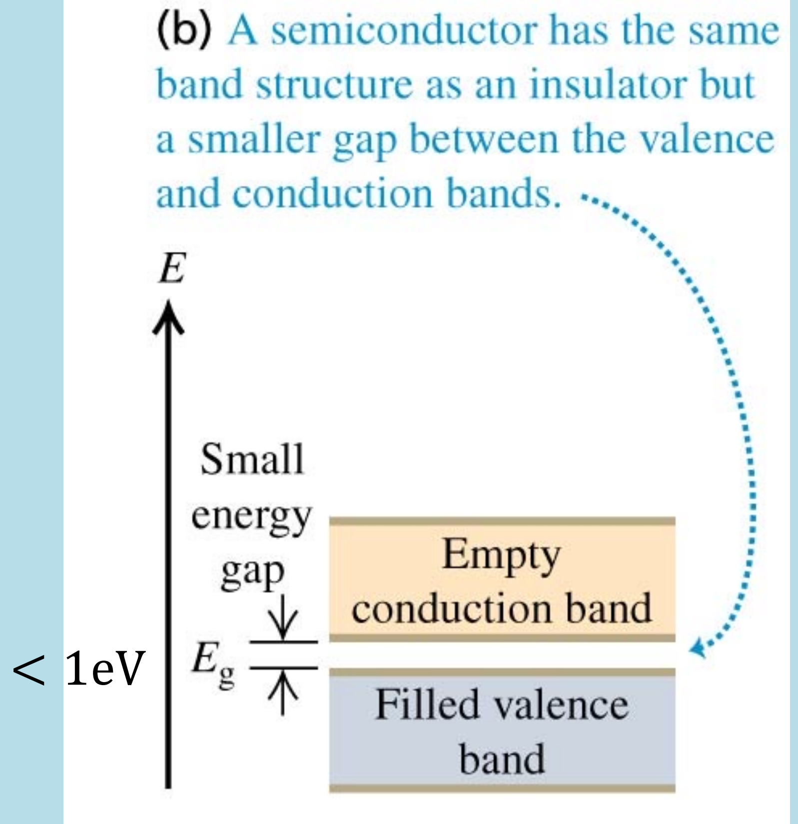
可見電洞的性質如帶正電！

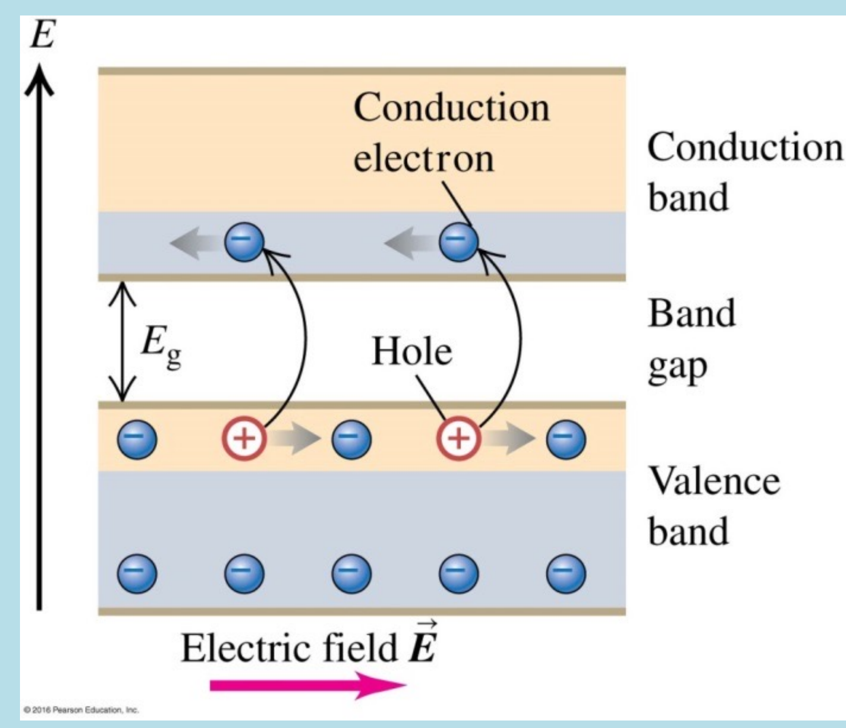
Similarly, we can write equations of motion for holes in the valence band

$$m_h^* \, d\mathbf{v}/dt = e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - m_h^* \, \mathbf{v}/\tau$$

where m_h^* is the hole effective mass. Note again that here the charge on the hole is *positive*. This should make sense—the electric field pulls on an electron in a direction opposite to the direction that it pulls on the absence of an electron!

半導體 Semiconductor



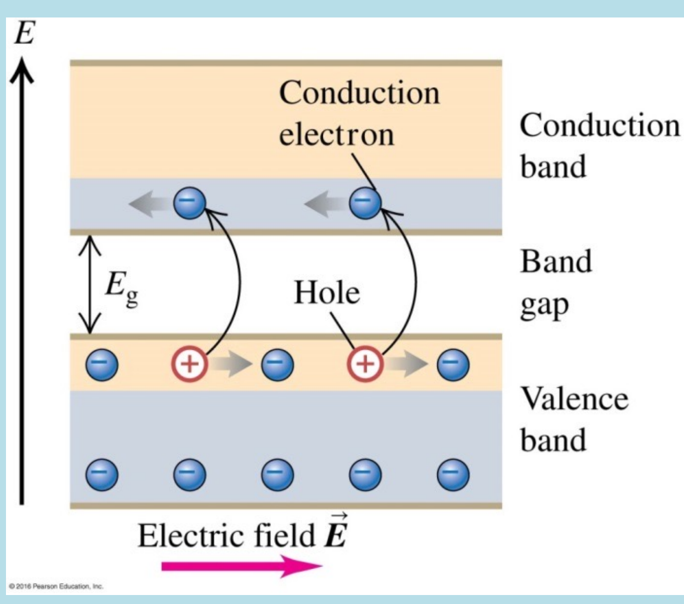


半導體的能帶間隙小，在室溫時即可以有電子由Valence跳上Conduction。

Conduction帶內的電子及Valence帶內的電洞形成導電的載體carrier。

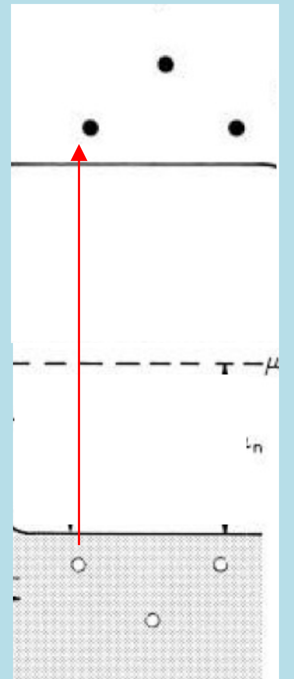
而且兩者都是自由自在、如同沒有交互作用而機動。

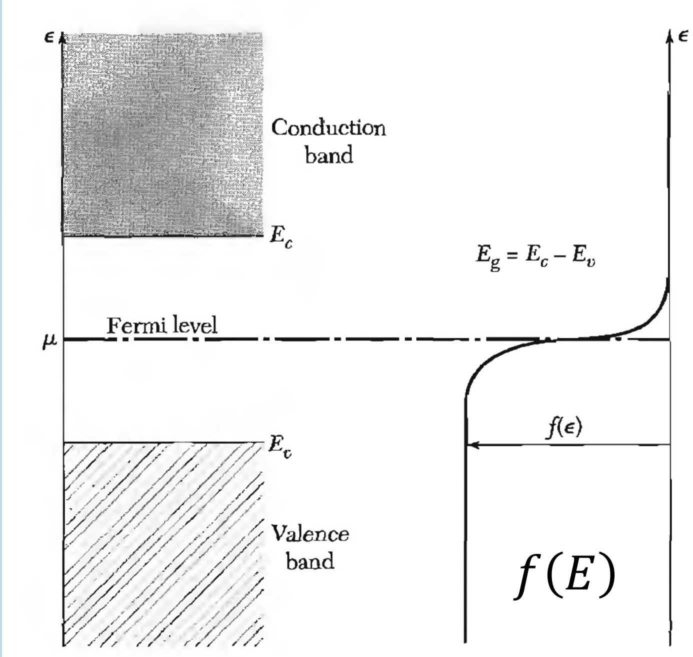
從這個事實的基礎就能建立整個半導體理論，幾乎無需再回到能帶等等概念！

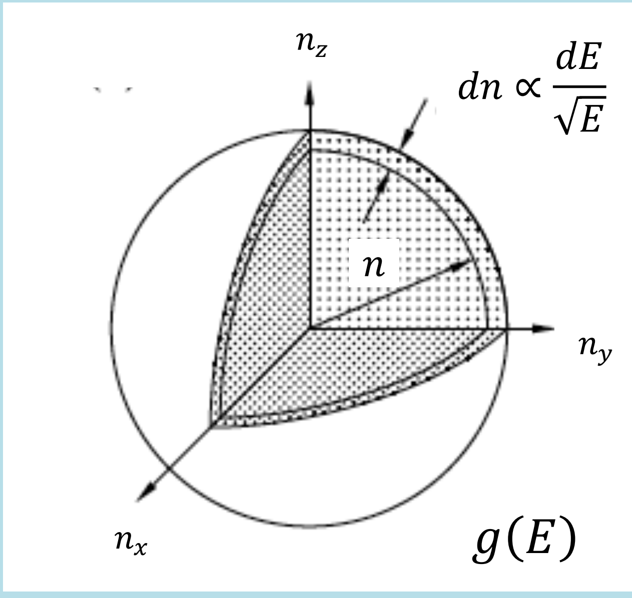


半導體內電洞也能導電！

半導體的能帶間隙小，在室溫時即可以有電子由Valence跳上Conduction。
溫度為T時，導帶的電子數，也就是價帶的電洞數，
可以以狀態發生機率Fermi-Dirac Factor $f(E)$及狀態數密度$g(E)$計算：

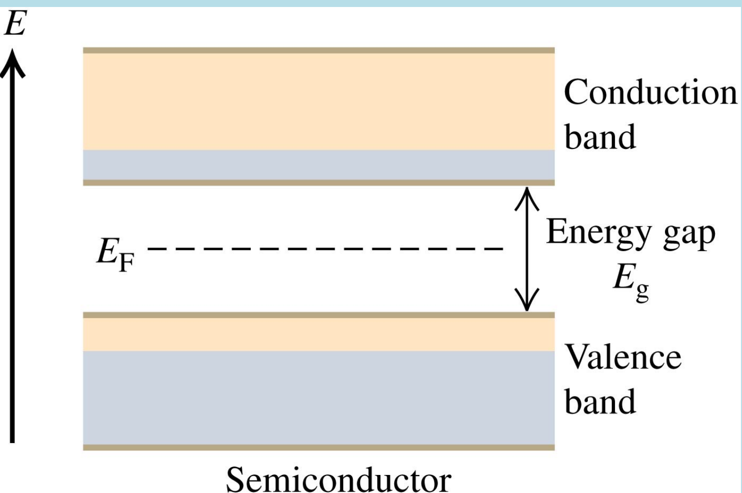






$$n = \int_{E_G}^{\infty} dE \cdot g(E) \cdot f(E)$$

$$= \frac{1}{\sqrt{2}} \left(\frac{k_B T}{\pi \hbar^2} \right)^{3/2} (m_e^* m_h^*)^{3/4} \quad e^{-\frac{E_G}{2kT}}$$



導電電子密度大約可以以波茲曼facto估計：

$n \propto e^{-E_g/2kT}$ 導電電子密度由能隙決定！

$$\frac{E_g}{kT} \sim \frac{0.2\text{eV}}{8.617\times10^{-5}\text{eV/K}\cdot300\text{K}} \sim 7.736$$

$$n \propto 2.00\times10^{-2} \sim 9.22\times10^{15}\text{m}^{-3}$$

EXAMPLE 42.9 JUMPING A BAND GAP

Consider a material with the band structure described above, with its Fermi energy in the middle of the gap (**Fig. 42.24**). Find the probability that a state at the bottom of the conduction band is occupied at $T = 300$ K, and compare that with the probability at $T = 310$ K, for band gaps of (a) 0.200 eV; (b) 1.00 eV; (c) 5.00 eV.

SOLUTION

IDENTIFY and SET UP: The Fermi–Dirac distribution function gives the probability that a state of energy E is occupied at temperature T. Figure 42.24 shows that the state of interest at the bottom of the conduction band has an energy $E = E_F + E_g/2$ that is greater than the Fermi energy E_F, with $E - E_F = E_g/2$. Figure 42.23 shows that the higher the temperature, the larger the fraction of electrons with energies greater than the Fermi energy.

EXECUTE: (a) When $E_g = 0.200$ eV,

$$\frac{E - E_F}{kT} = \frac{E_g}{2kT} = \frac{0.100 \text{ eV}}{(8.617 \times 10^{-5} \text{ eV/K})(300 \text{ K})} = 3.87$$

$$f(E) = \frac{1}{e^{3.87} + 1} = 0.0205$$

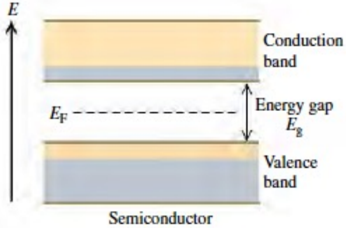
For $T = 310$ K, the exponent is 3.74 and $f(E) = 0.0231$, a 13% increase in probability for a temperature rise of 10 K.

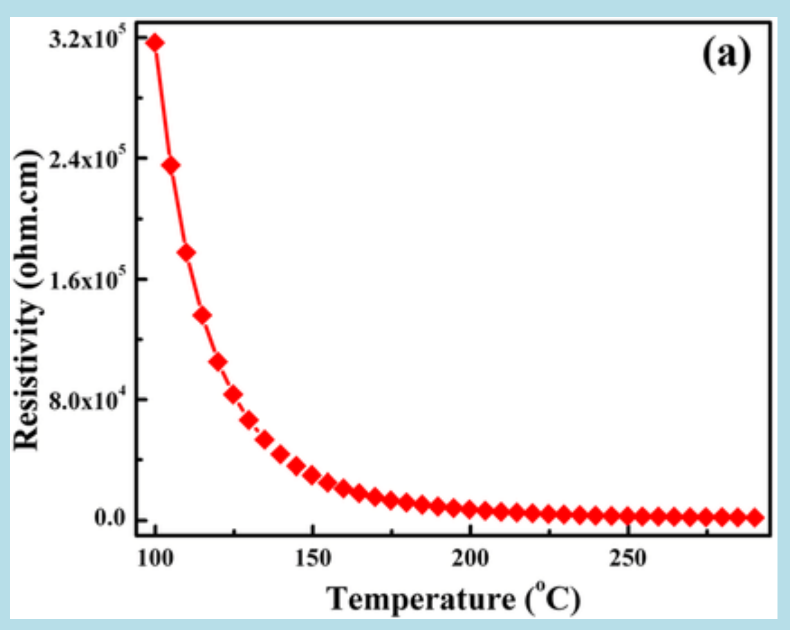
(b) For $E_g = 1.00$ eV, both exponents are five times as large as in part (a), namely 19.3 and 18.7; the values of $f(E)$ are 4.0×10^{-9} and 7.4×10^{-9}. In this case the (low) probability nearly doubles with a temperature rise of 10-K.

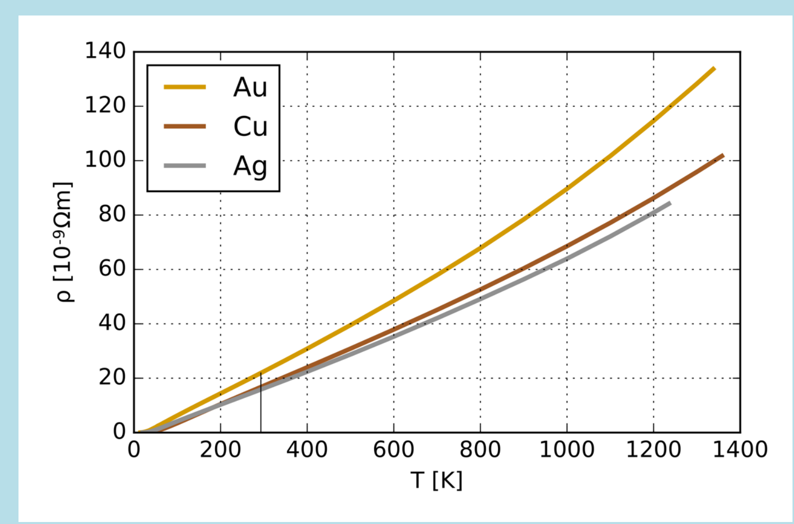
(c) For $E_g = 5.0$ eV, the exponents are 96.7 and 93.6; the values of $f(E)$ are 1.0×10^{-42} and 2.3×10^{-41}. The (extremely low) probability increases by a factor of 23 for a 10-K temperature rise.

EVALUATE: This example illustrates two important points. First, the probability of finding an electron in a state at the bottom of the conduction band is extremely sensitive to the width of the band gap. At room temperature, the probability is about 2% for a 0.200-eV gap, a few in a thousand million for a 1.00-eV gap, and essentially zero for a 5.00-eV gap. (Pure diamond, with a 5.47-eV band gap, has essentially no electrons in the conduction band and is an excellent insulator.) Second, for any given band gap the probability depends strongly on temperature, and even more strongly for large gaps than for small ones.

42.24 Band structure of a semiconductor. At absolute zero a completely filled valence band is separated by a narrow energy gap E_g of 1 eV or so from a completely empty conduction band. At ordinary temperatures, a number of electrons are excited to the conduction band.







半導體的電阻率隨溫度增加快速降低。

相對的、導體的電阻率隨溫度增加而增加。

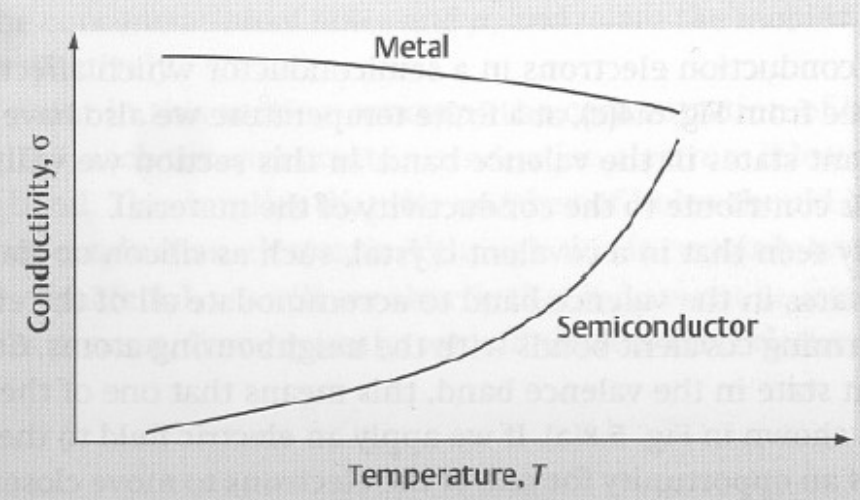


Figure 5.6 Variation of conductivity with temperature for a typical metal and semiconductor.

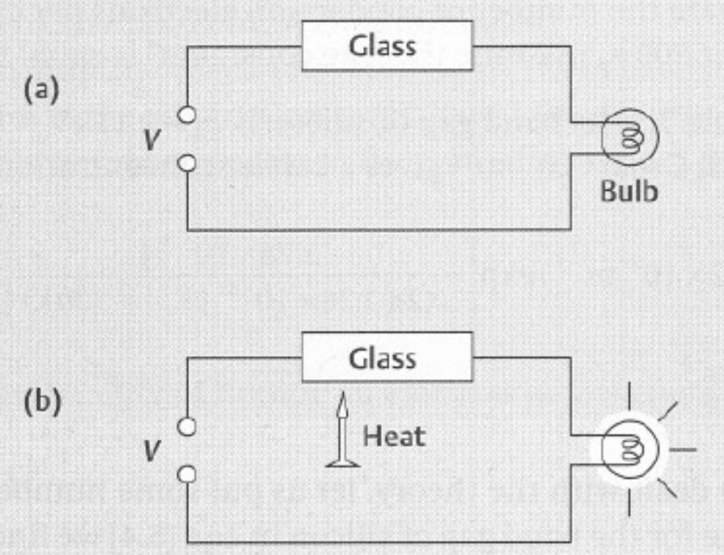


Figure 5.7 (a) A simple circuit consisting of a glass bar in series with a light bulb. At room temperature the bulb does not light because glass is an insulator. (b) But if the glass bar is heated (e.g. using a Bunsen burner), the conductivity of the glass increases and the bulb lights.

但E_g~1.0eV能跳上Conduction的電子數量還是少於導體，

電阻率比起導體還是來得大！

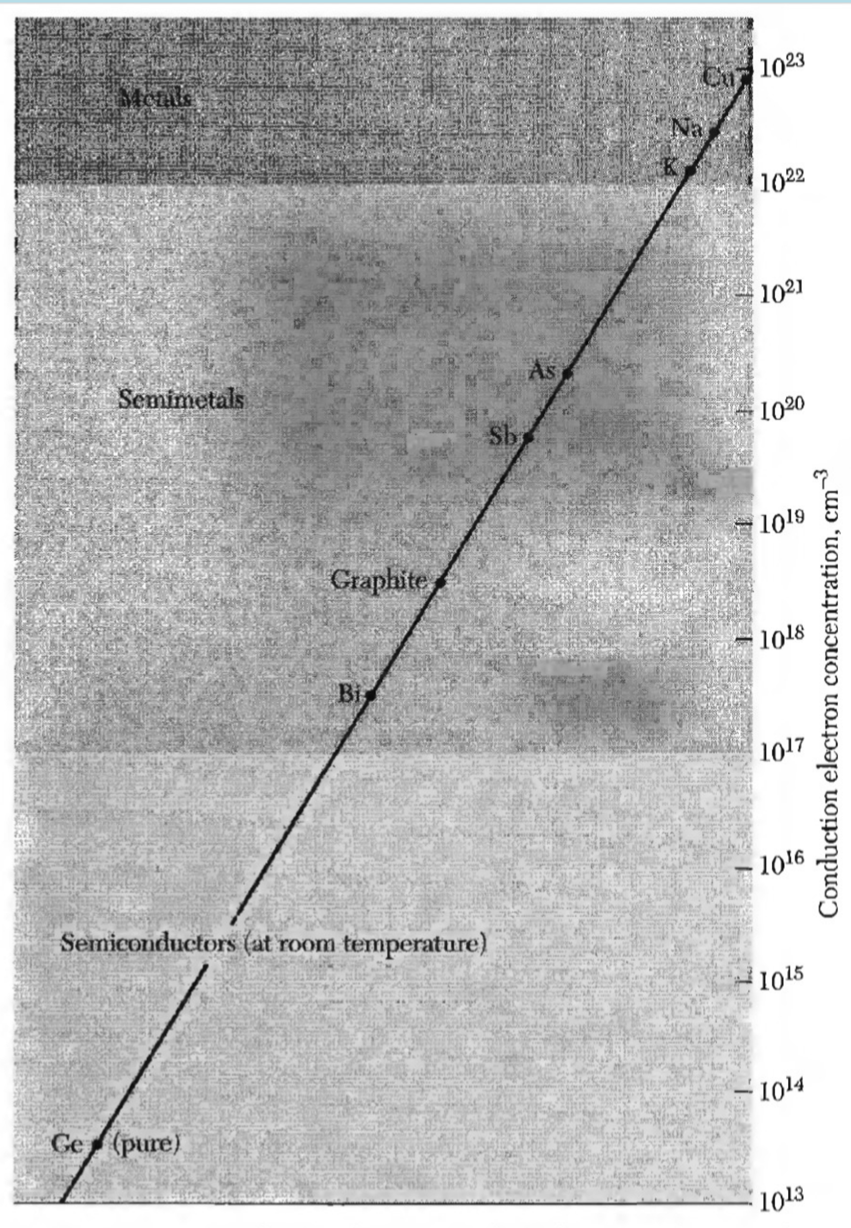


Figure 1 Carrier concentrations for metals, semimetals, and semiconductors. The semiconductor range may Screenshot ward by increasing the impurity concentration, and the range can be extended downwar .o merge eventually with the insulator range.

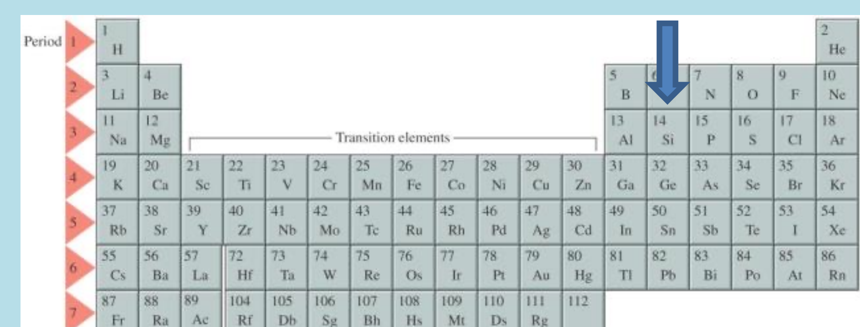
野生的半導體幾乎毫無用處！

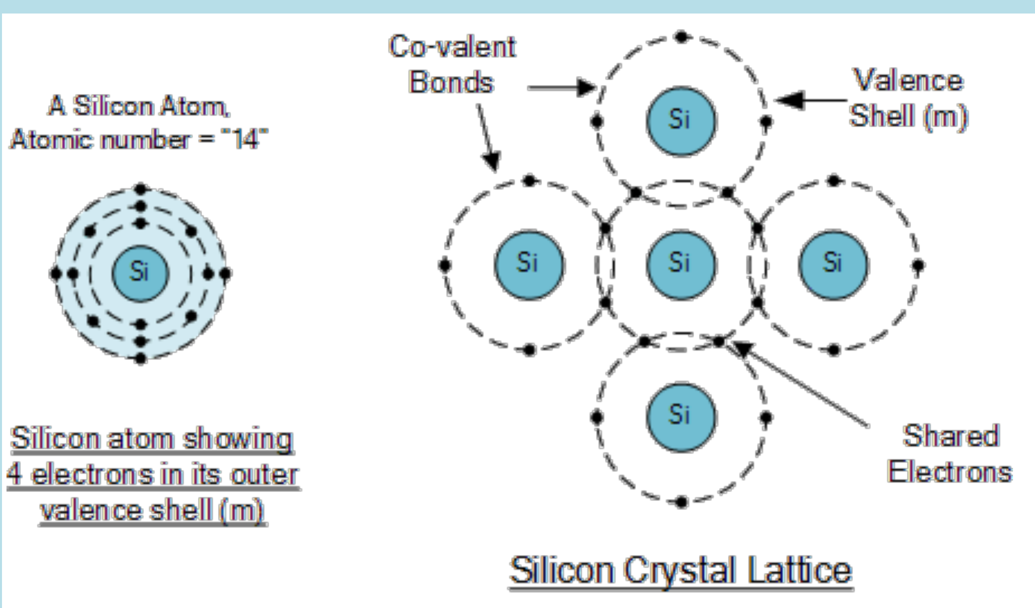
但E_g~1.0eV能跳上Conduction的電子數量還是少於導體，

電阻率比起導體還是來得大！

但我們可以用雜質Doping來增加半導體的導電性：

加入五個價電子的磷！





Silicon atom showing 4 electrons in its outer valence shell (m)

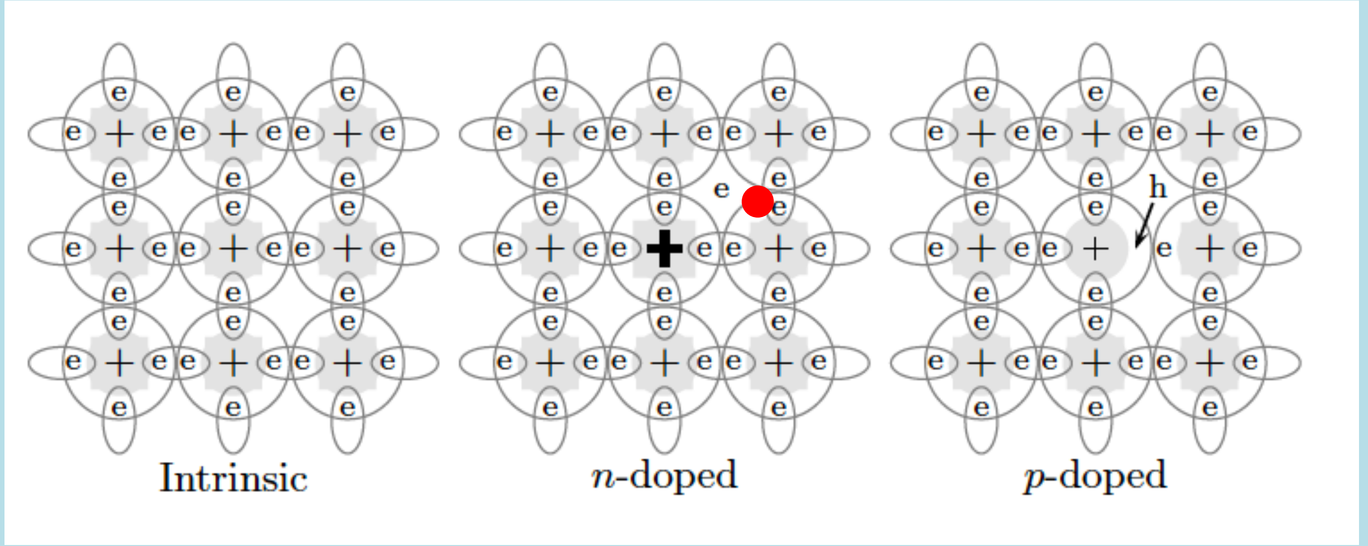
Silicon Crystal Lattice

Si Si Si Si Si
Si Si Si Si Si
Si Si P Si Si
Si Si Si Si Si
Si Si Si Si Si

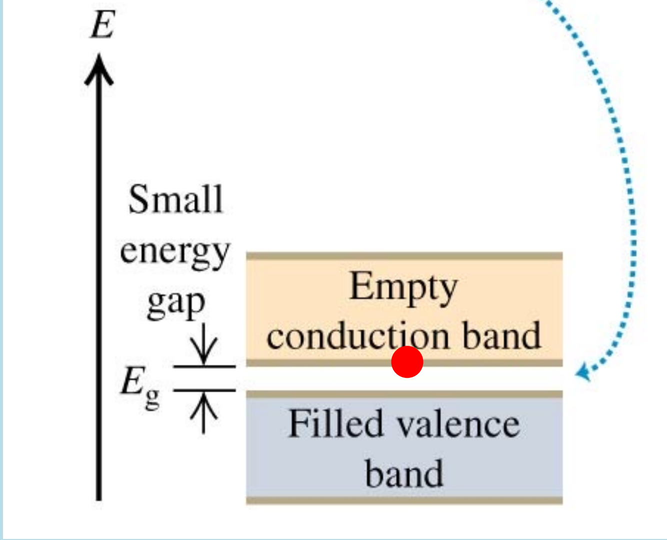
=

Si Si Si Si Si
+one free electron
Si Si Si Si Si
Si Si Si Si Si
+proton
Si Si Si Si Si
Si Si Si Si Si

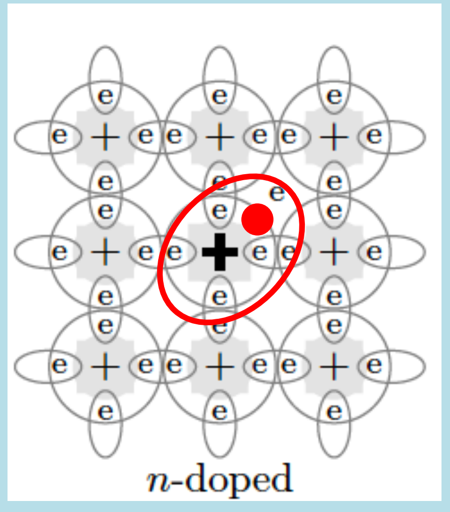
如此晶體結構幾乎不變，但電子會多出一個。



價能帶已填滿，多出來的電子，就會進入全空的傳導帶。



但不完全……



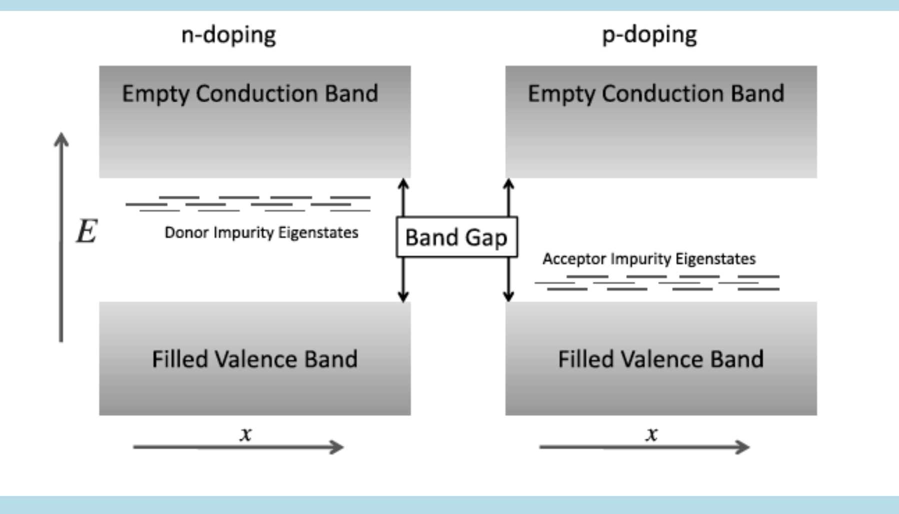
多出來的電子，與多出來的磷原子核正電荷，會如氫原子，形成束縛態。

但因此電子的有效質量一般小於電子質量，

而且必須考慮半導體內的介電性，一般極大。

因此束縛能~0.1 eV遠小於氫原子束縛能，以及能隙E_G，而半徑遠大~30Å。

這些束縛態的能量略低於傳導帶下端，與導帶的間隙就是束縛能~0.1 eV 。



Escape of the electron to large distances leaves the impurity atom with a net positive charge; at finite separations the positive charge exerts an attractive force on the electron and leads to the existence of a bound state for the electron. The 'charged impurity plus electron' system is analogous to the 'proton plus electron' system and we can therefore estimate the strength of this binding by adapting the standard result for the energy levels of the hydrogen atom to allow for the fact that the electron is moving through a crystal rather than a vacuum. Thus we use m_e for the electron mass and assume that the crystal has a dielectric constant (relative permittivity) ε to obtain

(5.10) $$E_n = -\frac{m_e e^4}{2\varepsilon^2 \hbar^2 n^2 (4\pi\varepsilon_0)^2}.$$

To estimate the spatial extent of the bound state wavefunctions we use the radii of the corresponding orbits as given by the Bohr theory,

(5.11) $$r_n = \frac{\varepsilon n^2 \hbar^2}{m_e e^2} 4\pi\varepsilon_0.$$

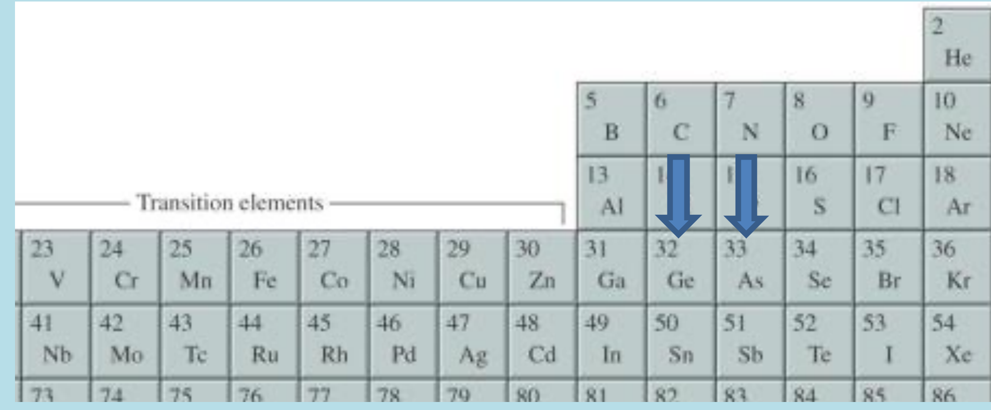
The effective mass of electrons in germanium is 0.2 electron masses and the dielectric constant is 15.8. Using these values in Eqs. (5.10) and (5.11) gives an estimate

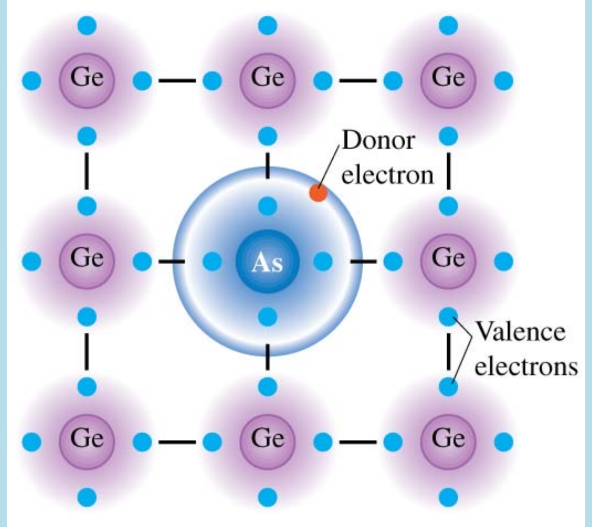
(5.12) $$E_1 = -\left(\frac{m_e}{m\varepsilon^2}\right) \times 13.6\ \text{eV} \approx -0.01\ \text{eV}$$

for the ground state binding energy of the extra electron and

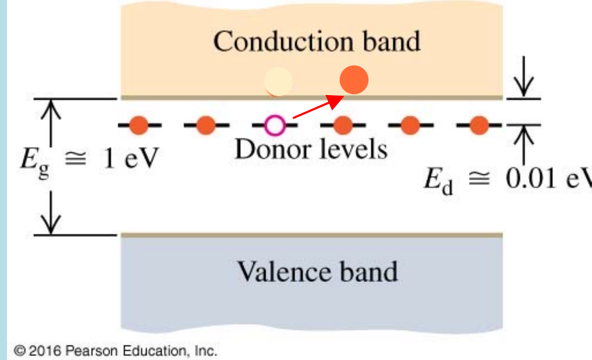
(5.13) $$r_1 = \left(\frac{\varepsilon m}{m_e}\right) \times 0.53\ \text{Å} \approx 40\ \text{Å}$$

for the radius of the corresponding orbit (−13.6 eV and 0.53 Å are the corresponding values for hydrogen). Thus the combination of small effective mass and large dielectric constant gives very weak binding of the extra electron to the impurity and a very extended wavefunction for the bound state. Since the bound state wavefunction extends over many





(a) A donor (n-type) impurity atom has a fifth valence electron that does not participate in the covalent bonding and is very loosely bound.



(b) Energy-band diagram for an n-type semiconductor at a low temperature. One donor electron has been excited from the donor levels into the conduction band.

© 2016 Pearson Education, Inc.

鍺 Ge

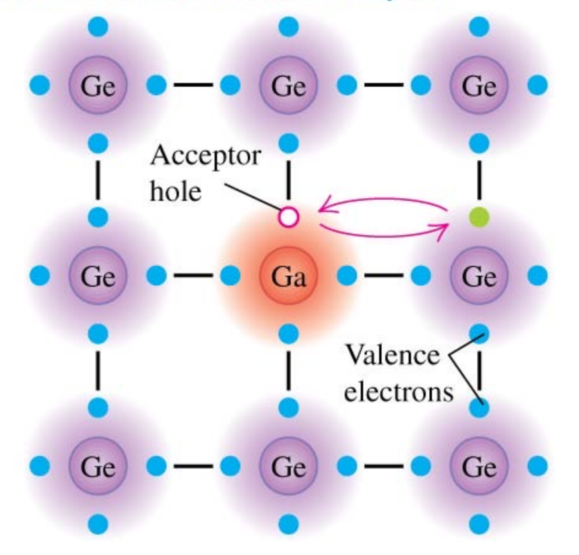
砷 As Arsenic

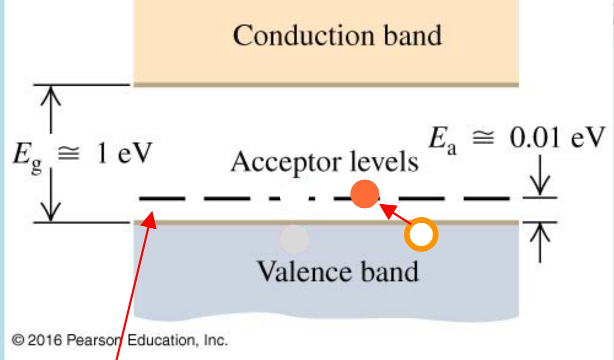
加入五價雜質提供鍵結以外多一顆電子。

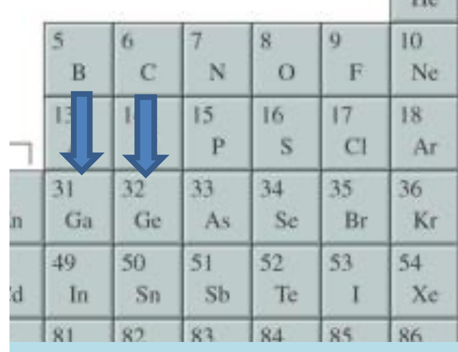
此電子的能態，在傳導帶之下，且間隙極小，稱為Doner態。

因此室溫時即可以有大量電子跳上Conduction帶，可以導電。

作為載體的電子帶負電，此類固體稱為n type半導體。







Ga Gallium 鎵

反之，加入三價雜質使鍵結內少一顆電子，等於價帶出現一個電洞。

此電洞與帶負電原子核的束縛態，稱為Acceptor態，在價帶上方，間隙也極小，

因此室溫時即可以有電子由價帶跳上空的Acceptor態。

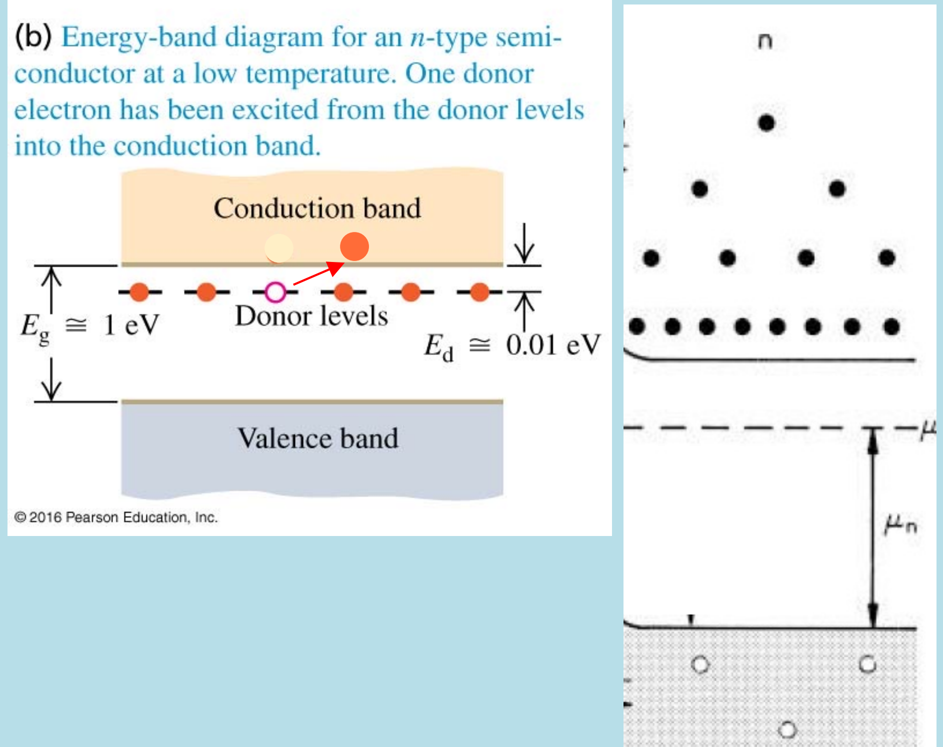
價帶出現電洞，電洞可以移動，就可以導電。

作為載體的電洞帶正電，此類固體稱為p type半導體。

以帶正電的粒子來導電的固態導體，在自然界是不存在的，

因此這是一種人類利用半導體所發明的新材料

室溫下，雜質半導體內的電子與電洞分佈：



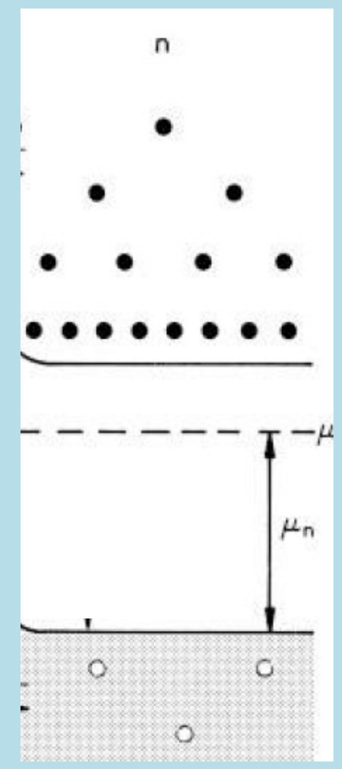
(b) Energy-band diagram for an *n*-type semiconductor at a low temperature. One donor electron has been excited from the donor levels into the conduction band.

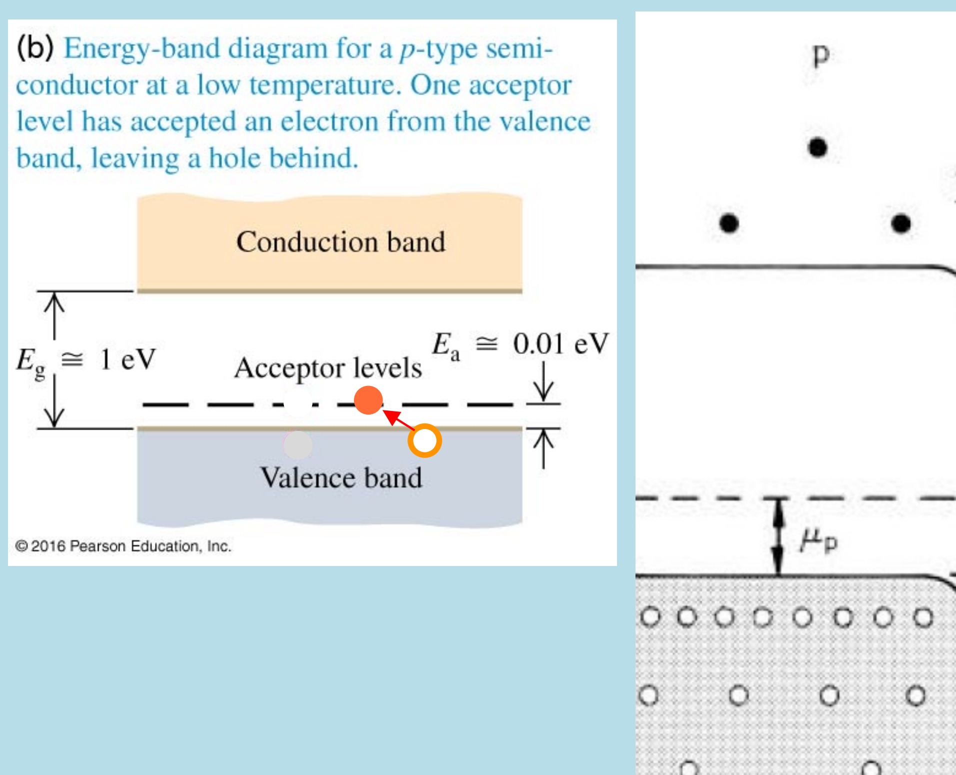
n type半導體內，

因能量間隙E_d很小，定溫下，大部分Doner Level電子會上到傳導帶，如氫原子的游離。

在導帶上，這些電子的能量分佈大致是波茲曼分佈$\sim e^{-(E-E_G)/kT}$ 。

價帶上也有一些電子會跳上導帶而留下可導電的電洞，但數量很少。





n type半導體內，

p type半導體內，電子從價帶跳上Acceptor Level，在價帶留下大量電洞的分佈。

同時，還是有比較少的電子會跳上導帶，

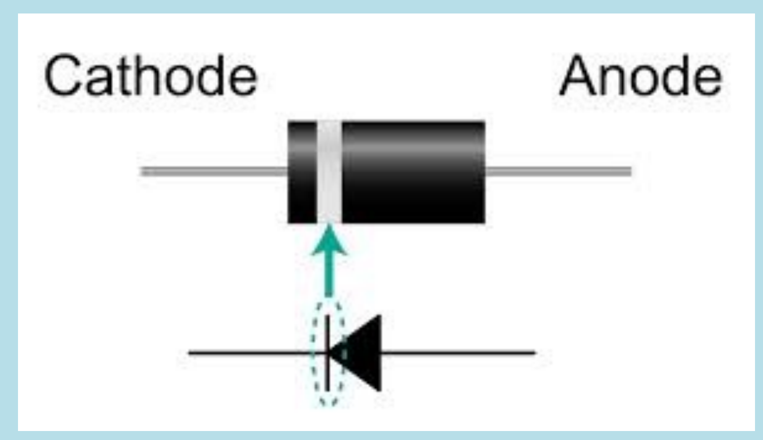
當溫度不高時，雜質貢獻的載體密度會比溫度產生的載體密度重要！

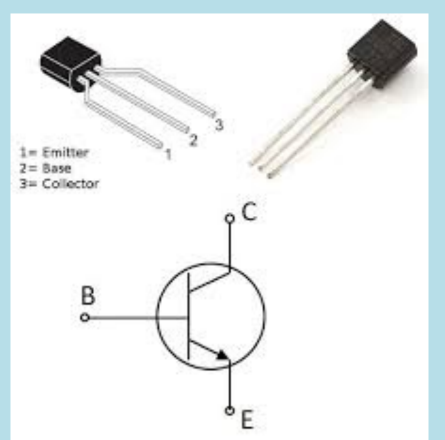
$$n - p = (\text{density of donors}) - (\text{density of acceptors}).$$

This, along with the law of mass action, gives us two equations with two unknowns which can be solved.[21] In short, the result is that if we are at a temperature where the undoped intrinsic carrier density is much greater than the dopant density, then the dopants do not matter much, and the chemical potential is roughly midgap as in Eq. 17.11 (this is the *intrinsic* regime). On the other hand, if we are at a temperature where the intrinsic undoped density is much smaller than the dopant density, then we can think of this as a low-temperature situation where the carrier concentration is mainly set by the dopant density (this is the *extrinsic* regime). In the n-doped case, the bottom of the conduction band gets filled with the density of electrons from the donors, and the chemical potential gets shifted up towards the conduction band. Correspondingly, in the p-doped case, holes fill the top of the valence band, and the chemical potential gets shifted down towards the valence band. Note that in this case of strong doping, the majority carrier concentration is obtained just from the doping, whereas the minority carrier concentration—which might be very small—is obtained via law of mass action. The ability to add carriers of either charge to semiconductors by doping is absolutely crucial to being able to construct semiconductor devices, as we will see in the next chapter.

利用雜質滲入的技術，在一塊半導體晶體內，可以自由製成兩種類似導體的材料。

將不同型的半導體組合在一起，可以製造出各式半導體元件，來控制電路中的電流：

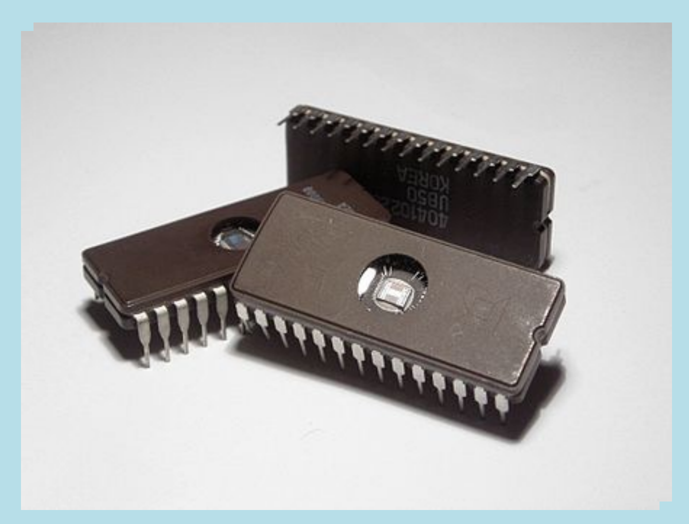


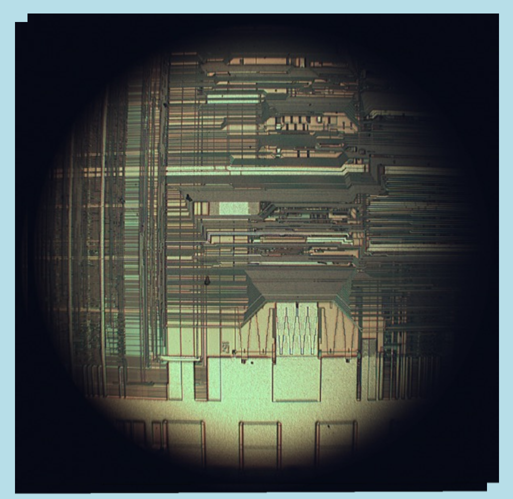


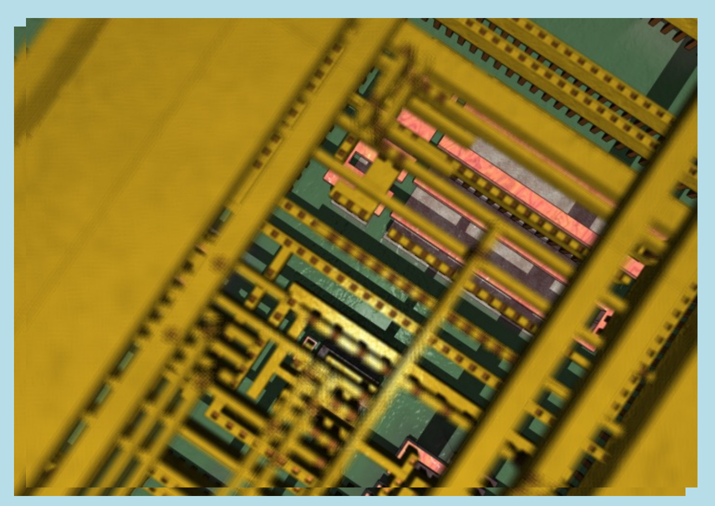
半導體元件非常不自然、完全人工，這是一個工程問題！

It is all about control. 控制！

control freak

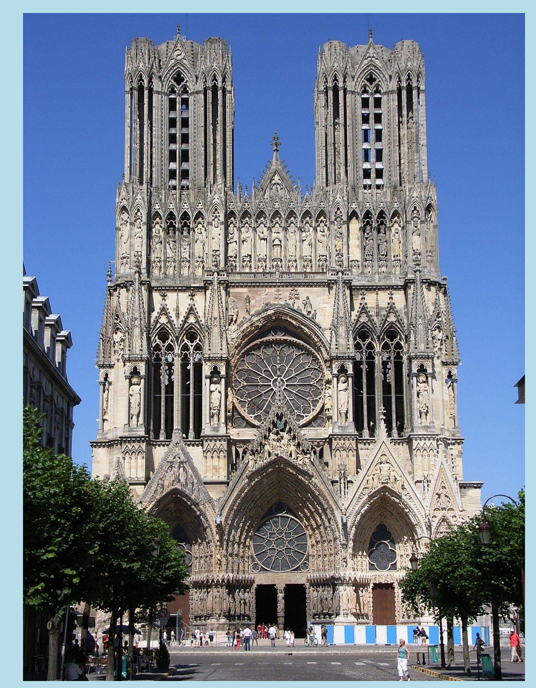


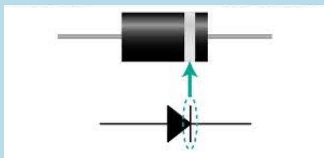




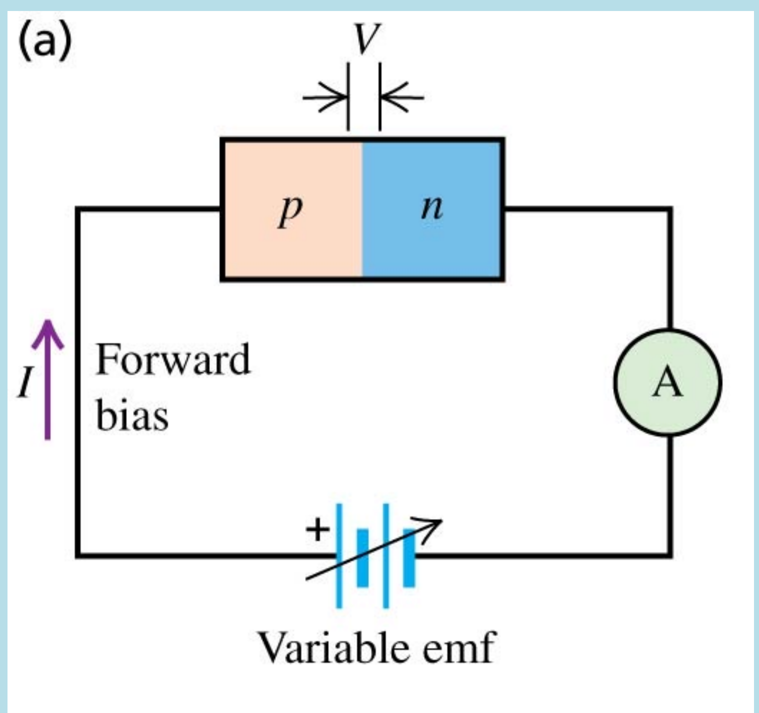
把元件與彼此的連接製作於一塊半導體板內，就稱Integrated Circuit IC 積體電路

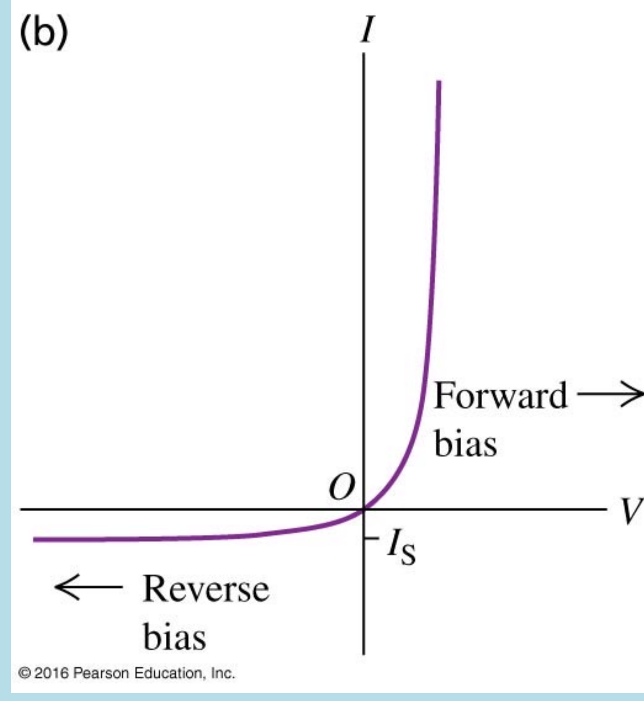
這是一個建築問題！元件就如微觀世界的歌德教堂！

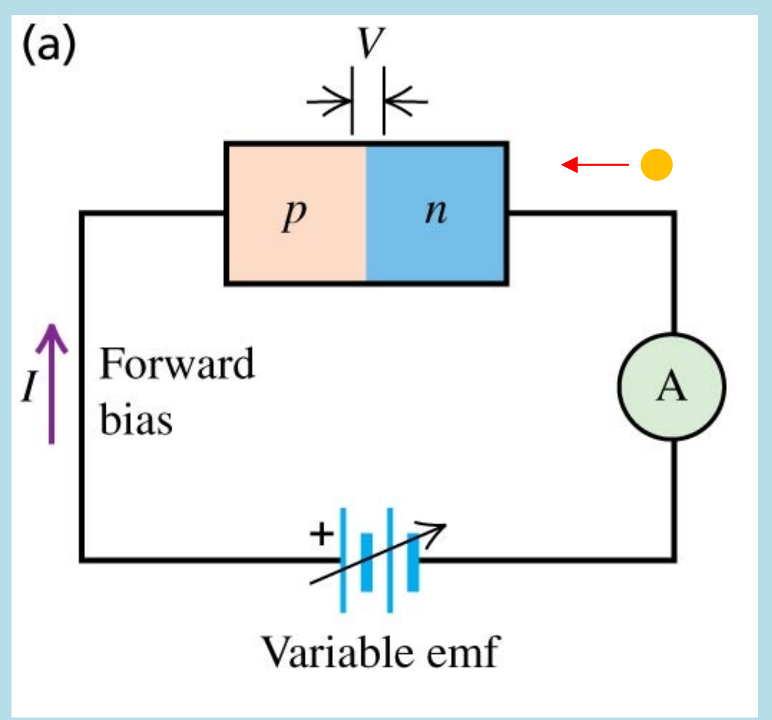


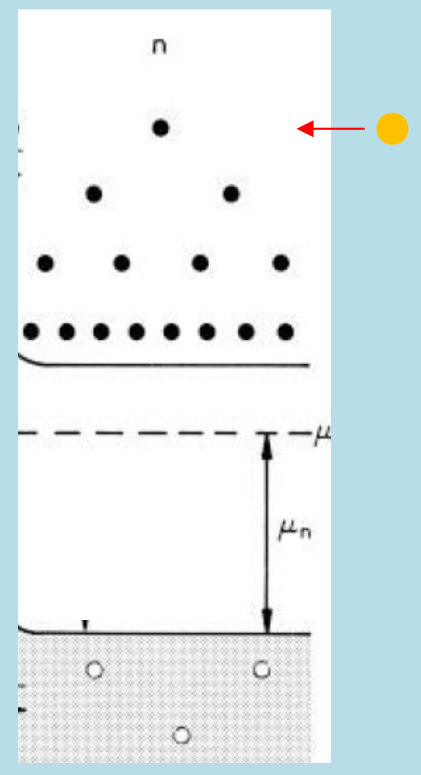


p-n Junction, Diode二極體：電流只能朝單一方向p→n流動！整流器



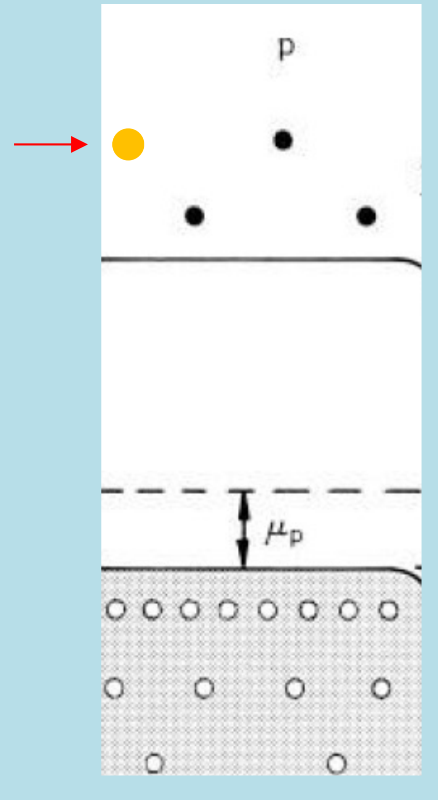


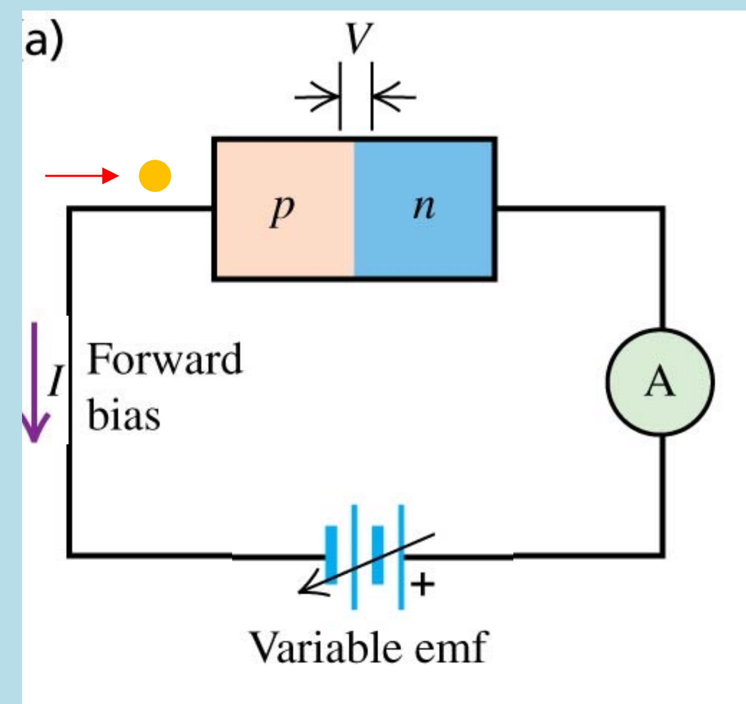




在Forward Bias流向，電子流入n，可以推動導帶中電子向p流動。

同時，電子從p流走，等於加入電洞，電洞在p中可以流動到介面，與電子抵消。

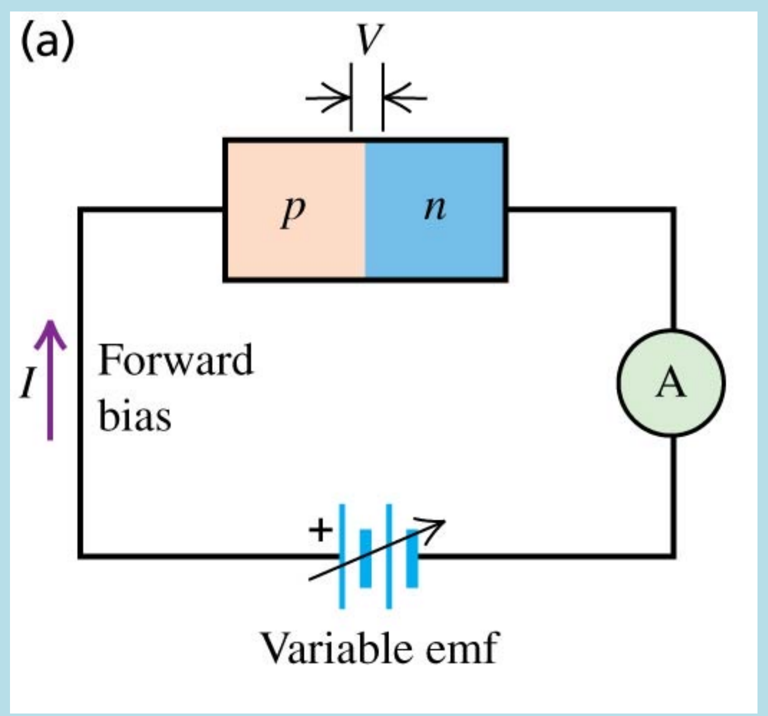


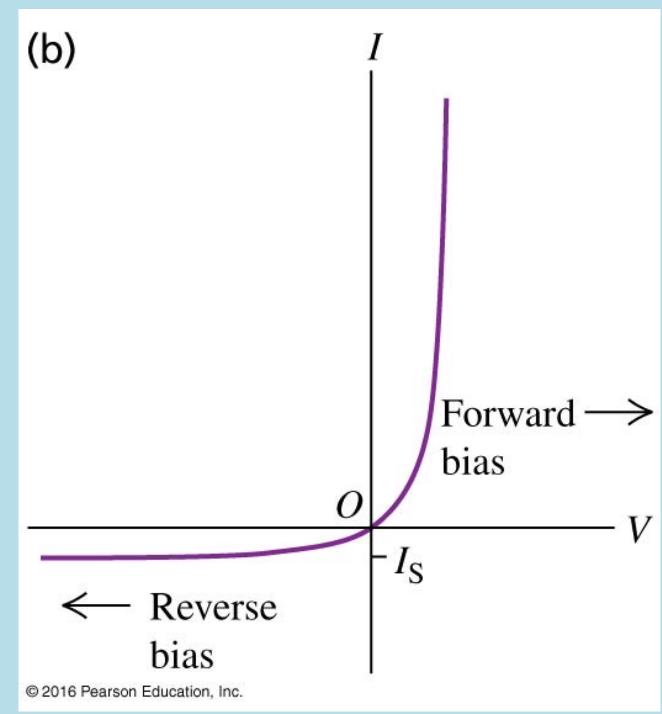


在Reverse Bias流向，電子從左流入p，

而p中導帶的電子，數量稀少。因此電子幾乎無法流過p ，到達介面。

因此反向電壓時電流無法流動。

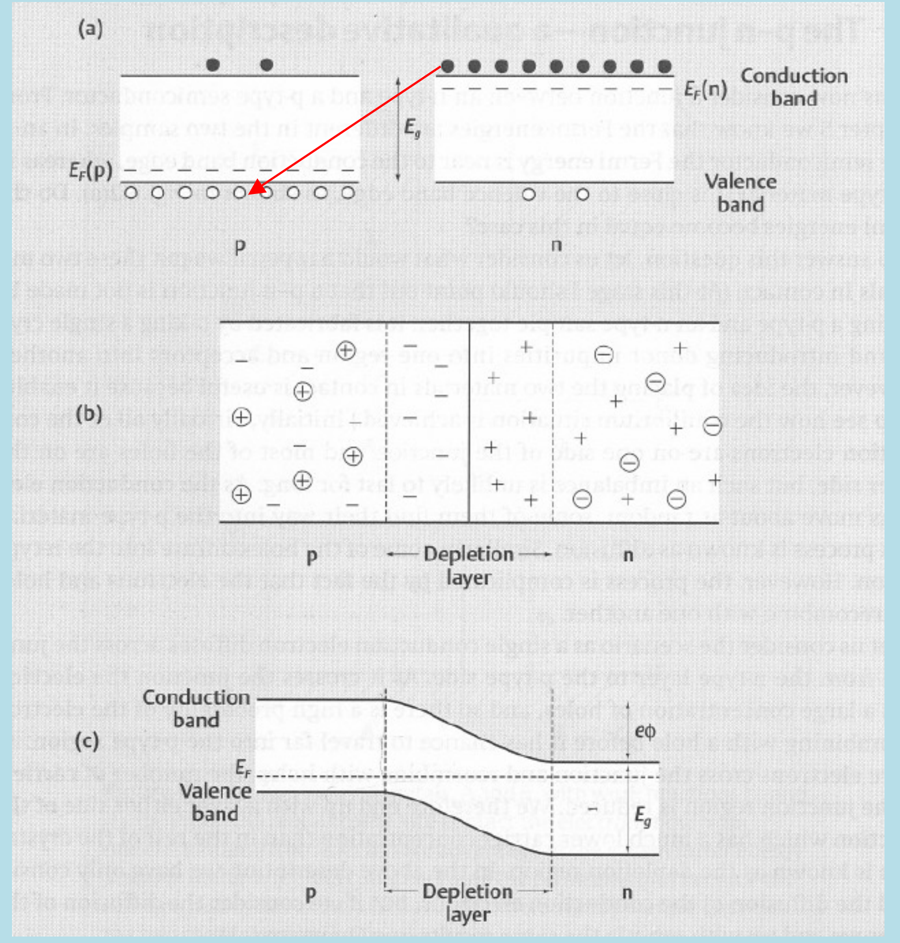


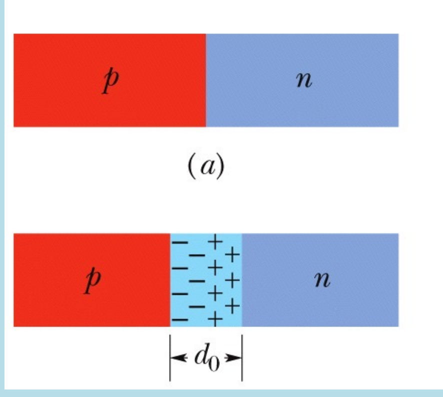


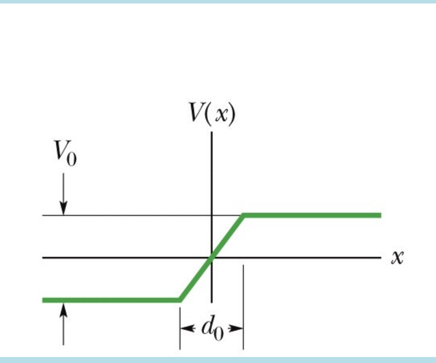
正向電壓時，二極體是一個導體。

反向電壓時，二極體是一個絕緣體！

比較精細的推導顯示：二極體的關鍵在p-n介面！







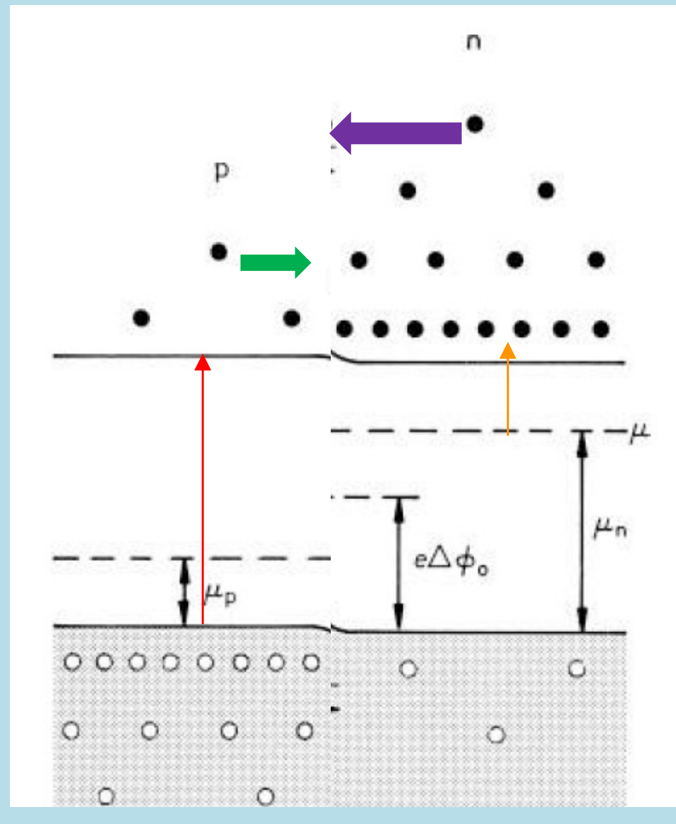
介面上右邊n的電子會滲透進入左邊p，填入電洞之中，

因此介面處會形成一層無載體區域，

右邊電子離開後留下正電離子，左邊電子進入帶負電，薄層中會有一向右電場。

因此n與p之間出現電位差！

Depletion Zone產生前：考慮兩種雜質半導體內的電子電洞分佈：

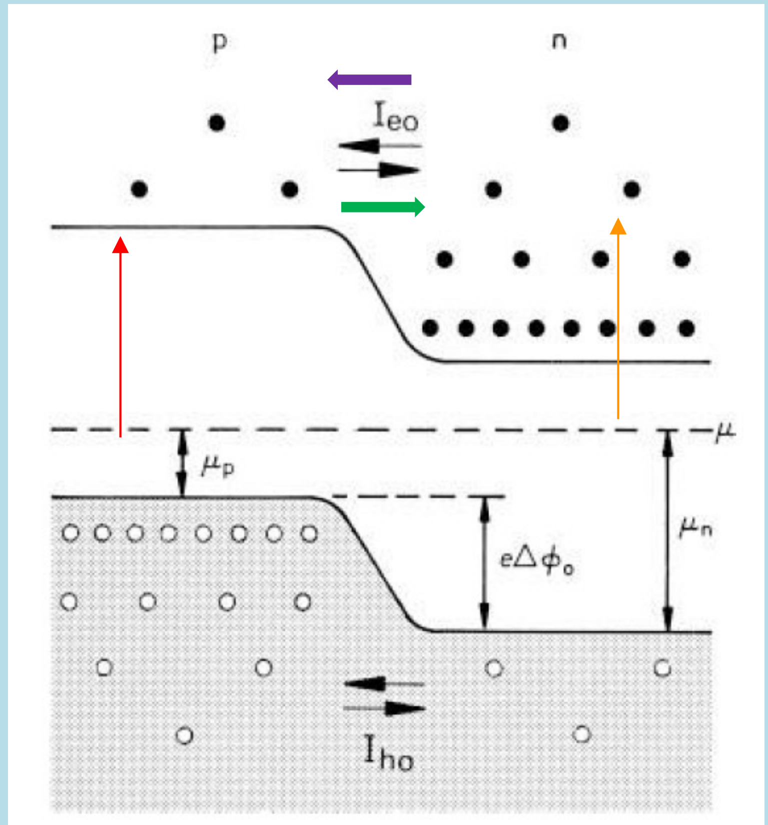


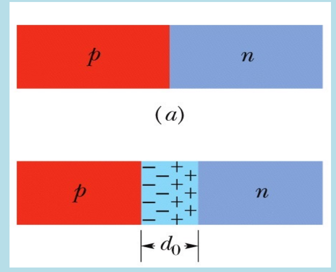
讓我們專注於導帶內電子可能的流動：

左端p，價帶上方少量電子，因熱擾動由價帶跳上傳導帶，$\propto e^{-\frac{E_G}{2kT}}$。向右流。

右端n，Noner內電子，也會因熱到達傳導帶，$\propto e^{-\frac{E_D}{kT}}$。間隙較小，電子數量較大。

因此電子淨向左流，再填入價帶的電洞，如前述，產生了Depletion Zone。





Depletion Zone產生的電子位能差異$\Delta\phi$，應該加在兩端n與p的能帶圖上：

左右兩端導帶的能量高度出現差距，也就是$\Delta\phi$構成了一個障礙。

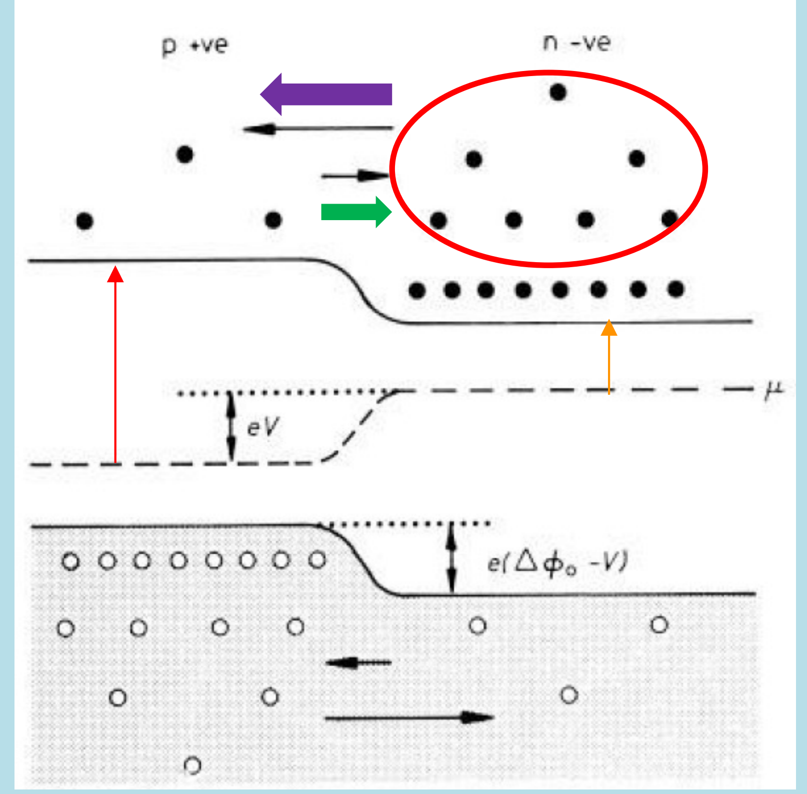
現在右端n的導帶電子，必須跳上到達左邊導帶的能高，才能往左流。

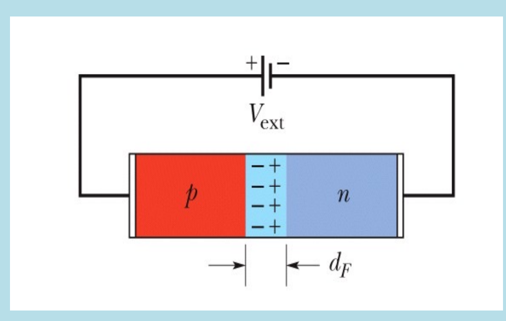
向左電流變小，但向右電流並不被影響。

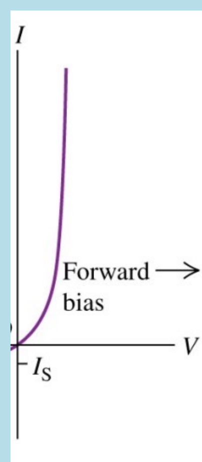
$\Delta\phi$累積到使到達左邊導帶高，兩邊電子數量相同，電流就會抵消而達到穩定。

可以說Depletion Zone出現的電位差，阻止了電子由右向左的擴散繼續進行。

現在p-n間加上一順向的、正的電位差V，在介面左右能量差將縮小，如下圖：







左端p的價帶上方電子，依舊不受所加電壓影響。

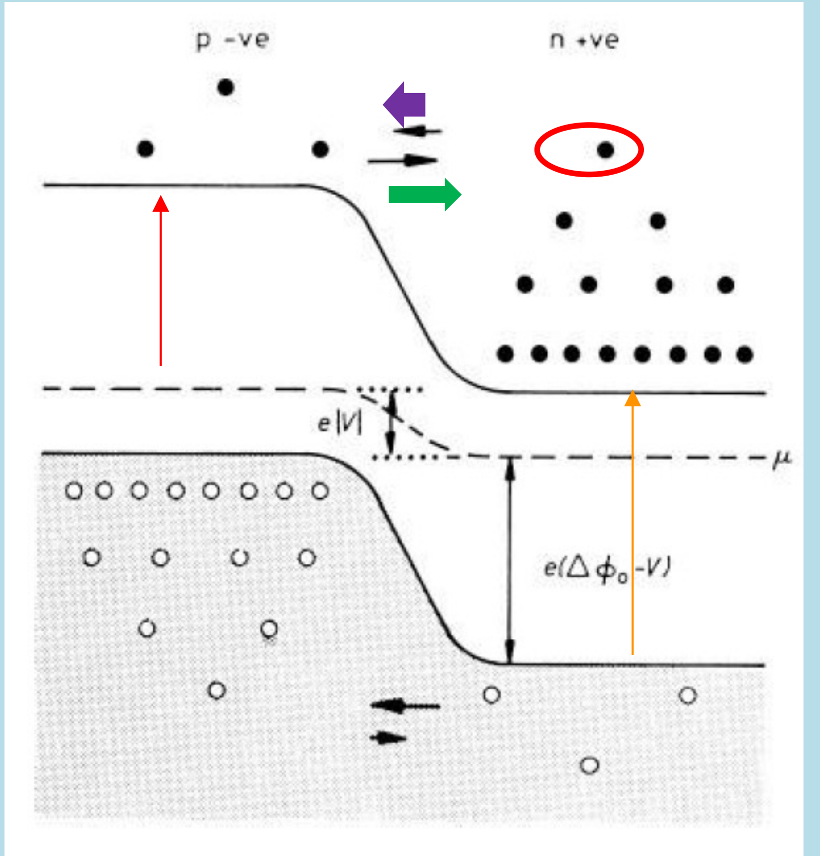
右端n的導帶下方，因熱達到左邊導帶能高的電子增加！

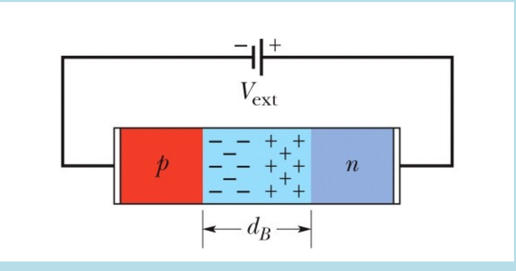
就是電子要跨越的門檻能差因加電壓變小，

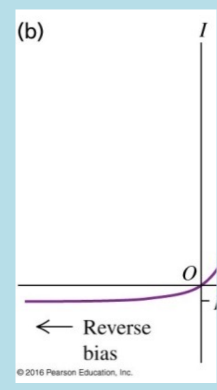
在導帶上電子的能量分佈是波茲曼分佈$\sim e^{-(E-E_G)/kT}$。

門檻降低V，達到的電子數就增加$\sim e^{V/kT}$倍！

因此電子會淨流向左，隨電壓依指數增加的電流向右流。







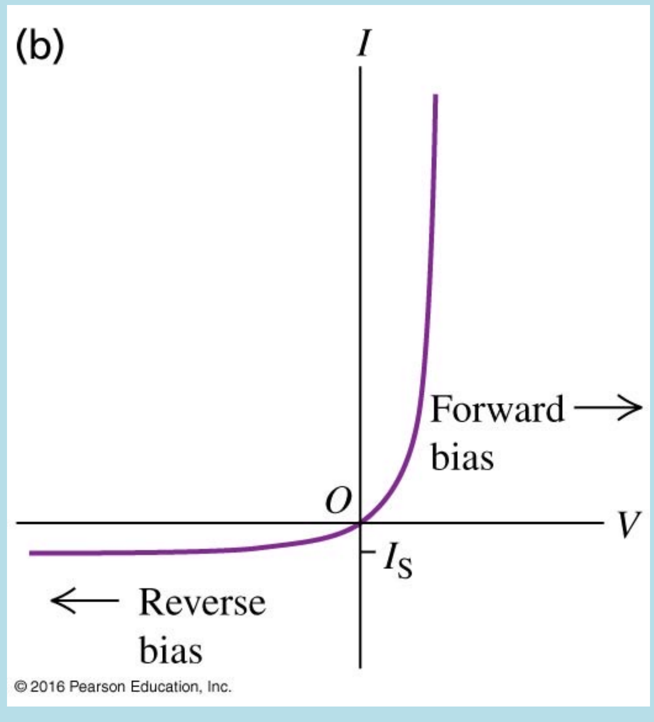
若p-n間加上一負的反向電位差，左右能量差加大，

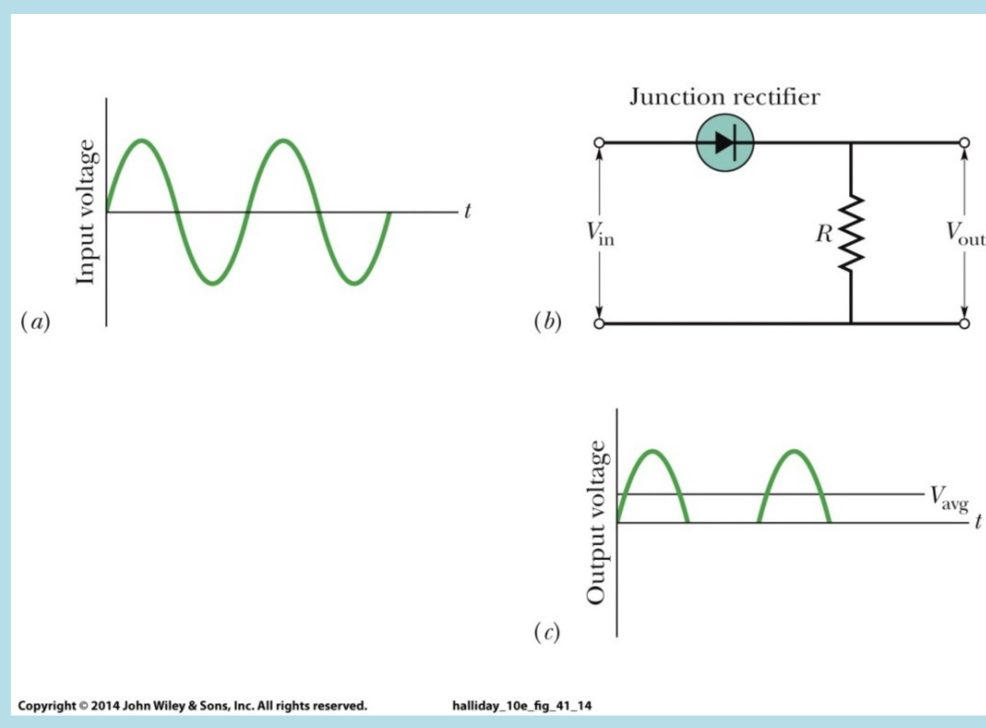
左端p的價帶上方電子，依舊不受所加電壓影響。

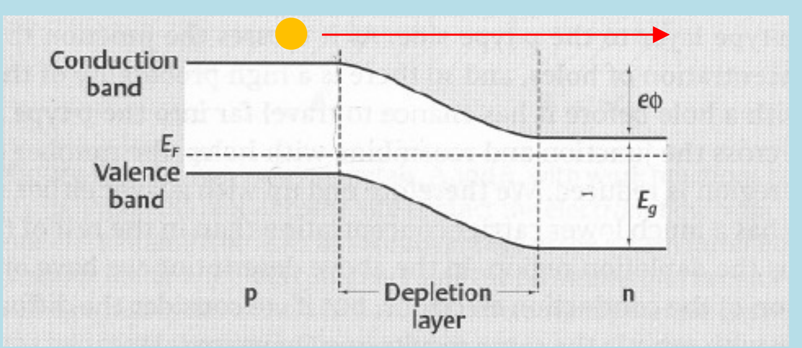
右端n的導帶下方，因熱達到左邊導帶能高的電子則因門檻增加而減少！

因此電子會淨流向右，但只剩下半導體原來因室溫擾動產生的很小的導電度。

電流只能朝單一方向流動！稱為整流器。

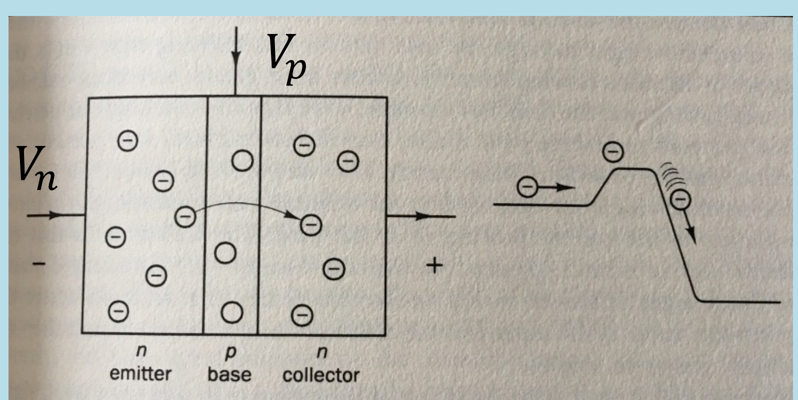






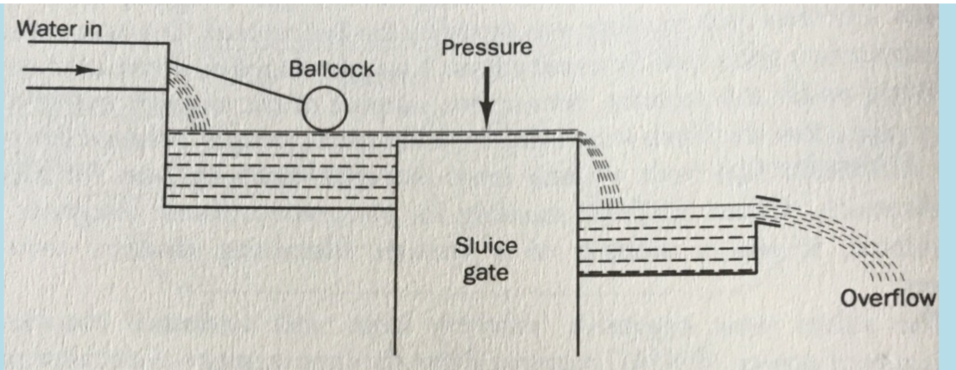
注意n-p介面中，n與p之間會有電位差，推動電子向右移動！。

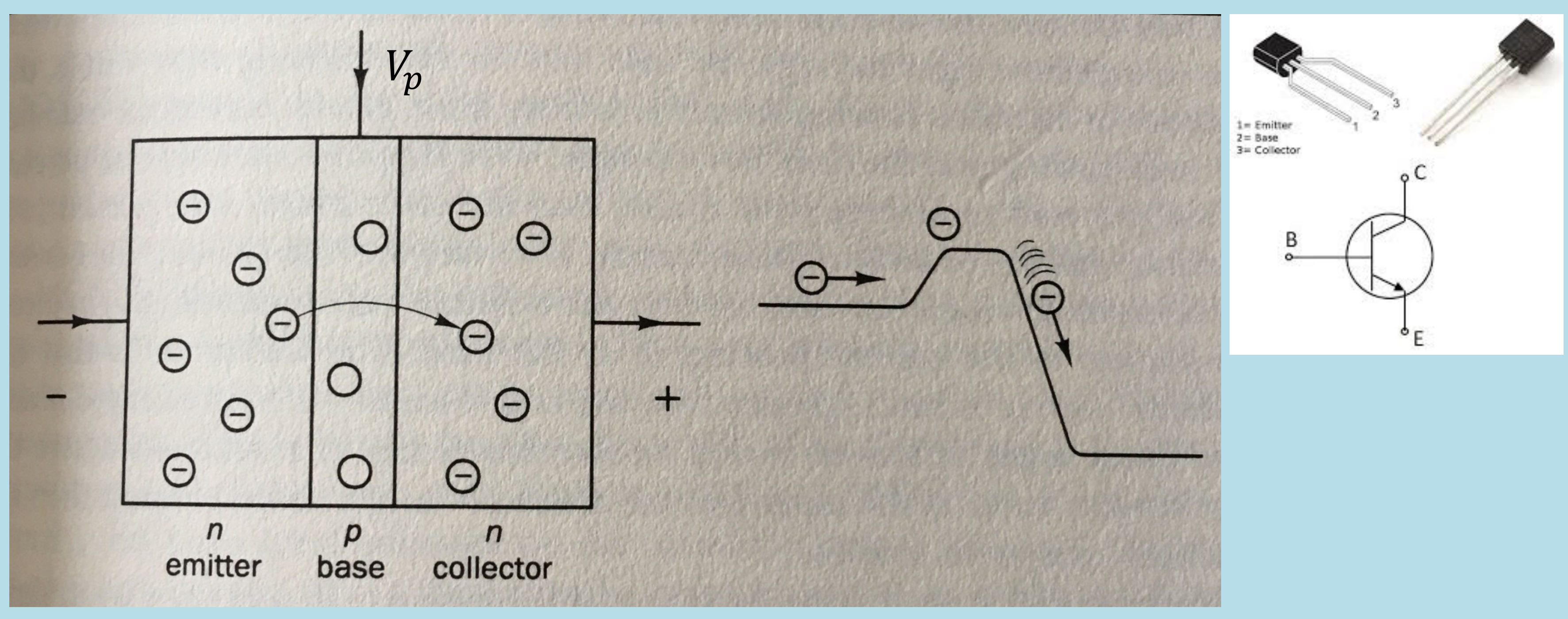
如果對p內額外輸入傳導電子，他們可以大量地流入n。



如果在p的左邊再放一個n，並施以順向電壓$V_p > 0$，

傳導電子就可以由左邊的n被推動流入p，再流入右邊n。





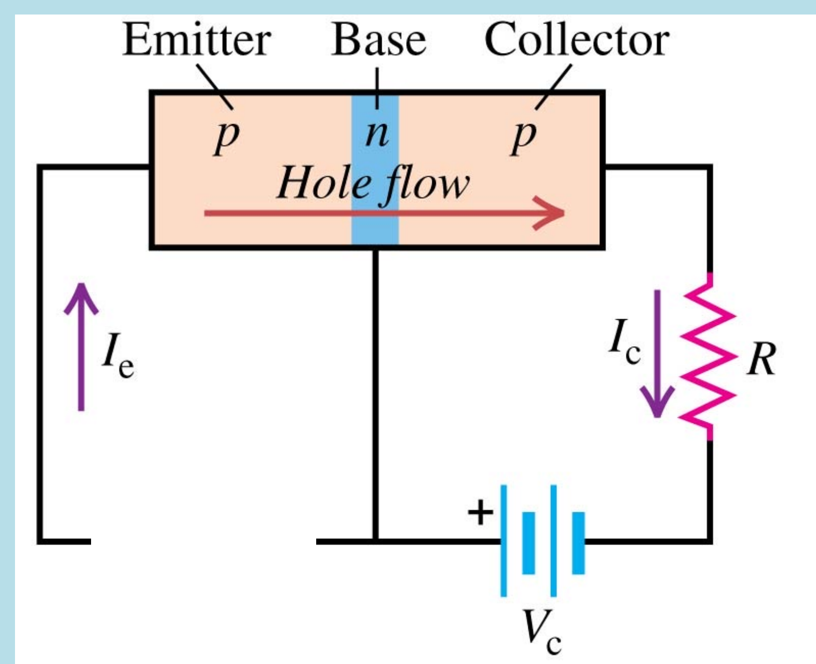
左邊的二極體的順向電壓 V_p 控制流到p的電子，也就控制了流到右邊n的電流大小。

Bipolar Transistor 雙極性電晶體

如果電壓V_e很小而且有訊號，電壓V_c很大，所產生的大I_c就會攜帶訊號。

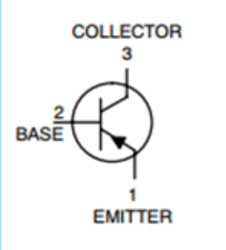
這就是訊號放大器！

電晶體 transistor



- When $V_e = 0$, the current is very small.
- When a potential V_e is applied between emitter and base, holes travel from the emitter to the base.
- When V_c is sufficiently large, most of the holes continue into the collector.

© 2016 Pearson Education, Inc.



右邊是一個Reverse Bias的電壓V_c ，電子進到Collector的p，在介面遇左方來的電子。

電子無法繼續往左由流入n，因此I_c很小。

但如果左方加一個電壓V_e，電子會由Base的n被抽走進入Emitter，

如此Collector來的，到介面上電子被電壓 V_c 推動，就能由繼續流入Base，產生 I_c 。

如此以電壓V_e做為條件，來控制電壓V_c是否能產生I_c。

如果電壓V_e很小而且有訊號，電壓V_c很大，所產生的大I_c就會攜帶訊號。

這就是訊號放大器！

金屬氧化物半導體、場效型電晶體 MOSFET

Metal-Oxide-Semiconductor Field Effect Transistor

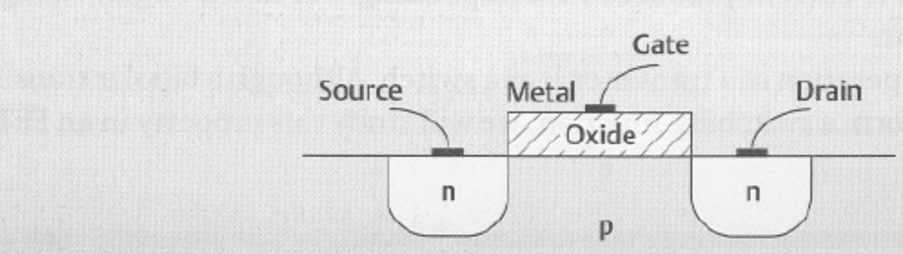


Figure 6.10 The structure of an n-channel MOSFET showing the source, gate and drain region. The electrical contact to the gate is separated from the semiconductor by a thin layer of insulator, typically silicon dioxide.

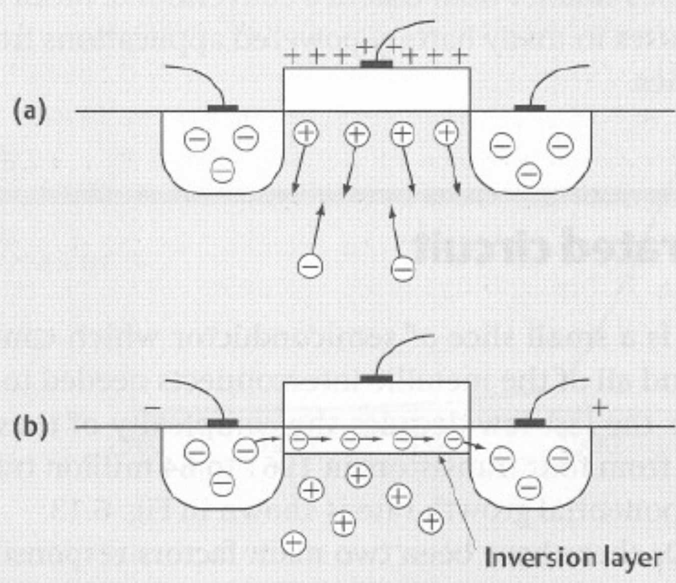
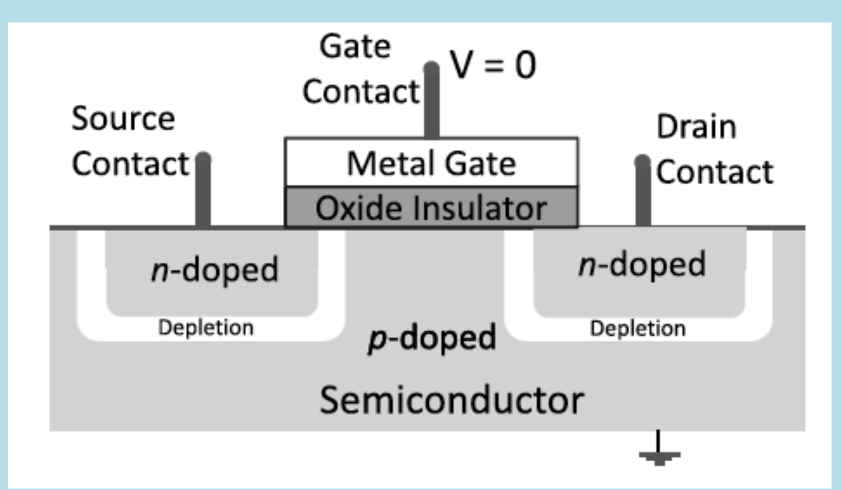
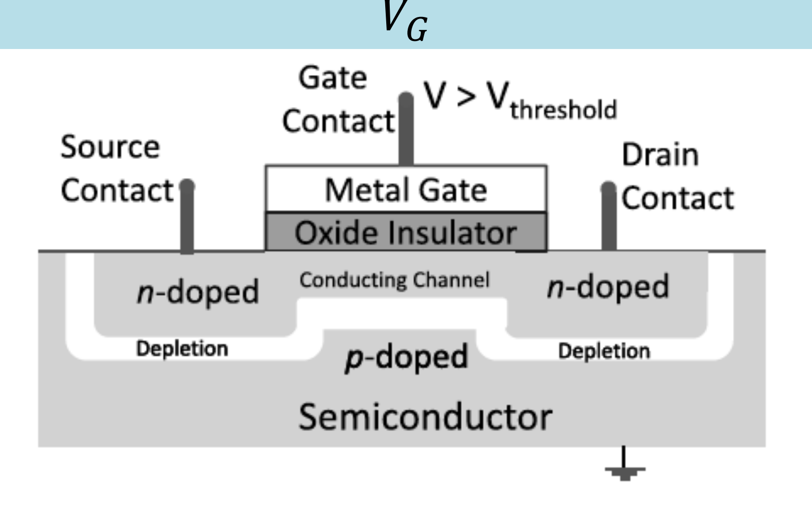


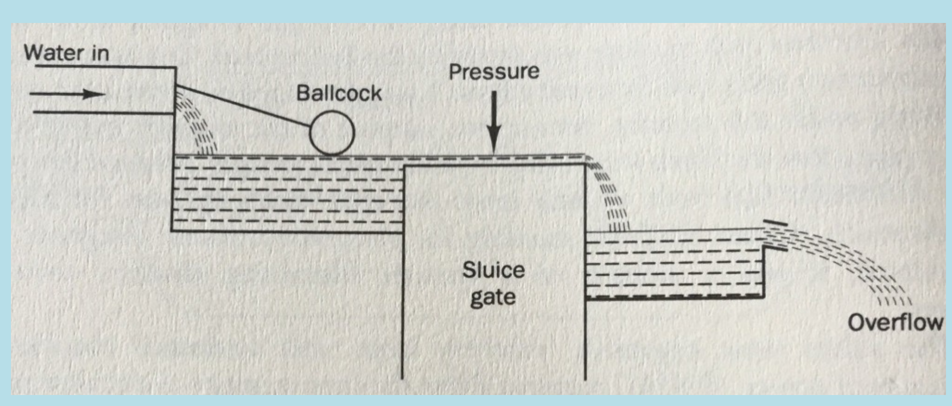
Figure 6.11 (a) When a positive voltage is applied to the gate the holes in the p-type semiconductor are repelled from the surface, and the minority carrier conduction electrons are attracted to the surface. (b) If the gate voltage exceeds the threshold value then an inversion layer is created near the surface. In this layer the material behaves as an n-type semiconductor and so provides a conducting channel between the source and the drain.

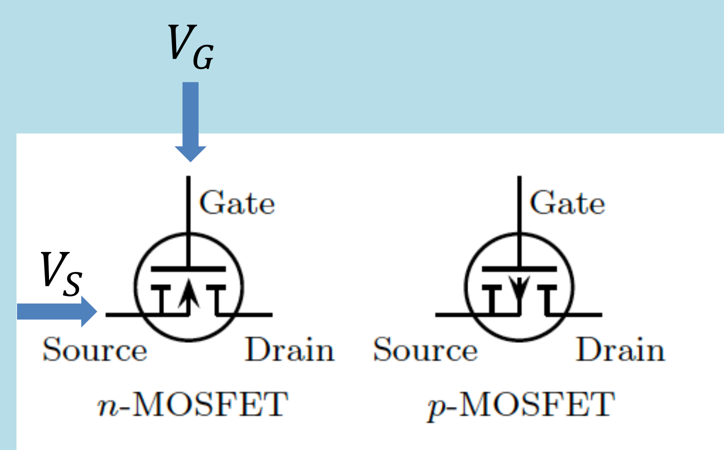




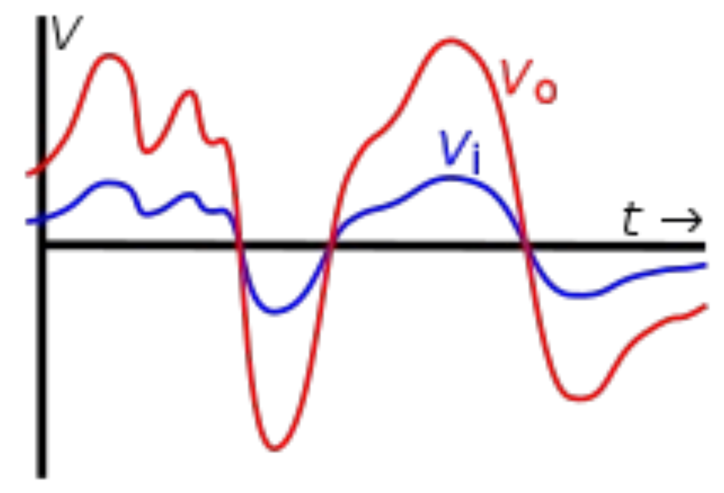
如此以閘電壓V_G做為條件，來控制電壓V_S是否能產生I_S。

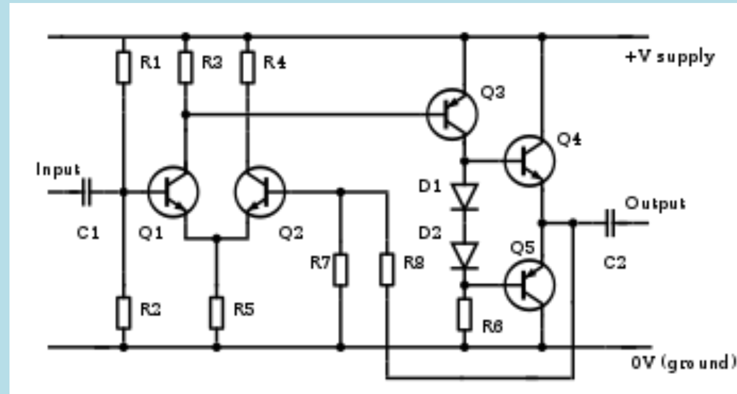
如果電壓V_G很小而且有訊號，電壓V_S很大，所產生的大I_S就會攜帶訊號。





audio amplifier 音響放大器





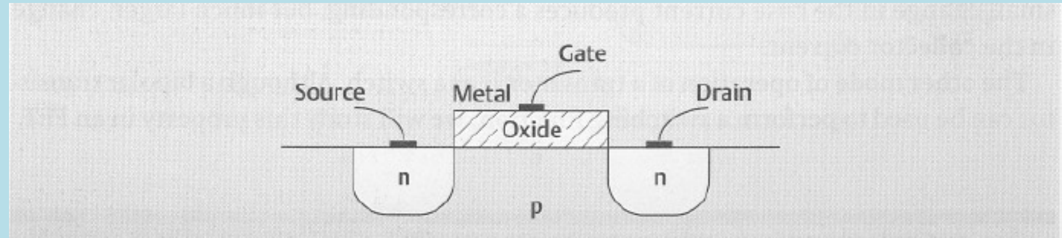
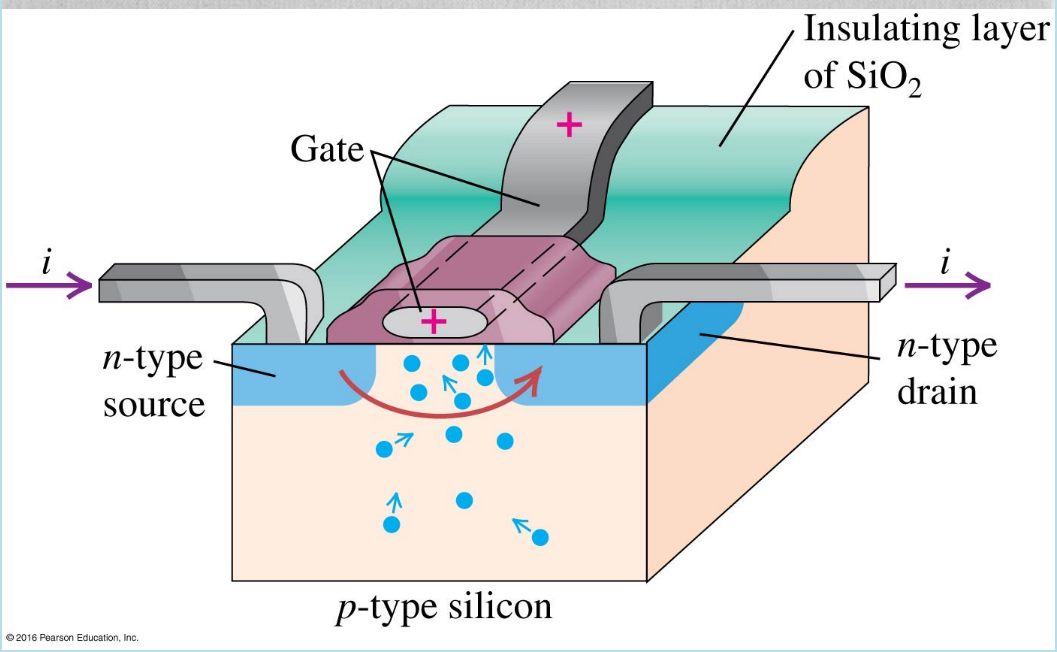


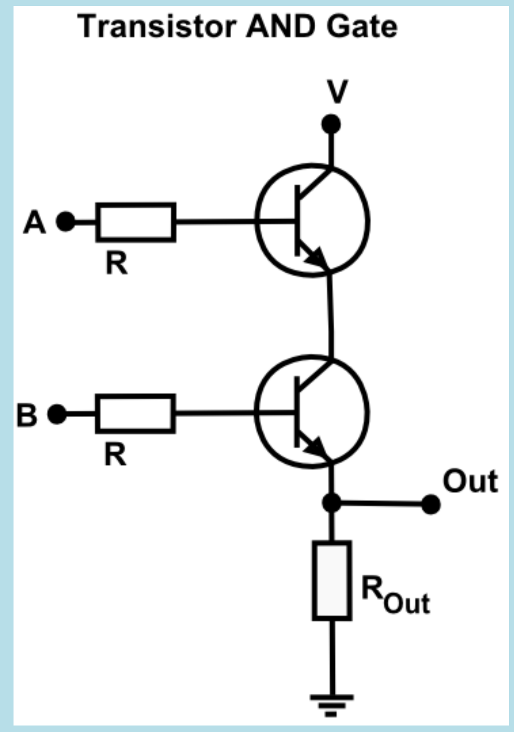
Figure 6.10 The structure of an n-channel MOSFET showing the source, gate and drain region. The electrical contact to the gate is separated from the semiconductor by a thin layer of insulator, typically silicon dioxide.

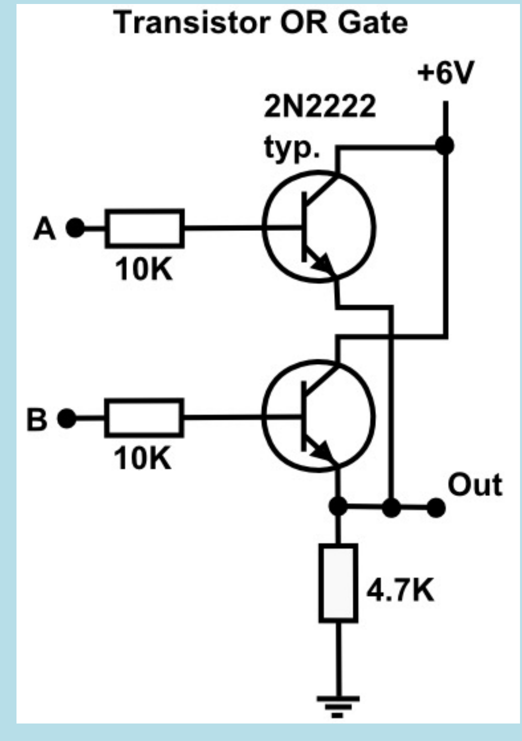


© 2016 Pearson Education, Inc.

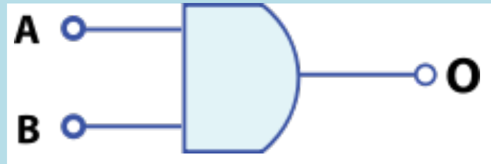
Integrated Circuit 積體電路

Logical Gates





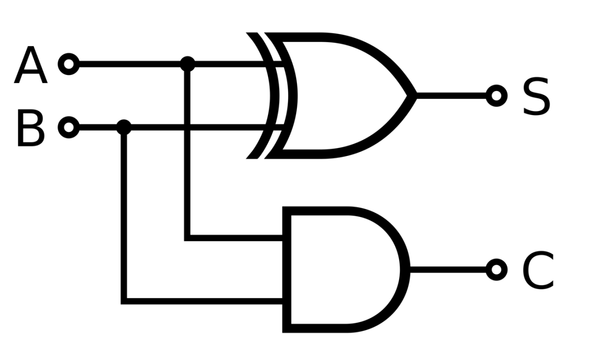
Input		Output
A	B	A XOR B
0	0	0
0	1	1
1	0	1
1	1	0

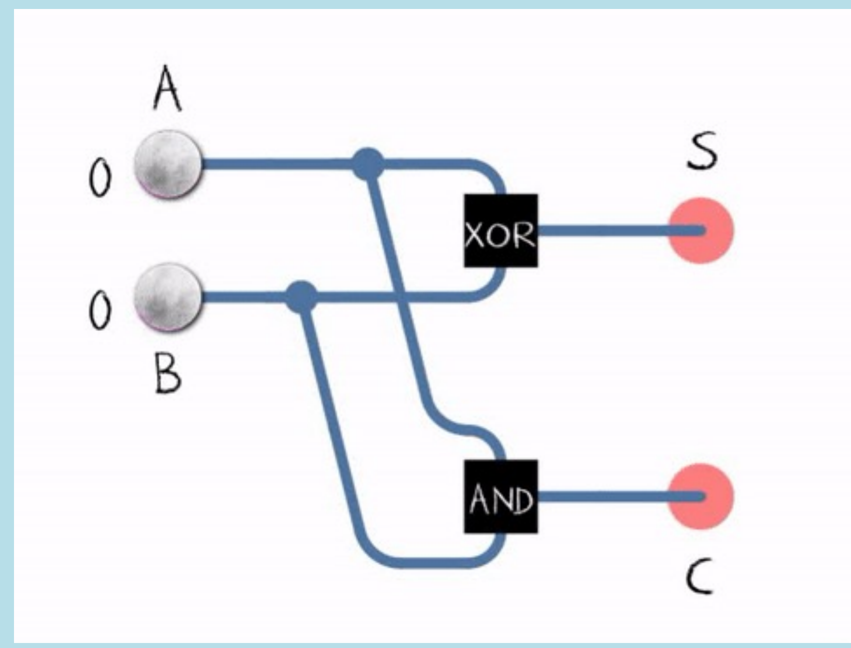


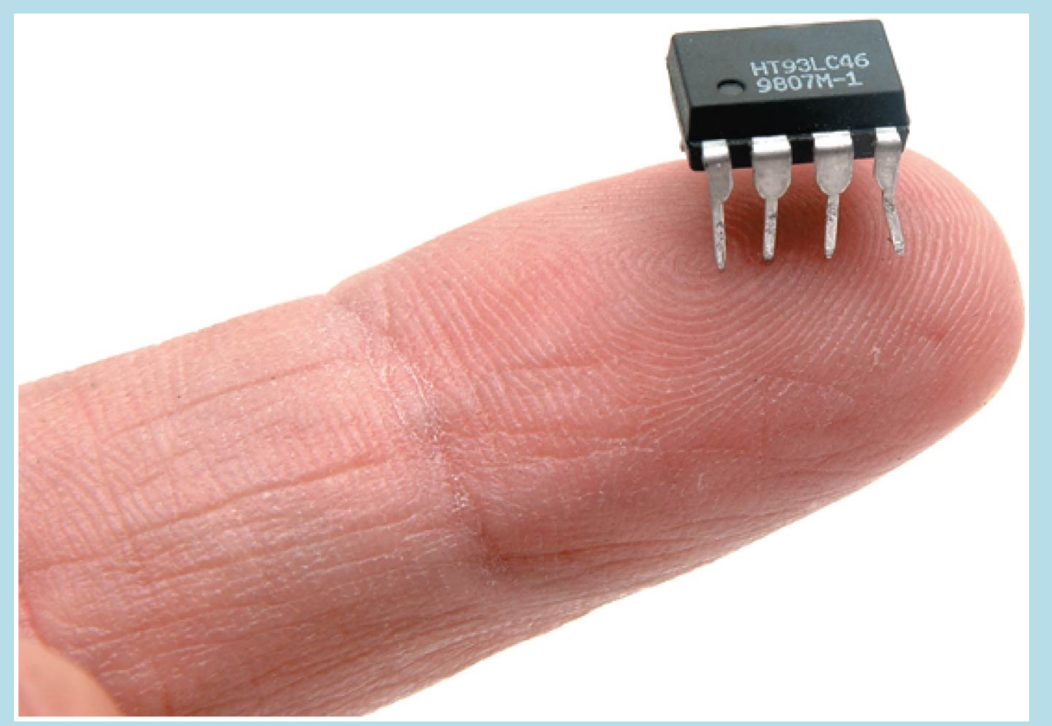
電晶體可以組成邏輯閘門！

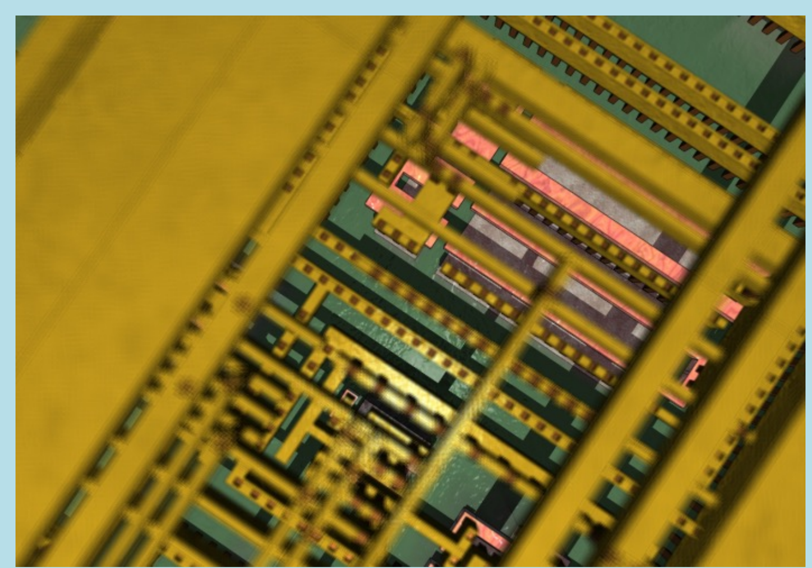
邏輯閘門可以組成演算電路！

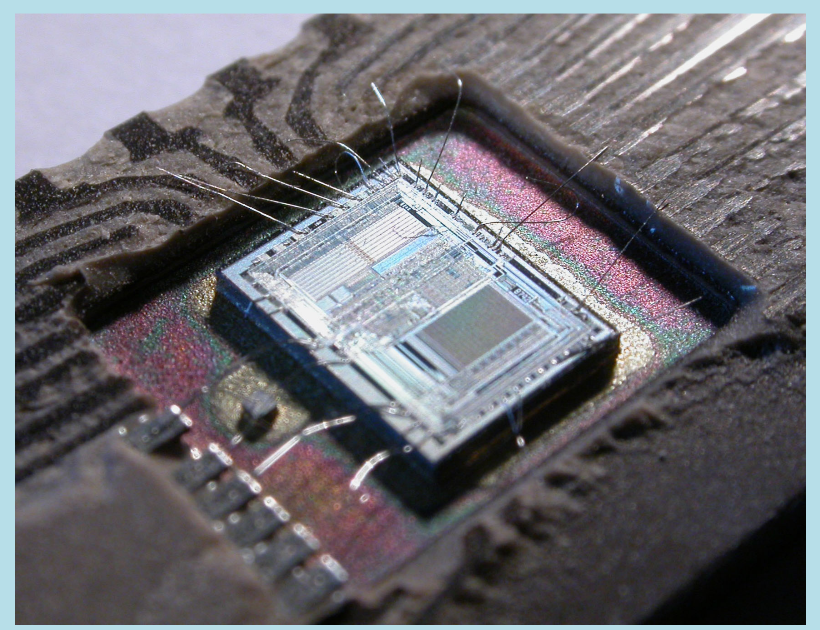
Half adder logic circuits

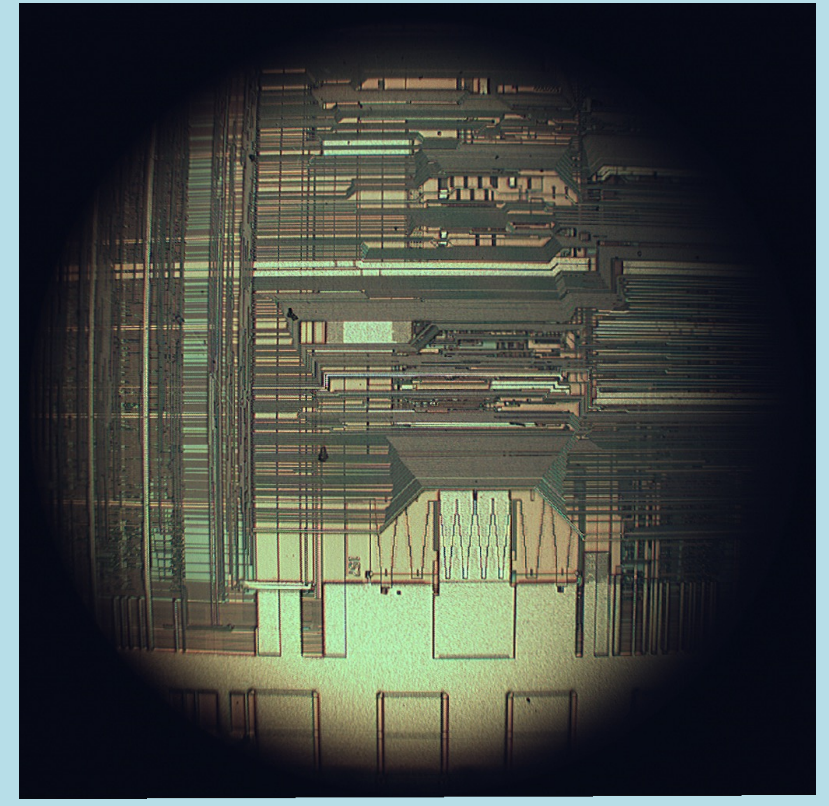


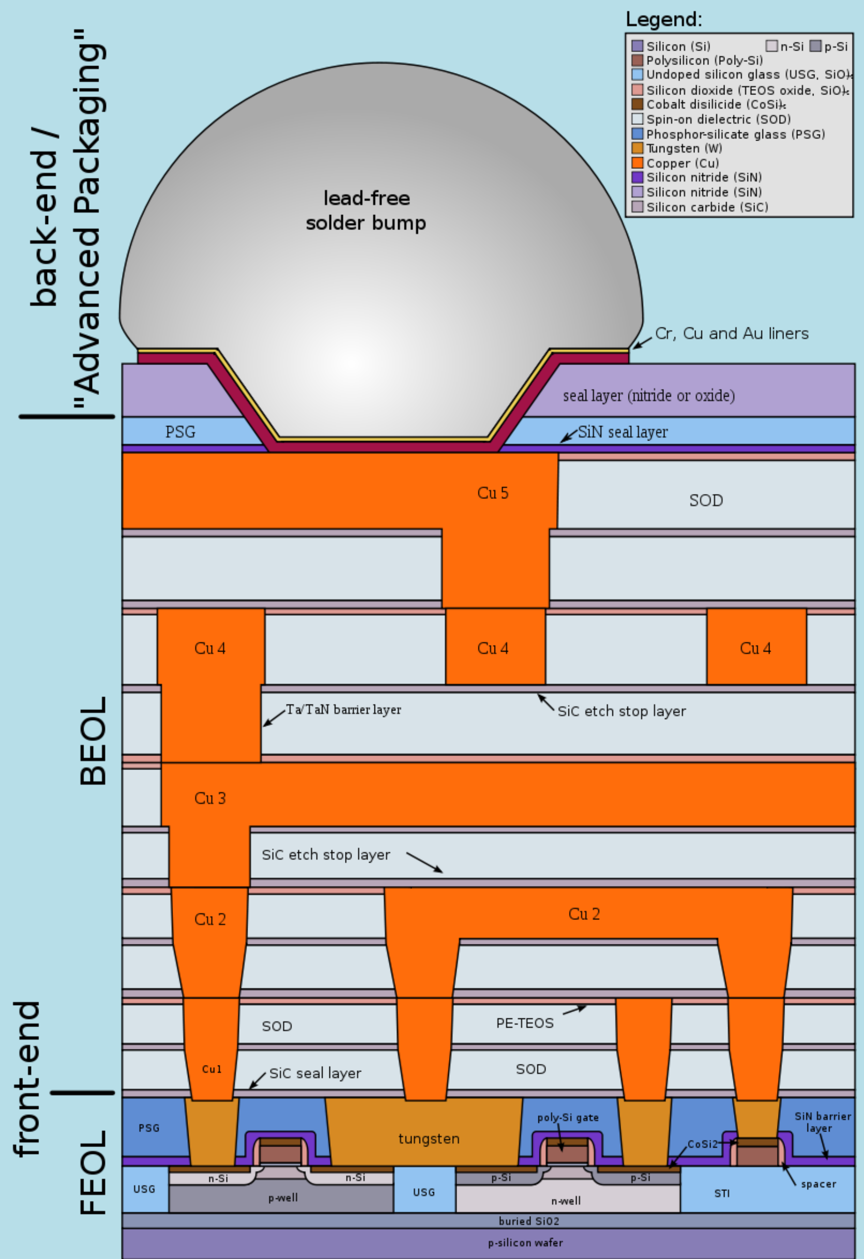



HT93LC46
9807M-1









back-end /
"Advanced Packaging"
BEOL
front-end
FEOL
Legend:
Silicon (Si)
n-Si
p-Si
Polysilicon (Poly-Si)
Undoped silicon glass (USG, SiO₂)
Silicon dioxide (TEOS oxide, SiO₂)
Cobalt disilicide (CoSi₂)
Spin-on dielectric (SOD)
Phosphor-silicate glass (PSG)
Tungsten (W)
Copper (Cu)
Silicon nitride (SiN)
Silicon nitride (SiN)
Silicon carbide (SiC)
lead-free
solder bump
Cr, Cu and Au liners
seal layer (nitride or oxide)
PSG
SiN seal layer
Cu 5
SOD
Cu 4
Cu 4
Cu 4
Ta/TaN barrier layer
SiC etch stop layer
Cu 3
SiC etch stop layer
Cu 2
Cu 2
SOD
PE-TEOS
Cu1
SiC seal layer
SOD
PSG
tungsten
poly-Si gate
SiN barrier layer
CoSi2
n-Si
n-Si
p-Si
p-Si
spacer
USG
p-well
USG
n-well
STI
buried SiO2
p-silicon wafer