ME 697R: Computational Methods for Nanoscale Energy Transport

Chapter 5: First Principles Method

Section 5.2: Electronic Structure of Solids

Reading: Kittel, pp. 174-182

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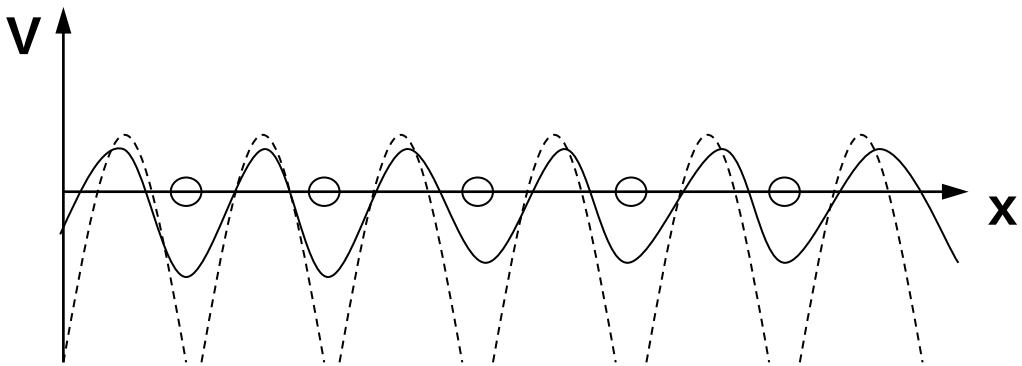
Electron Motion in a Periodic Potential

- The motion of an electron in a crystalline solid can be reduced to the problem of an electron in a periodic potential.
- The lattice determines the form of the potential:

$$V(\mathbf{r}+\mathbf{a}) = V(\mathbf{r}) \quad \text{for any lattice vector } \mathbf{a}$$



Typical crystalline potential

- Now seek to solve: $$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

- Bloch's Theorem: $$\boxed{\begin{array}{l}\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_{n\mathbf{k}}(\mathbf{r}) \\ \text{where} \quad u_{n\mathbf{k}}(\mathbf{r}+\mathbf{a}) = u_{n\mathbf{k}}(\mathbf{r})\end{array}}$$

The Bloch Function Description

- F. Bloch proved important theorem that the solutions to the Schrödinger equation for a periodic potential must be of a form:

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

cell periodic part with periodicity of the lattice

plane-wave component

- We now give a simplified proof of the Bloch theorem, which assumes 1D lattice with atoms at positions x = 0, a, 2a, …, *N*a, that are arranged on a ring. Guided by the symmetry of the ring, we now make the periodic assumption, that leads to:

$$\psi(x+a) = C\psi(x) \quad \rightarrow \quad \psi(x+Na) = C^N \psi(x) = \psi(x)$$

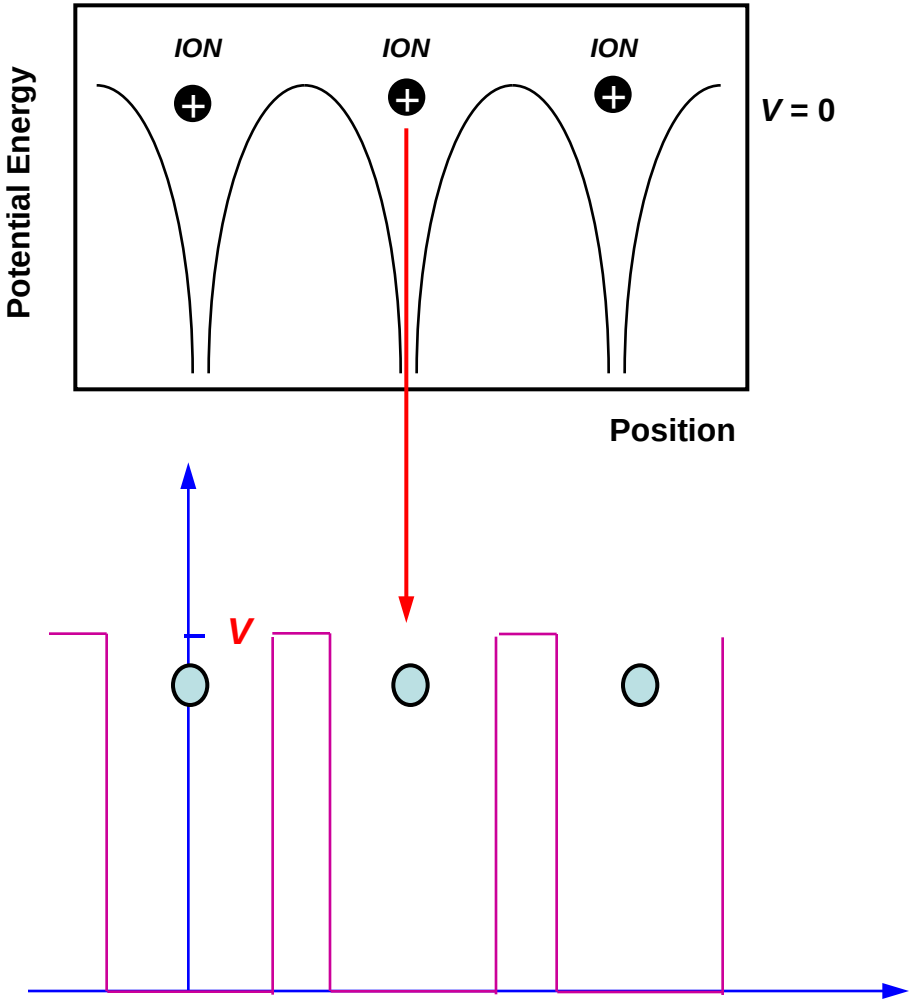
$$\Rightarrow C^N = 1 \quad \Rightarrow \quad C = e^{i2\pi n/N}$$

Let $\psi(x) = u_k(x) e^{ik_n x}$ where $k_n = 2\pi n / Na$, and $u_k(x) = u_k(x+a)$

Then $\psi(x+a) = u_k(x+a) e^{ik_n(x+a)} = u_k(x) e^{i\frac{2\pi n}{Na}(x+a)} = u_k(x) e^{i\frac{2\pi n}{Na}x + i\frac{2\pi n}{N}} = C\psi(x)$

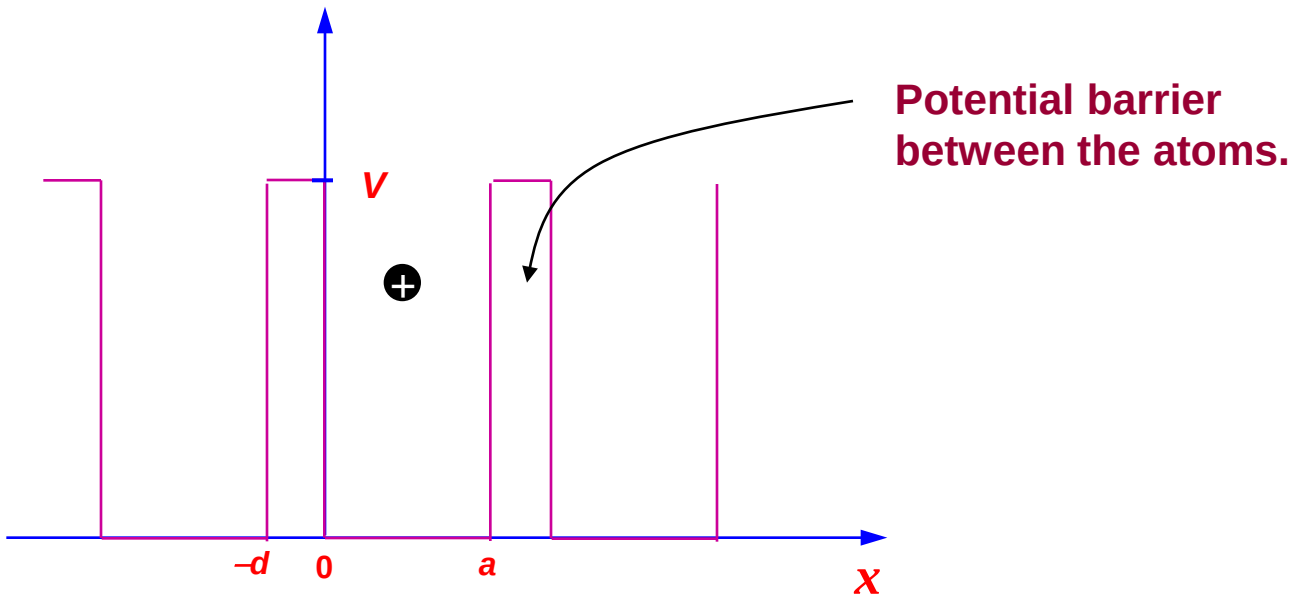
The Kronig-Penney Model

- Coulomb potential



- We simplify the potential, in order to be able to solve the problem analytically.

The Kronig-Penney Model



- We will eventually let $V \to \infty$ and $d \to 0$ in the problem.

The Kronig-Penney Model

- We now solve the time-independent Schrödinger equation.

$$0 < x < a$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} = E\psi_1$$

$$\frac{d^2\psi_1}{dx^2} + \alpha^2\psi_1 = 0$$

NOTE

$$\alpha^2 = \frac{2mE}{\hbar^2}$$

$$-d < x < 0$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + V\psi_2 = E\psi_2$$

$$\frac{d^2\psi_2}{dx^2} - \gamma^2\psi_2 = 0$$

$$\gamma^2 = \frac{2m(V-E)}{\hbar^2}$$

- So, we seek a general solution of the Bloch form:

$$\psi_i(x) = e^{ikx}u_i(x), \qquad u_i(x+a+d) = u_i(x)$$

The Kronig-Penney Model

$$\frac{d^2u_1}{dx^2} + 2ik\frac{du_1}{dx} + (\alpha^2 - k^2)u_1 = 0$$

$$\frac{d^2u_2}{dx^2} + 2ik\frac{du_2}{dx} - (\gamma^2 + k^2)u_2 = 0$$

$$u_i = e^{\delta x}$$

$$\delta_1^2 + 2ik\delta_1 + (\alpha^2 - k^2) = 0$$

$$\delta_1 = -ik \pm i\alpha$$

$$\delta_2^2 + 2ik\delta_2 - (\gamma^2 - k^2) = 0$$

$$\delta_2 = -ik \pm \gamma$$

$$u_1 = Ae^{-ikx+i\alpha x} + Be^{-ikx-i\alpha x}$$

$$u_2 = Ce^{-ikx+\gamma x} + De^{-ikx-\gamma x}$$

The Kronig-Penney Model

- Continuity boundary condition

$$u_1(0) = u_2(0) \longrightarrow A + B = C + D$$

$$\left.\frac{du_1}{dx}\right|_{x=0} = \left.\frac{du_2}{dx}\right|_{x=0} \longrightarrow \begin{aligned} &-i(k-\alpha)A - i(k+\alpha)A \\ &= -(ik-\gamma)C - (ik+\gamma)D \end{aligned}$$

- Periodic boundary condition

$$u_1(a) = u_2(a) = u_2(-d) \longrightarrow \begin{aligned} &Ae^{-i(k-\alpha)a} + Be^{-i(k+\alpha)a} \\ &= Ce^{(ik-\gamma)d} + De^{(ik+\gamma)d} \end{aligned}$$

$$\left.\frac{du_1}{dx}\right|_{x=a} = \left.\frac{du_2}{dx}\right|_{x=-d} \longrightarrow \begin{aligned} &-i(k-\alpha)Ae^{-i(k-\alpha)a} - i(k+\alpha)Be^{-i(k+\alpha)a} \\ &= -(ik-\gamma)Ce^{(ik-\gamma)d} - (ik+\gamma)De^{(ik+\gamma)d} \end{aligned}$$

The Kronig-Penney Model

- In the matrix form:

$$\begin{bmatrix} 1 & 1 & -1 & -1 \\ -i(k-\alpha) & -i(k+\alpha) & (ik-\gamma) & (ik+\gamma) \\ e^{-i(k-\alpha)a} & e^{-i(k+\alpha)a} & -e^{(ik-\gamma)d} & -e^{(ik+\gamma)d} \\ -i(k-\alpha)e^{-i(k-\alpha)a} & -i(k+\alpha)e^{-i(k+\alpha)a} & -(ik-\gamma)e^{(ik-\gamma)d} & -(ik+\gamma)e^{(ik+\gamma)d} \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = 0$$

- This requires the determinant of the large square matrix to vanish:

$$\det[coeff.] = 0$$

The Kronig-Penney Model

$$\frac{\gamma^2-\alpha^2}{2\alpha\gamma}\sinh(\gamma d)\sin(\alpha a)+\cosh(\gamma d)\cos(\alpha a)=\cos[k(a+d)]$$

- To simplify this, we take the limit $V \to \infty$ and $d \to 0$ in such a manner that $Vd = Q$.

$$\cosh(\gamma d)\to 1 \quad , \quad \frac{\sinh(\gamma d)}{\gamma d}\to 1$$

$$\frac{\gamma^2 d}{2\alpha}\sin(\alpha a)+\cos(\alpha a)=\cos(ka)$$

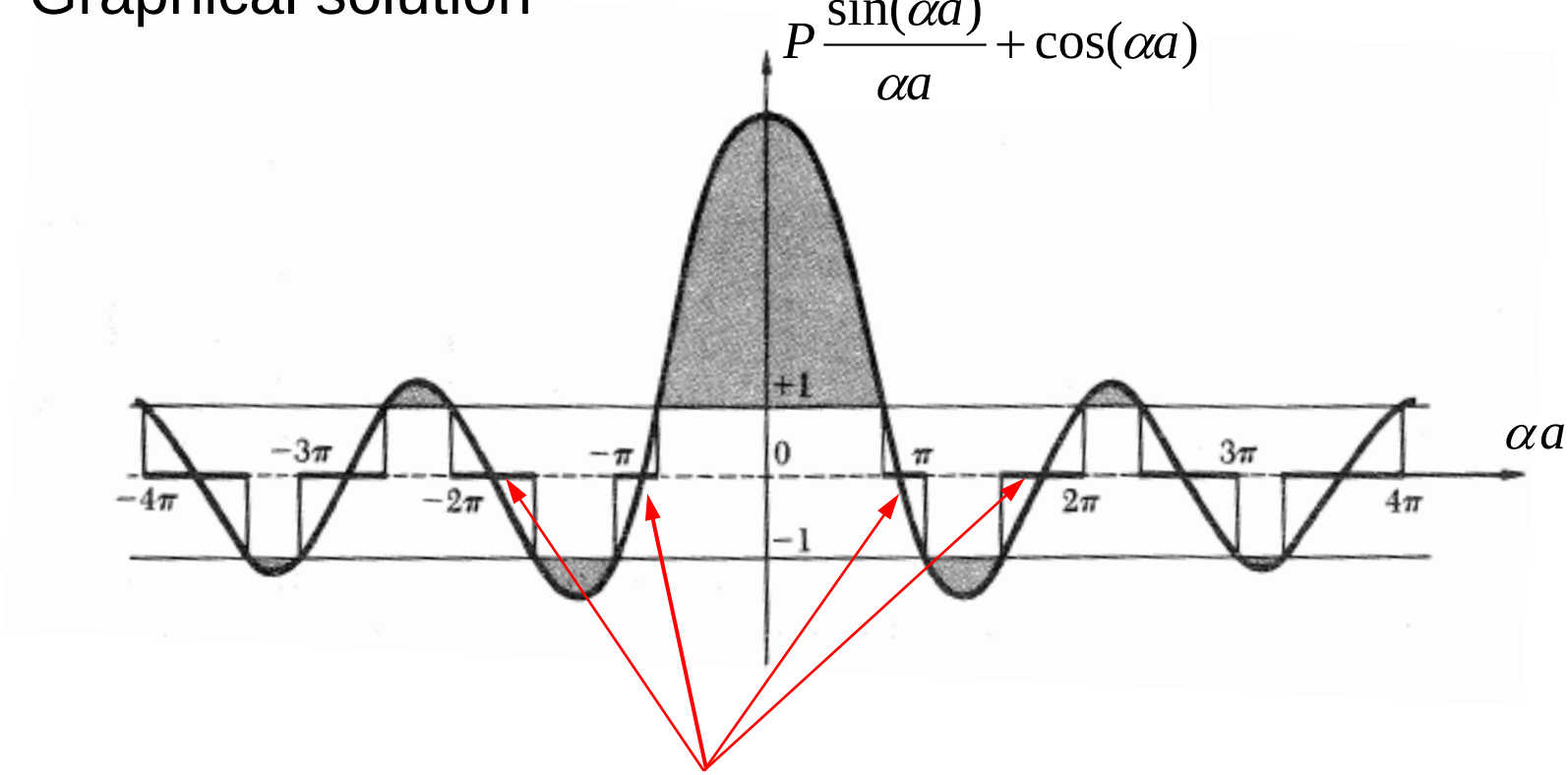
Function of the energy E

Depends only on the Wavevector k

- The wavevector *k* is real only for certain allowed ranges of *E*.

The Kronig-Penney Model

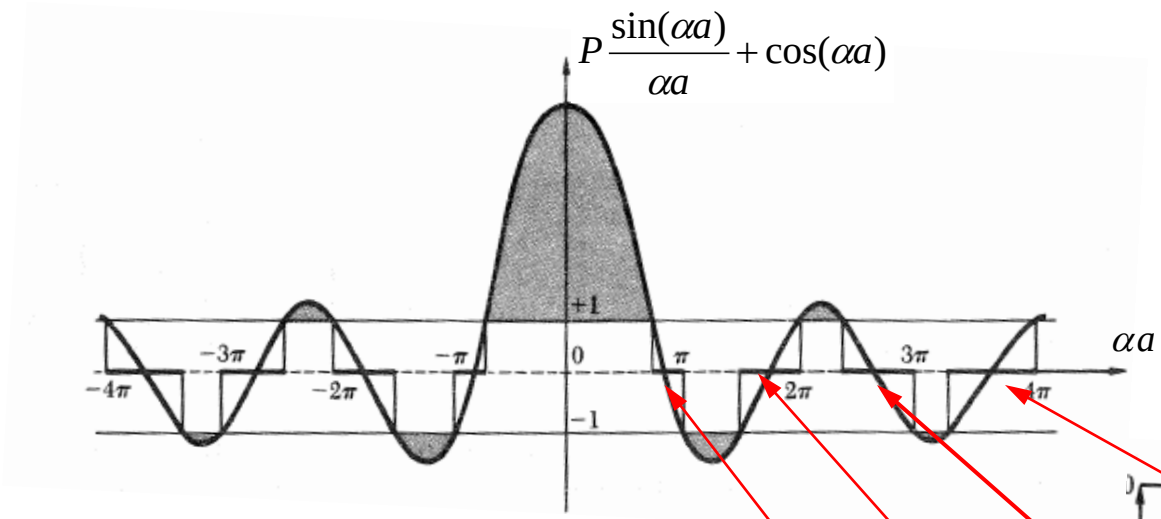
- Graphical solution

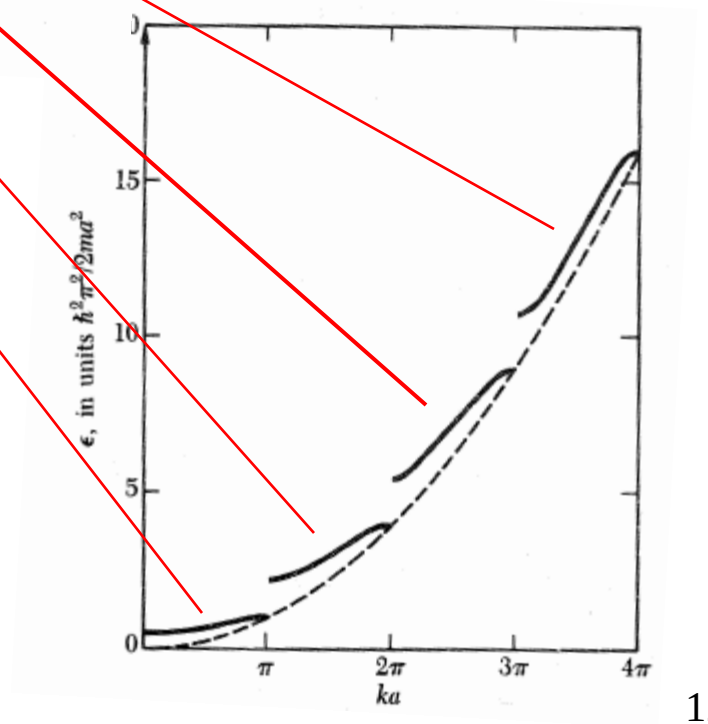


Regions where the equation is satisfied, hence where the solution exists.

- In general, as the energy increases (αa increases), each successive band gets wider, and each successive gap gets narrower.

Band Structure

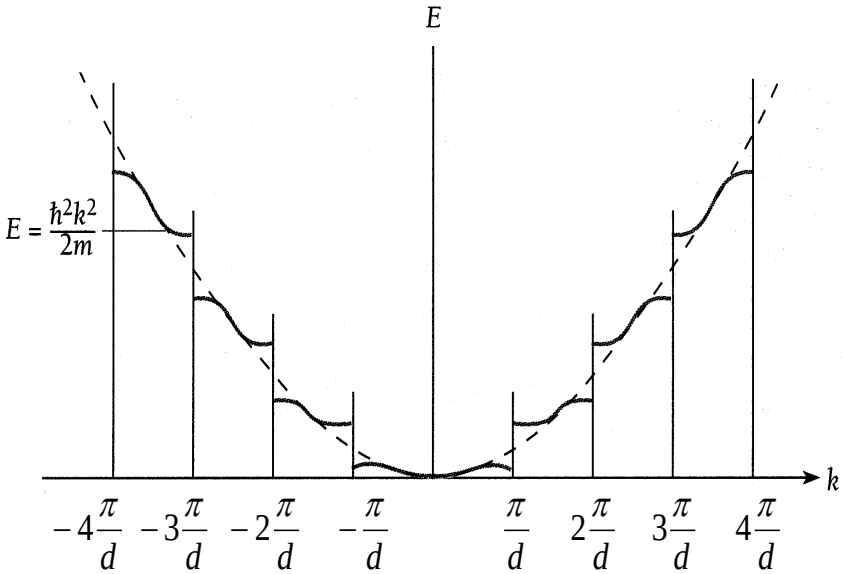




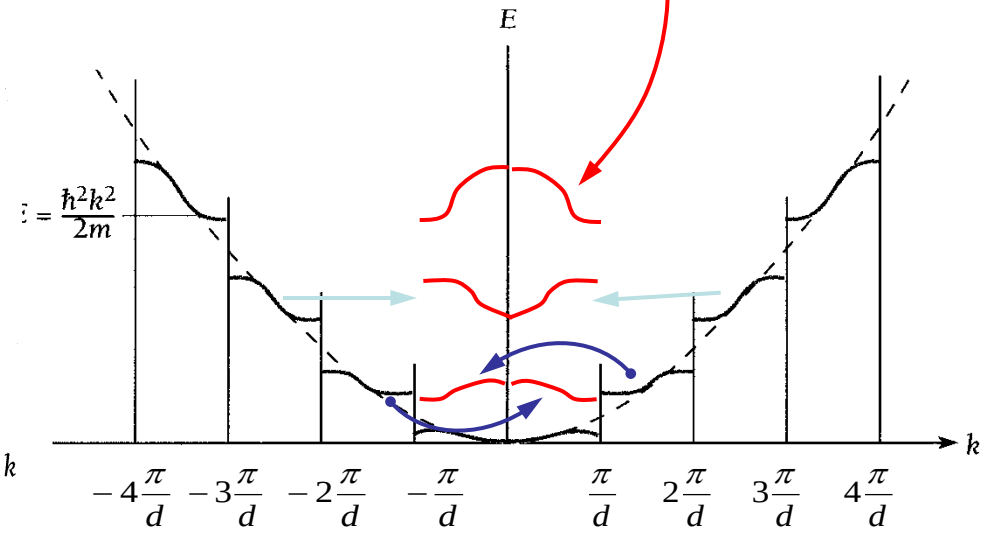
- Note:

$$\alpha^2 = \frac{2mE}{\hbar^2} \Rightarrow E = \frac{\alpha^2\hbar^2}{2m} = f(ka)$$

As energy increases, the bands get WIDER and the gaps get NARROWER



Extended zone scheme



Reduced zone scheme

Band Structure of Silicon

- In 3D, k can be along many different directions.