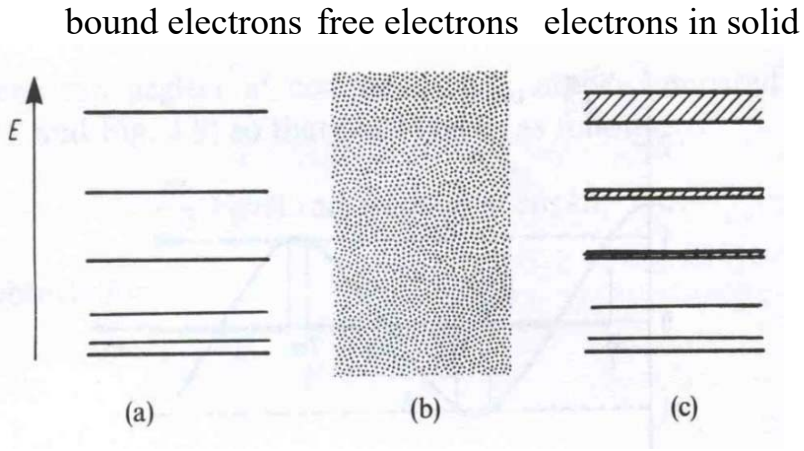
Chapter 7. Energy Bands

Energy bands in solids

- In free electron model, electrons occupy positive energy levels from E=0 to higher values of energy. They are valence electron so called “Valence band”.
- The free electrons and other electrons can be thought as belonging to the whole crystal → band rather than the discrete energy level
- There are three ways to look at bands.
  1. Bands resulting from a periodic potential.
  2. Bands resulting from interacting atoms. <tight binding interaction>
  3. Bands resulting from periodic perturbation of free electrons.

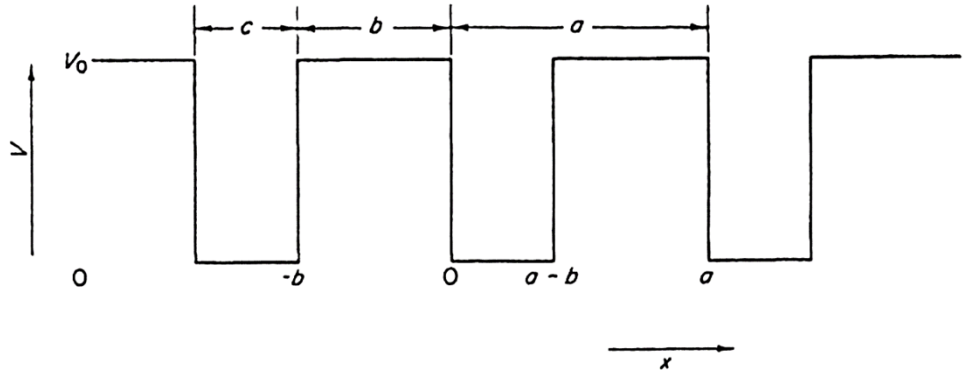
     <weak binding approximation>

- The energy gap can be though of as energy required to remove an electron from the chemical bond in the material and to allow it to be free enough to move through the material under electric field.
- In a crystal, there is a periodic potential, which results in a series of allowed energy separated by energy gap.



One-dimensional periodic potential

- Square-well potential arranged periodically in one-dimension



- From Schrodinger equation in two regions where V=V_o and V=0

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

For $V = 0$ $(x = 0 \sim (a - b))$

$$\psi_0 = Ae^{+i\beta x} + Be^{-i\beta x}$$

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

For $V = V_0$ and $E < V_0$ $(x = -b \sim 0)$

$$\psi_V = Ce^{+\alpha x} + De^{-\alpha x}$$

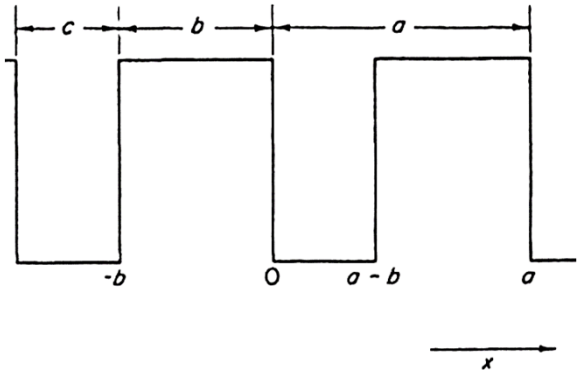
$$\alpha = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

One-dimensional periodic potential

[B.C.] Continuity of ψ_0 and ψ_V at $x = 0$

$$\psi_0(0) = \psi_V(0) \quad \text{----------} \quad (1)$$

$$\left.\frac{\partial \psi_0}{\partial x}\right|_{x=0} = \left.\frac{\partial \psi_V}{\partial x}\right|_{x=0} \quad \text{----------} \quad (2)$$



Since $V(x + a) = V(x)$, Schrodinger equation is also periodic.
For $\psi(x + a) = \psi(x)$, $\psi(x + a) = \mathrm{e}^{-ika}\,\psi\,(x)$
At $x = -b$ and $x = (a - b)$, $\psi(-b) = \mathrm{e}^{-ika}\,\psi\,(a - b)$

[B.C.] Continuity of ψ_0 and ψ_V at $x = -b$ and $x = (a - b)$

$$\psi_V(-b) = exp(-ikx)\psi_0(a - b) \quad \text{----------} \quad (3)$$

$$\left.\frac{\partial \psi_V}{\partial x}\right|_{x=-b} = exp(-ikx)\left.\frac{\partial \psi_0}{\partial x}\right|_{x=(a-b)} \quad \text{----------} \quad (4)$$

One-dimensional periodic potential

From (1), (2), (3), and (4)

(a) $A + B = C + D$

(b) $i\beta(A - B) = \alpha(C - D)$

(c) $Cexp(-\alpha b) + Dexp(\alpha b)$
$= exp(-ika)[Aexp\{i\beta(a - b)\} + Bexp\{-i\beta(a - b)\}]$

(d) $\alpha Cexp(-\alpha b) - \alpha Dexp(\alpha b)$
$= exp(-ika)i\beta[Aexp\{i\beta(a - b)\} - Bexp\{-i\beta(a - b)\}]$

→ Energy restricting condition

$$\cos k\,a = \{(\alpha^2 - \beta^2)/2\alpha\beta\}\sinh\alpha\,b\sin\beta\,(a - b) + \cosh\alpha\,b\cos\beta\,(a - b)$$

This oscillating function with increasing energy must lie between +1 and -1.

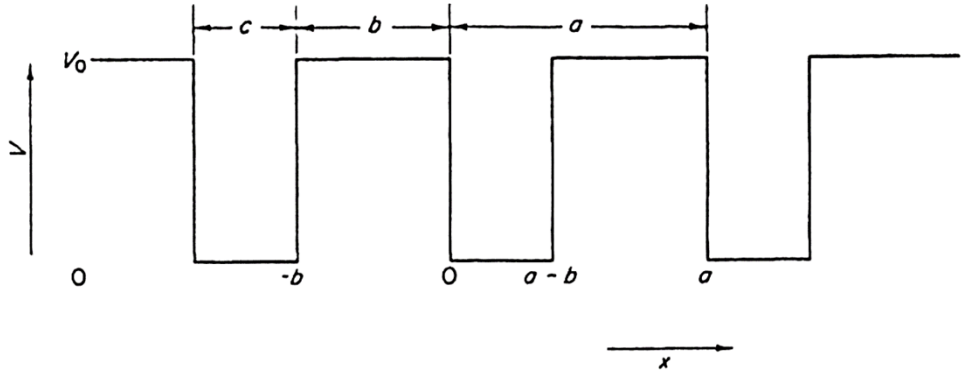
- The certain range of energy (allowed energy values), separated by ranges of energy for which the value of the function lies outside the range of +1 to -1 (forbidden energy values)

Kronig-Penney approximation

Take limit of $b \to 0,\ V_0 \to \infty$

so as to maintain

$$P = \left(\frac{ma}{\hbar^2}\right) bV_0 = \text{constant}$$



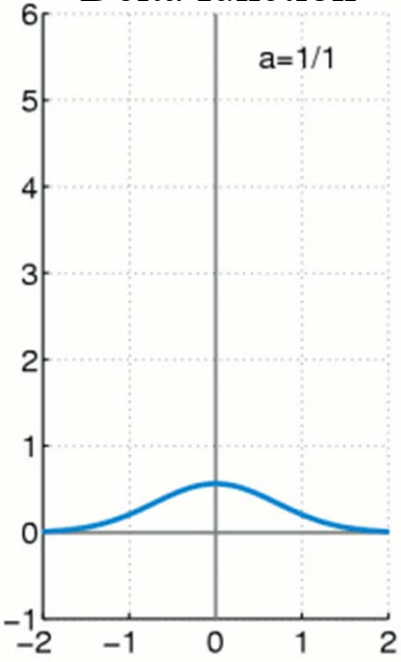
*This is equivalent to maintaining constant barrier area while proceeding to the limit in which the square potential wells are replaced by delta function.

then, $(V_0 - E) \to V_0$, $\sinh \alpha b \to \alpha b$, $\cosh \alpha b \to 1$

$$\cos ka = P\frac{\sin \beta a}{\beta a} + \cos \beta a$$

note: k is a real constant so that $-1 < \cos ka < +1$

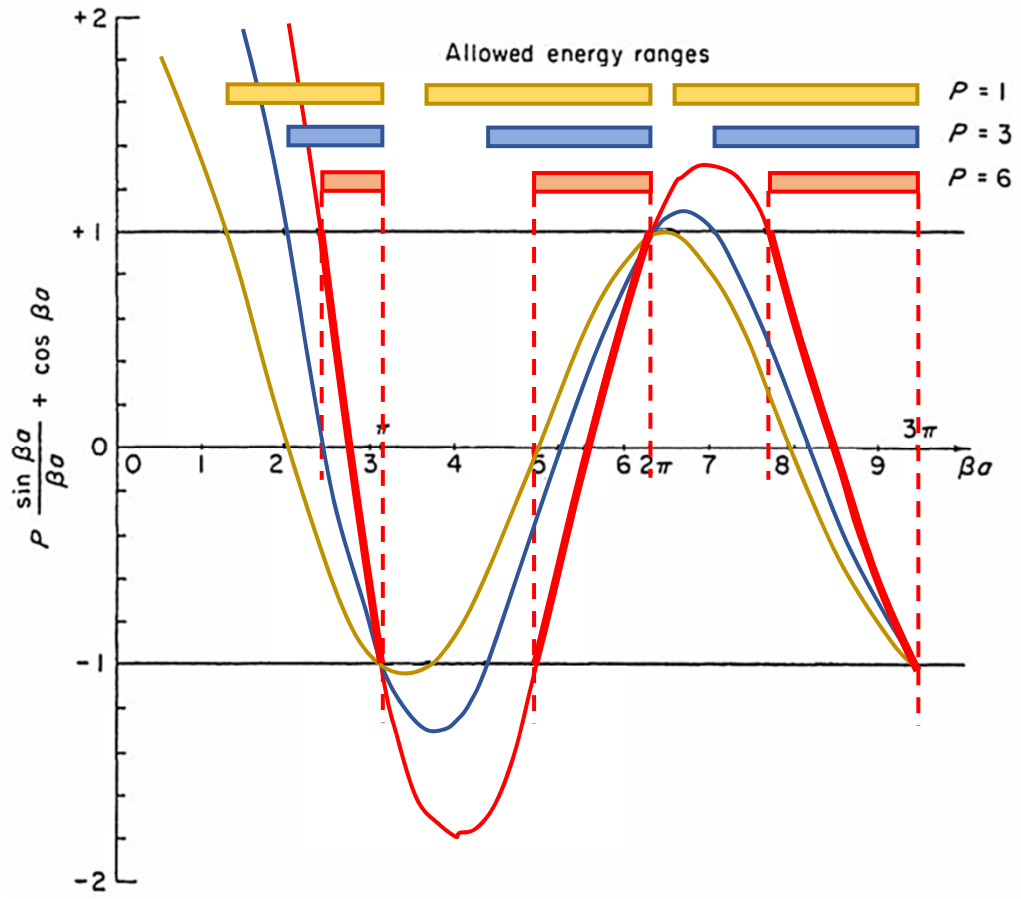
Delta function



Kronig-Penney approximation

$$-1 < P\frac{\sin \beta a}{\beta a} + \cos \beta a < 1 \quad : \text{ allowed}$$

elsewhere : not allowed; forbidden



Kronig-Penney approximation

(1) The points of transition between allowed and forbidden bands occur at $\beta a = n\pi$

$$\cos ka = \cos \beta a \qquad \therefore k = \frac{n\pi}{a},\ n\frac{\lambda}{2} = a$$

At these value of k, we have standing waves.

$n\lambda = 2a$: correspond to 1-D Bragg reflection condition.

This can be understood by the periodic nature of the crystal.

An allowed energy band terminates at a condition correspond to a Bragg reflection.

Electron waves with $k = n\frac{\pi}{a}$ are not able to propagate in the crystal, and hence correspond physically to forbidden energies for the electrons.

Kronig-Penney approximation

(2) Allowed energy band width increases and forbidden band gap width decreases with increasing energy

For very high energies, all energies are allowed.

Lower energy bands = tightly bound electrons to isolated atoms

Inner shell electrons have narrower energy bands than outer shell electrons.

(3) Width of the bands is a function of P (potential area) and a measure of binding tightness. (Width of bands decreases as P increases.)

$$P = \left(\frac{ma}{\hbar^2}\right) bV_0$$

If $P \sim 0$, free electron and continuum of allowed energies

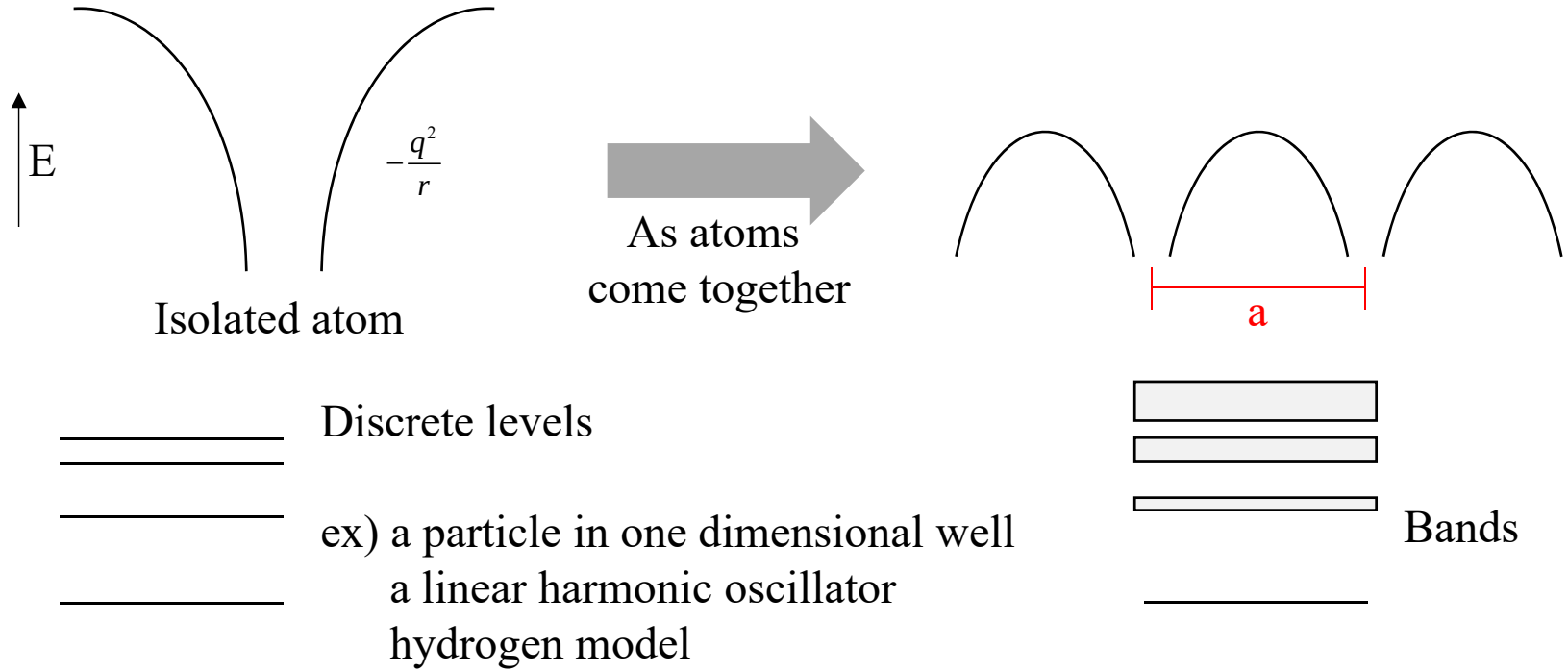
If $P \rightarrow \infty$, no interaction between potential wells

So, discrete energy levels (no bands)

If $0 < P < \infty$, allowed band width decreases as P increases.

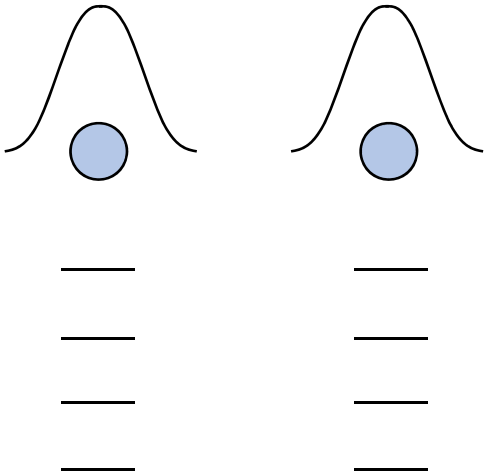
(more tightly bound electrons, less interaction between electrons, smaller allowed band width)

Tight binding model

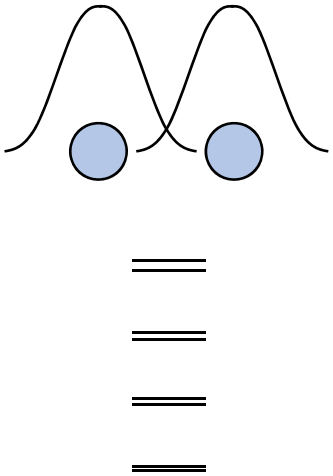


- Electrons in a crystal effectively belong to the whole crystal (solid).
- No two electrons can have same energy. Therefore, for N atoms, energy level breaks up into slightly different levels.

Tight binding model



Isolated atoms
Less tight
Less interaction bet/n atoms
Less overlaps bet/n wave functions
Discrete energy levels



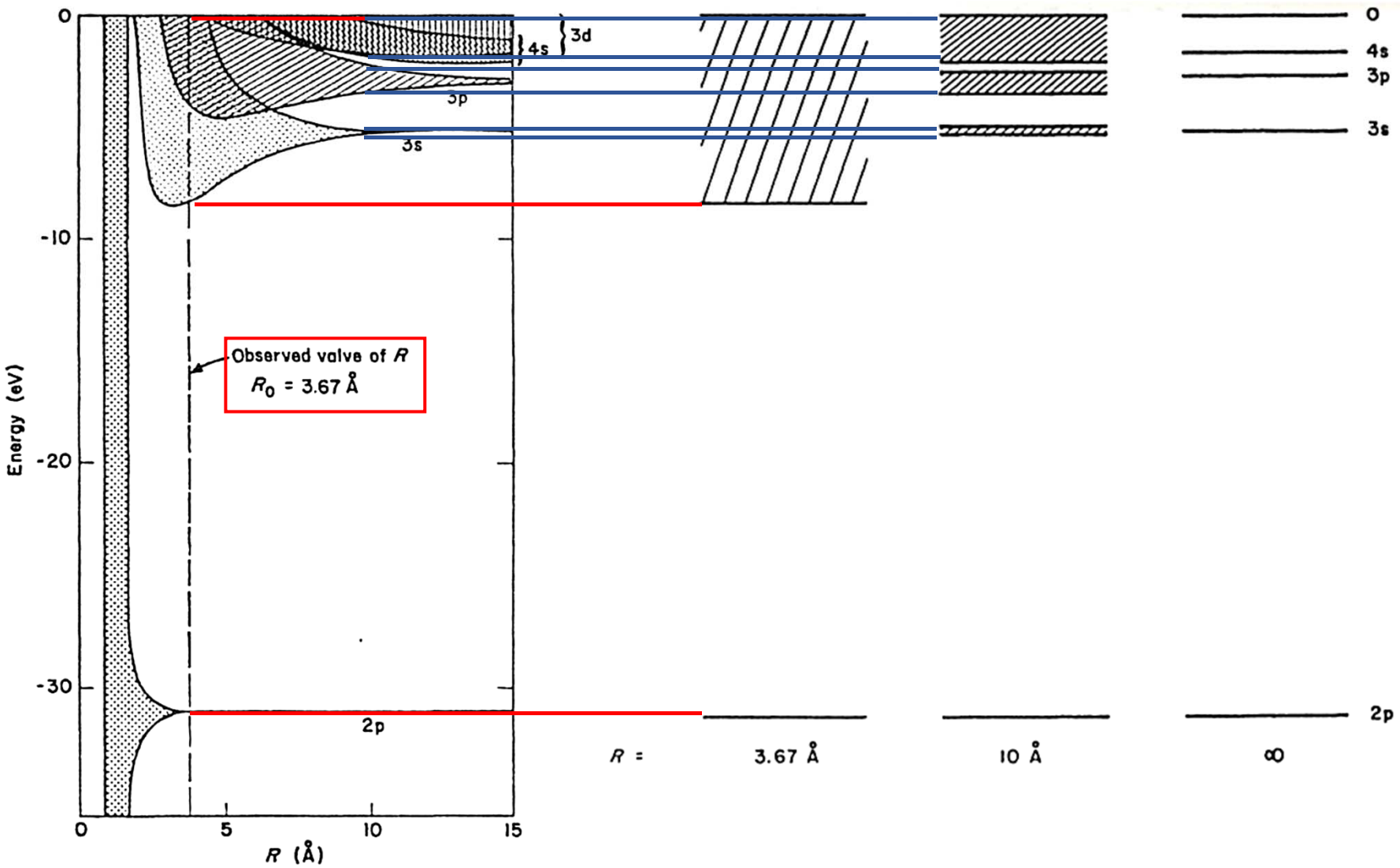
A linear combination of atomic wave functions, located on a periodic lattice with a periodic potential energy
→ solve Schrodinger eq.

N atoms

N atoms → N different levels
Belong to the whole crystal

Tight binding model

- Na : $1s^2 2s^2 2p^6 3s$



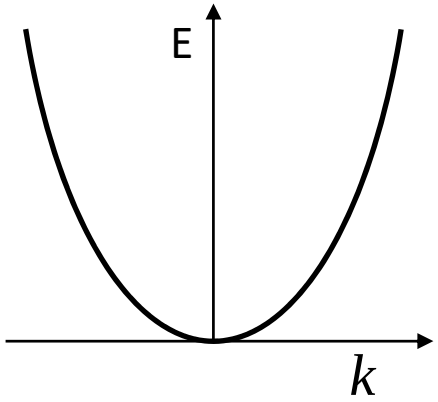
Weak binding model

- Free electrons superimposed by a small periodic potential on the free electrons (introduce a small periodic potential as a perturbation in the Schrodinger equation)

For free electrons

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

k : all values



In a small periodic potential,

- Electron waves with particular value of k cannot propagate through the crystal because of the Bragg reflection. $\rightarrow v_g = 0$
- Waves with $k = \frac{n\pi}{a}$ is standing waves.
- Opening up of the energy gaps at $k = \frac{n\pi}{a}$

Weak binding model

At $k = \frac{\pi}{a}$, two wave functions for standing waves:

$$\psi_+ \propto exp\left(\frac{i\pi x}{a}\right) + exp\left(-\frac{i\pi x}{a}\right) = 2\cos\frac{\pi x}{a}$$

$$\psi_- \propto exp\left(\frac{i\pi x}{a}\right) - exp\left(-\frac{i\pi x}{a}\right) = 2\sin\frac{\pi x}{a}$$

The electron waves with specific energies (band gap) cannot propagate through the crystal along the crystalline direction (*k*: reciprocal lattice).

Energy gap ~ $V(|\psi_+|^2) - V(|\psi_-|^2)$