

## II Periodic Potential

The prime example of periodical structures in nature are solids.

In this chapter, I will attempt to capture their main physical characteristics by studying the 1-D periodic potential.

In particular, I will focus on three following important characteristics of the electron dynamics:

- a) The form of the wavefunction as specified by Bloch's theorem.
- b) the development of an energy gap in the spectrum of the electrons.
- c) the approximation, whereby the dynamics of the electron in the solid can be described by assigning to the electron an effective mass and still consider the electron as a free particle.

We shall start by proving Bloch theorem (also called Floquet's Theorem).

### A) Translation operator

Define the translation operator through its action on a function  $f(x)$ . Specifically:

$$T_a f(x) = f(x+a)$$

where  $a$  is the translation (displacement) distance. We shall choose  $a$  to be the period of the lattice.

This operator commutes with a single particle Hamiltonian of the form

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

$$\text{if } V(x+a) = V(x)$$

Proof: If we let  $x' = x + a$

$\frac{d}{dx} = \frac{d}{dx'}$   
and the only requirement for  
 $[T_a, H] = 0$  is that  $V(x+a) = V(x)$

In the case that two operators commute they admit the same eigenfunctions, i.e if  $\phi(x)$  is an eigenfunction of  $H$ , then it is also an eigenfunction of  $T_a$

$$H\phi(x) = E\phi(x)$$

$$T_a\phi(x) = \lambda\phi(x)$$

Clearly applying  $T_a$  to  $\phi(x)$   $N$  times gives

$$T_a^N\phi(x) = \lambda^N\phi(x) = \phi(x+Na)$$

If we apply periodic boundary conditions with period  $N$ , then  $\phi(x+Na) = \phi(x)$ , from which we conclude that  $\lambda^N = 1$ . Thus  $\lambda$  itself must be the  $N$  root of unity

$$\lambda = e^{i\frac{2\pi}{N}n}$$

where  $n = 0, \pm 1, \pm 2, \dots$  and we can write  $\lambda$  as

$$\lambda = e^{ika} \quad (\text{where } k = \frac{2\pi n}{Na})$$

It is apparent that two values of  $k$  which differ by  $\frac{2\pi}{a}$  times an integer give identical values of  $\lambda$ . We choose the  $N$  independent values of  $k$  to be those in the range  $-\frac{2\pi}{a} < k < \frac{2\pi}{a}$

This interval for  $k$  is called the first Brillouin zone.

B) Bloch's Theorem

We have demonstrated that

$$T_a \phi(x) = \phi(x+a) - e^{ika} \phi(x)$$

Now define a function

$$u_k(x) = e^{-ikx} \phi(x)$$

Now act on this function with  $T_a$

$$\begin{aligned} T_a u_k(x) &= T_a [e^{-ikx} \phi(x)] \\ &= e^{-ikx} e^{-ika} \phi(x+a) \\ &= e^{-ikx} \phi(x) \\ &= u_k(x) \end{aligned}$$

therefore we can write

$$\phi(x) = e^{ikx} u_k(x)$$

where  $u_k(x) = u_k(x+a)$

Direct consequence

If the wavefunction is described at a certain point by

$$\phi(x) = A e^{ik_1 x} + B e^{-ik_1 x}$$

and at another point by,

$$\phi(x) = C e^{ik_2 x} + D e^{-ik_2 x}$$

then the coefficients, A, B and C, D are related through

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} P_{11} & P_{12} \\ P_{21} & P_{22} \end{pmatrix} \begin{pmatrix} C \\ D \end{pmatrix}$$

over a period, Bloch theorem implies that

$$C = A e^{ika}$$

$$D = B e^{-ika}$$

or  $\begin{pmatrix} A \\ B \end{pmatrix} = e^{-ika} \begin{pmatrix} C \\ D \end{pmatrix}$

which means that

$$P \begin{pmatrix} C \\ D \end{pmatrix} = e^{-ika} \begin{pmatrix} C \\ D \end{pmatrix}$$

which may be written in the form

$$\begin{pmatrix} P_{11} - e^{-ika} & P_{12} \\ P_{21} & P_{22} - e^{-ika} \end{pmatrix} \begin{pmatrix} C \\ D \end{pmatrix} = 0$$

this is a set of homogeneous equations.  
this set of equations has a solution if the determinant of the above matrix is zero or

that  $(P_{11} - e^{-ika})(P_{22} - e^{-ika}) - P_{12}P_{21} = 0$

but the matrix  $P$  is a special case of the transfer matrix

$$M = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix}$$

whose general properties are

$$M_{21} = M_{12}^* \quad \text{and} \quad M_{22} = M_{11}^*$$

The condition ~~on~~ on the determinant of the matrix  $P$  can now be written:

$$(P_{11} - e^{-ika})(P_{11}^* - e^{-ika}) - P_{12}P_{21}^* = 0$$

$$\Rightarrow e^{-i2ka} - 2\operatorname{Re}(P_{11})e^{-ika} + (P_{11}P_{11}^* - P_{12}P_{12}^*) = 0$$

but the determinant of the transfer matrix is always  $= 1$ , or  $P_{11}P_{11}^* - P_{12}P_{12}^* = 1$ . This means that

$$e^{-i2ka} - 2\operatorname{Re}(P_{11})e^{-ika} = -1$$

Multiplying both sides of this equation by  $e^{ika}$  gives:

$$\cos(ka) = \operatorname{Re}(P_{11})$$

This equation has a real root solution for  $k$  only if

$$|\operatorname{Re}(P_{11})| \leq 1 \Rightarrow \left| \frac{1}{2} t_F(P) \right| \leq 1 \text{ since } P_{11} = P_{22}$$

This implies that if we were to plot  $\operatorname{Re}(P)$  as function of energy, there will be regions where the condition is satisfied, these regions are called allowed bands.

and there are regions where the condition is not satisfied and these regions are called forbidden bands.

It should be noted that we use only Bloch Theorem, i.e. periodicity of the potential to prove the existence of bands.

c) Approximate Calculation of effective mass

The model consists of  $N$  atoms over a length  $L$  - the distance between two consecutive atoms being  $a$ , and we assume cyclic boundary conditions.

In the absence of interaction, the eigenfunctions of an electron is given by:

$$\phi_k(x) = \frac{1}{\sqrt{L}} \exp(i k x)$$

the cyclic BC requires that  $kL = 2n\pi$   
or  $kNa = 2n\pi \Rightarrow k = \frac{2\pi}{a} n = G \frac{n}{N}$

where  $G = \frac{2\pi}{a}$ .

The free electron kinetic energy is:

$$E_0(k) = \frac{\hbar^2 k^2}{2m}$$

Let us assume now that the interaction of the lattices and electrons is described by the potential

$$V(x) = -2 V_c \cos(Gx)$$

the interaction matrix element between two states  $|k_1\rangle$  and  $|k_2\rangle$  is given by

$$V_{12} = -\frac{V_c}{L} \int_0^L \left\{ \exp[i(k_2 - k_1 + G)x] + \exp[i(k_2 - k_1 - G)x] \right\} dx$$

Let us select  $k_1$  and  $k_2$  such

$$k_1 = -\frac{G}{2} + k'$$

$$k_2 = \frac{G}{2} + k'$$

these two modes are strongly coupled, the argument of the exponential is zero and

$$V_{12} \approx -V_G$$

- First consider the case that  $k' = 0$ , the Hamiltonian of the interacting two-level system is

$$\hat{H} = \begin{pmatrix} \varepsilon_0(-G/2) & -V_G \\ -V_G & \varepsilon_0(G/2) \end{pmatrix}$$

$$\text{where } \varepsilon_0(-G/2) = \varepsilon_0(G/2) = \frac{k^2 G^2}{8m} \equiv F$$

the eigenvalues of the above matrix are respectively.

$$\varepsilon_{\pm} = F \pm V_G$$

i.e the gap is equal to  $2V_G$ .

- Next consider  $k' \neq 0$ , then

$$\varepsilon_0\left(-\frac{G}{2} + k'\right) = \frac{k^2}{2m} \left(-\frac{1}{2}G + k'\right)^2$$

$$= F - 2\sqrt{F\varepsilon'} + \varepsilon'$$

$$\text{where } \varepsilon' = \frac{k^2}{2m} (k')^2$$

$$\mathcal{E}_0 \left( \frac{G}{2} + k' \right) = F + 2\sqrt{F\varepsilon'} + \varepsilon'$$

and the Hamiltonian matrix is:

$$\hat{H} = \begin{pmatrix} F - 2\sqrt{F\varepsilon'} + \varepsilon' & -V_G \\ V_G & F + 2\sqrt{F\varepsilon'} + \varepsilon' \end{pmatrix}$$

and the eigenvalues of this matrix are:

$$\mathcal{E}_{\pm} = F + \varepsilon' \pm \sqrt{4F\varepsilon' + V_G^2}$$

for small values of  $k'$ ,  $\varepsilon'$  is small and the square root can be expanded:

$$\sqrt{V_G^2 + 4F\varepsilon'} \approx V_G \left( 1 + \frac{2F\varepsilon'}{V_G^2} \right)$$

and the eigenvalues can be approximated

$$\mathcal{E}_+ = F + \varepsilon' + V_G + \frac{2F\varepsilon'}{V_G} = F + V_G + \varepsilon' \left( 1 + \frac{2F}{V_G} \right)$$

and

$$\mathcal{E}_- = F - V_G + \varepsilon' \left( 1 - \frac{2F}{V_G} \right)$$

but the above expressions can also be written as:

$$\varepsilon_+ = F + V_G + \frac{\hbar^2 k'^2}{2m_+}$$

and

$$\varepsilon_- = F - V_G + \frac{\hbar^2 k'^2}{2m_-}$$

where the effective masses  $m_+$  and  $m_-$  are given by

$$\frac{m}{m_+} = 1 + \frac{2F}{V_G}$$

and

$$\frac{m}{m_-} = \left(1 - \frac{2F}{V_G}\right)$$

i.e. the effective masses are not equal to each other and they are both not equal to the free electron mass

## 2) Refinement of the gap calculation

We can improve the accuracy of the calculation of the energy gap at  $k = \pm G/2$  by including the two additional plane waves at  $k = \pm 3G/2$  into the perturbation expansion, each of which couples to one of the plane waves, <sup>states</sup>, with  $k = \pm G/2$ . The unperturbed energies of these states are

$$\mathcal{E}_0 (\pm 3G/2) = \frac{9\hbar^2 G^2}{8m} = 9F$$

The secular determinant determining the eigenenergies is

$$\begin{vmatrix} 9F - \mathcal{E} & -V_G & 0 & 0 \\ -V_G & F - \mathcal{E} & -V_G & 0 \\ 0 & -V_G & F - \mathcal{E} & -V_G \\ 0 & 0 & -V_G & 9F - \mathcal{E} \end{vmatrix} = 0$$

This is a fourth order polynomial. The roots can be computed analytically, however the solutions of the problem can be seen more transparently if we use a different basis functions, define the new basis as follows:

$$|C,1\rangle = \underbrace{\left( |G/2\rangle + | -G/2\rangle \right)}_{\sqrt{2}} = \sqrt{\frac{2}{L}} \cos\left(\frac{Gx}{2}\right)$$

$$|C,3\rangle = \frac{1}{\sqrt{2}} \left( |3G/2\rangle + |-3G/2\rangle \right) = \sqrt{\frac{2}{L}} \cos\left(\frac{3Gx}{2}\right)$$

these are the even states and

$$|S,1\rangle = \frac{1}{\sqrt{2}} i \left( |G/2\rangle - | -G/2\rangle \right) = \sqrt{\frac{2}{L}} \sin\left(\frac{Gx}{2}\right)$$

$$\begin{aligned} |S,3\rangle &= \frac{1}{\sqrt{2}} \left( |3G/2\rangle - |-3G/2\rangle \right) \\ &= \sqrt{\frac{2}{L}} \sin\left(\frac{3Gx}{2}\right) \end{aligned}$$

these are the odd parity states

Because the sine and cosine have opposite parities, there will be no mixed matrix elements between them. The  $4 \otimes 4$  secular determinant factors into two  $2 \otimes 2$  determinants one for the even states and one for the odd states.

The values of the off-diagonal matrix elements are:

$$\begin{aligned} \langle C,1 | V | C,3 \rangle &= \\ &\frac{1}{2} (\langle G/2 | V | 3G/2 \rangle + \langle -G/2 | V | 3G/2 \rangle \\ &+ \langle G/2 | V | -3G/2 \rangle + \langle -G/2 | V | -3G/2 \rangle) \\ &= \frac{1}{2} (-V_g + 0 + 0 - V_g) = -V_g \end{aligned}$$

similarly

$$\langle S,1 | V | S,3 \rangle = -V_g$$

However in the new basis

$$\langle C,1 | V | C,1 \rangle = -V_g$$

$$\langle S,1 | V | S,1 \rangle = +V_g$$

$$\langle C,3 | V | C,3 \rangle = \langle S,3 | V | S,3 \rangle = 0$$

The secular equation for the even states become

$$\begin{vmatrix} F - V_g - \epsilon & -V_g \\ -V_g & 9F - \epsilon \end{vmatrix} = 0$$

for the even states and

$$\begin{vmatrix} F + V_g - \epsilon & -V_g \\ -V_g & 9F - \epsilon \end{vmatrix} = 0$$

the roots are respectively

$$\epsilon_{c,\pm} = 5F - \frac{1}{2}V_g \pm \sqrt{\left(4F + \frac{1}{2}V_g\right)^2 + V_g^2}$$

for the even states characteristic equation, and for the odd parity states, we have.

$$\epsilon_{s,\pm} = 5F + \frac{1}{2}V_g \pm \sqrt{\left(4F - \frac{1}{2}V_g\right)^2 + V_g^2}$$

In the limit of a vanishing perturbation  $V_g \rightarrow 0$ , the lower of the two roots  $\epsilon_{c,-}$  and  $\epsilon_{s,-}$  go over into the unperturbed energy at  $k = \pm G/2$  ( $\epsilon^{(0)} = F$ ), while the higher roots  $\epsilon_{c,+}$  and  $\epsilon_{s,+}$  go over into the unperturbed energy at  $k = \pm 3G/2$  ( $\epsilon^{(0)} = 9F$ ). The two lower roots represent the energy gap at  $\pm G/2$ , while the higher roots represent the new gap at  $\pm 3G/2$ .

**6.1** The potential energy in a periodic 1D lattice is given by:

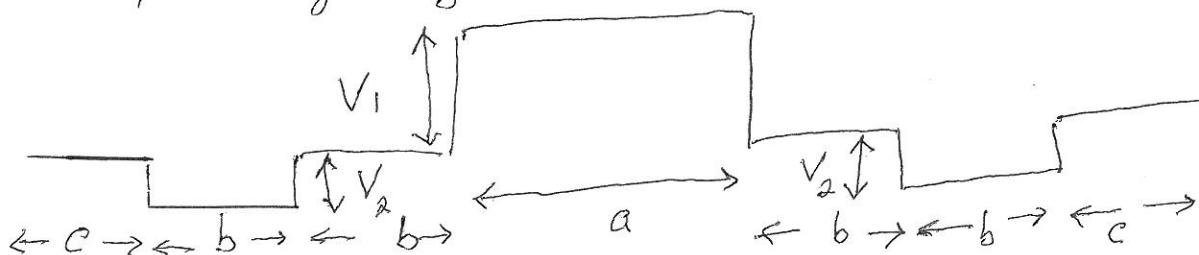
$$V(x) = \sum \lambda \delta(x - nL)$$

Use the expression previously derived in Chap V for the delta gap transfer matrix to find the forbidden bands for an electron in the interval  $0 \leq \varepsilon \leq 10$  eV.

Let  $\lambda = 0.3$  eV.nm and  $L = 0.4$  nm.

**6.2** The potential energy in a periodic 1D lattice, of period 0.4 nm, consists of rectangular barriers of width 0.2nm and height 1.5 eV. Find the forbidden bands for an electron in this structure in the interval  $0 \leq \varepsilon \leq 10$  eV. Compare your results with those of Pb 6.1

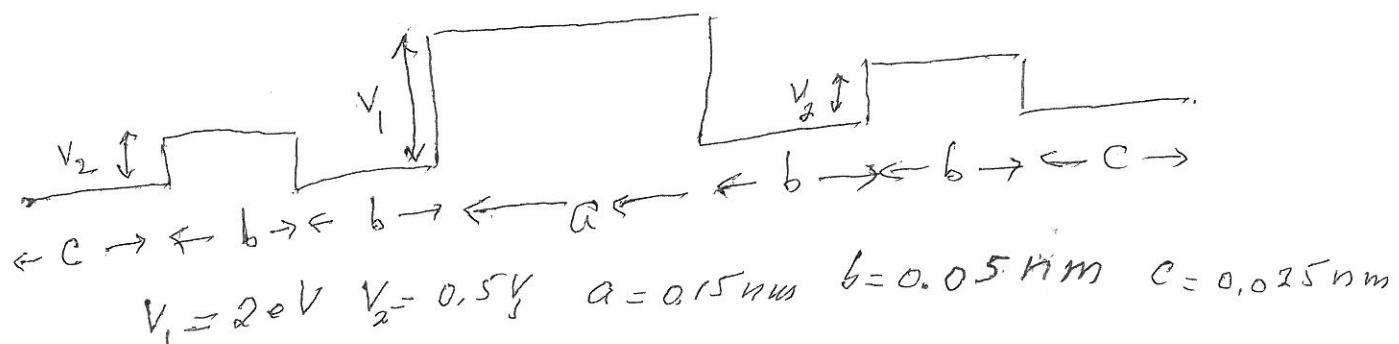
**6.3** Find the forbidden bands, in the interval  $0 \leq \varepsilon \leq 10$  eV, for the following periodic structure, with the following unit cell:



$$V_1 = 2 \text{ eV} \quad V_2 = 0.5 V_1 \quad a = 0.15 \text{ nm} \quad b = 0.05 \text{ nm} \quad c = 0.025 \text{ nm}$$

Compare your results with those of Pb 6.2.

**6.4** Find the forbidden bands, in the interval  $0 \leq \varepsilon \leq 10$  eV, for the following periodic structure, with the following unit cell



Compare your results with those of Pb 6.2.