Part I Fundamentals

Electron Theory : Matter Waves

Electromagnetic Theory : Maxwell Equations

(Electrons in Solids, 3rd Ed., R. H. Bube)

3. The Schrödinger Equation

3.1 The Time-Independent Schrödinger Equation

- Time-independent Schrödinger equation: *a vibration equation*

$$\boxed{\nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0}$$

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$$

3.2 The Time-Dependent Schrödinger Equation

- Time-dependent Schrödinger equation: *a wave equation*

$$\boxed{\nabla^2\Psi - \frac{2mV}{\hbar^2}\Psi - \frac{2mi}{\hbar}\frac{\partial\Psi}{\partial t} = 0}$$

$$\Psi(x,y,z,t) = \psi(x,y,z)\cdot e^{i\omega t}$$

4. Solution of Schrödinger Equation

4.1 Free Electrons

Suppose electrons propagating freely to the positive *x*-direction,

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \quad \longrightarrow \quad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0$$

$V = 0$ (potential-free space)

$$\psi(x) = Ae^{i\alpha x} \quad \text{because} \quad \Psi(x) = Ae^{i\alpha x}\cdot e^{i\omega t}$$

$$\alpha = \sqrt{\frac{2m}{\hbar^2}E} = k \qquad |\mathbf{k}| = \frac{2\pi}{\lambda} \quad \longrightarrow \quad E = \frac{\hbar^2}{2m}k^2$$

“energy continuum”

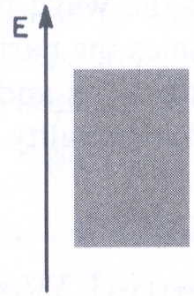


Figure 4.1. Energy continuum of a free electron (compare with Fig. 4.3).

4. Solution of Schrödinger Equation

4.2 Electron in a Potential Well (Bound Electron)

Suppose the electron can move freely between two infinitely high potential barriers

$\psi = 0$ $\qquad\qquad$ $\psi = 0$

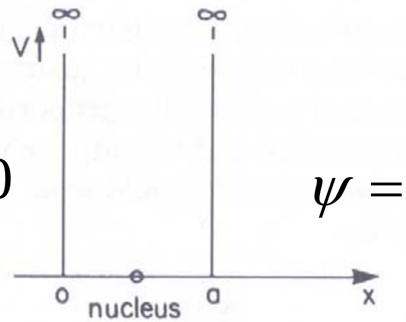


Figure 4.2. One-dimensional potential well. The walls consist of infinitely high potential barriers.

Within 1-dim potential well

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0$$

The solution $\psi = Ae^{i\alpha x} + Be^{-i\alpha x}$ where $\alpha = \sqrt{\frac{2m}{\hbar^2}E}$

$$E_n = \frac{\hbar^2}{2m}\alpha^2 = \frac{\hbar^2\pi^2}{2ma^2}n^2 \quad ,$$

$$n = 1,2,3,....$$

"energy quantization"

(If n = 0, no wave function !)

"energy levels"

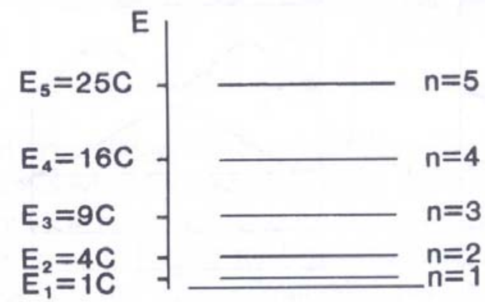


Figure 4.3. Allowed energy values of an electron that is bound to its atomic nucleus. E is the excitation energy in the present case. $C = \hbar^2\pi^2/2ma^2$, see (4.18). (E_1 is the zero-point energy.)

4. Solution of Schrödinger Equation

4.2 Electron in a Potential Well (Bound Electron)

The wave function : $\psi = 2Ai \cdot \sin \alpha x \quad \psi^* = 2Ai \cdot \sin \alpha x$ $\qquad \alpha = n\dfrac{\pi}{a}$

$$\psi\psi^* = 4A^2 \sin^2 \alpha x$$

$$\int_0^a \psi\psi^* d\tau = 4A^2 \int_0^a \sin^2(\alpha x)dx = \frac{4A^2}{\alpha}[-\frac{1}{2}\sin \alpha x \cos \alpha x + \frac{\alpha x}{x}]_0^a = 1 \qquad A = \sqrt{\frac{1}{2a}}$$

Condition for the orbit stability

$$2\pi r = n\lambda$$

$$r = \frac{\lambda}{2\pi} n$$

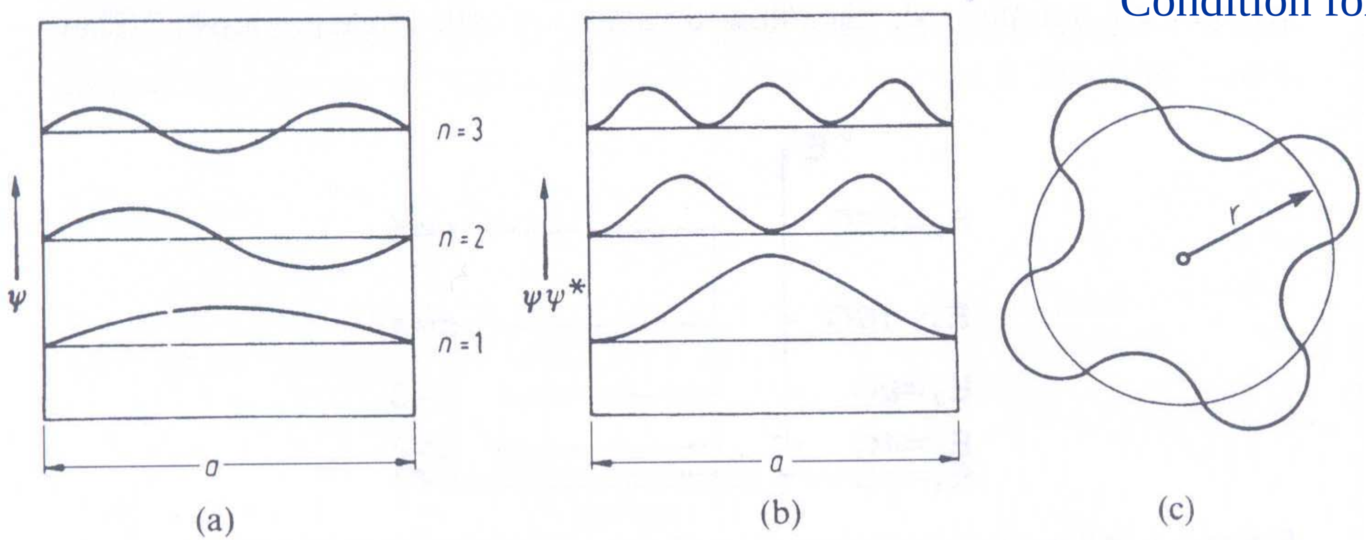


Figure 4.4. (a) ψ function and (b) probability function $\psi\psi^*$ for an electron in a potential well for different n-values. (c) Allowed electron orbit of an atom.

4.2 Electron in a Potential Well (Bound Electron)

For a hydrogen atom,
Coulombic potential

$$E = \frac{me^4}{2(4\pi\varepsilon_0\hbar)^2}\frac{1}{n^2} = -13.6\cdot\frac{1}{n^2}(eV)$$

$$V = -\frac{e^2}{4\pi\varepsilon_0 r}$$

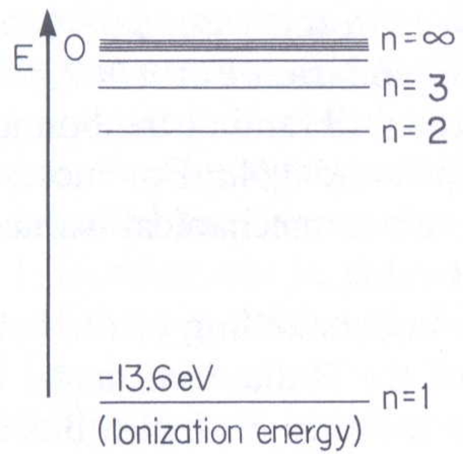


Figure 4.5. Energy levels of atomic hydrogen. E is the binding energy.

In 3-dim potential well
(electron in a box)

$$E_n = \frac{\hbar^2\pi^2}{2ma^2}(n_x^{\,2} + n_y^{\,2} + n_z^{\,2})$$

The same energy but different quantum numbers: “degenerate” states

4. Solution of Schrödinger Equation

4.3 Finite Potential Barrier (Tunnel Effect)

Suppose electrons propagating in the positive x-direction encounter a potential barrier V_0 (> total energy of electron, E)

- Region (I) $x < 0$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0$$

- Region (II) $x > 0$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0$$

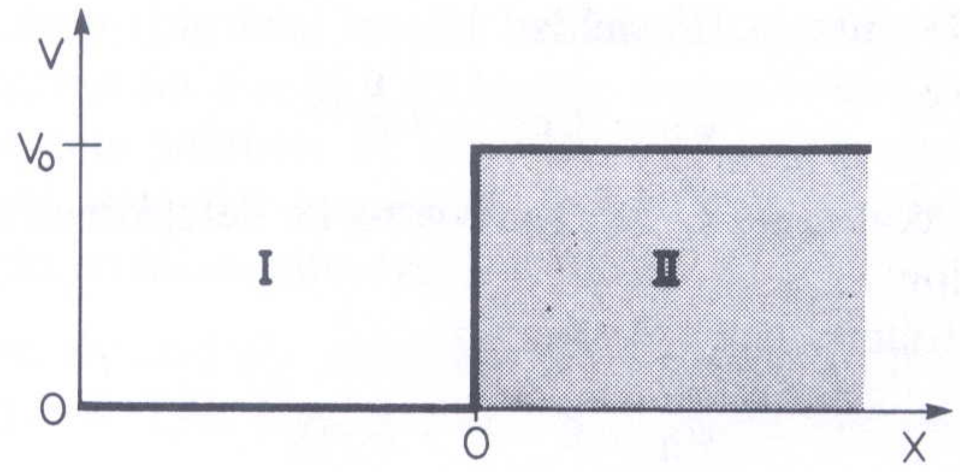


Figure 4.6. Finite potential barrier.

The solutions (see Appendix 1)

$$\psi_I = Ae^{i\alpha x} + Be^{-i\alpha x} \qquad \alpha = \sqrt{\frac{2m}{\hbar^2}E}$$

$$\psi_{II} = Ce^{i\beta x} + De^{-i\beta x} \qquad \beta = \sqrt{\frac{2m}{\hbar^2}(E - V_0)}$$

4.3 Finite Potential Barrier (Tunnel Effect)

Since E - V_0 is negative, $\beta = \sqrt{\frac{2m}{\hbar^2}(E - V_0)}$ becomes imaginary.

To prevent this, define a new parameter, $\gamma = i\beta$

Thus, $\gamma = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$, and $\psi_{II} = Ce^{i\beta x} + De^{-i\beta x} \longrightarrow \psi_{II} = Ce^{\gamma x} + De^{-\gamma x}$

Determination of C or D by B.C. For x $\rightarrow \infty$ $\psi_{II} = C \cdot \infty + D \cdot 0$

Since $\Psi\,\Psi^*$ can never be lager than 1, $\psi_{II} \rightarrow \infty$ is no solution, and thus,

$C \rightarrow 0$, which reveals Ψ-function decreases in Region II

$$\psi_{II} = De^{-\gamma x}$$

Using (A.27) + (4.39) in textbook, the damped wave becomes

$$\Psi = De^{-\gamma x} \cdot e^{i(\omega t - kx)}$$

4. Solution of Schrödinger Equation

4.3 Finite Potential Barrier (Tunnel Effect)

As shown by the dashed curve in Fig 4.7, a potential barrier is penetrated by electron wave : ***Tunneling***

* For the complete solution,

(1) At $x = 0$ $\quad \psi_I = \psi_{II}$: continuity of the function

$$Ae^{i\alpha x} + Be^{-i\alpha x} = De^{i\gamma x} \longrightarrow A + B = D$$

(2) At $x = 0$ $\quad \frac{d\psi_I}{dx} \equiv \frac{d\psi_{II}}{dx}$: continuity of the slope of the function

$$Ai\alpha e^{i\alpha x} - Bi\alpha e^{-i\alpha x} = -\gamma De^{-\gamma x}$$

With $x = 0$ $\quad Ai\alpha - Bi\alpha = -\gamma D$

Consequently, $\quad A = \frac{D}{2}(a + i\frac{\gamma}{\alpha})$

$$B = \frac{D}{2}(1 - i\frac{\gamma}{\alpha})$$

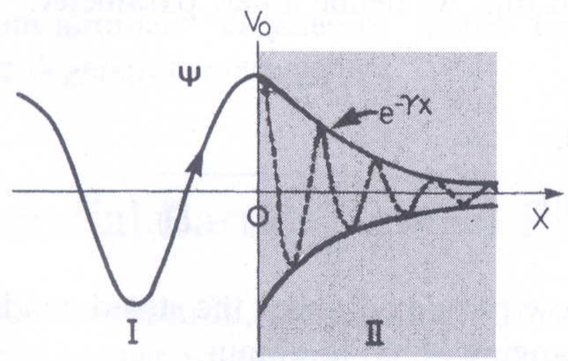


Figure 4.7. ψ-function (solid line) and electron wave (dashed line) meeting a finite potential barrier.

4.3 Finite Potential Barrier (Tunnel Effect)

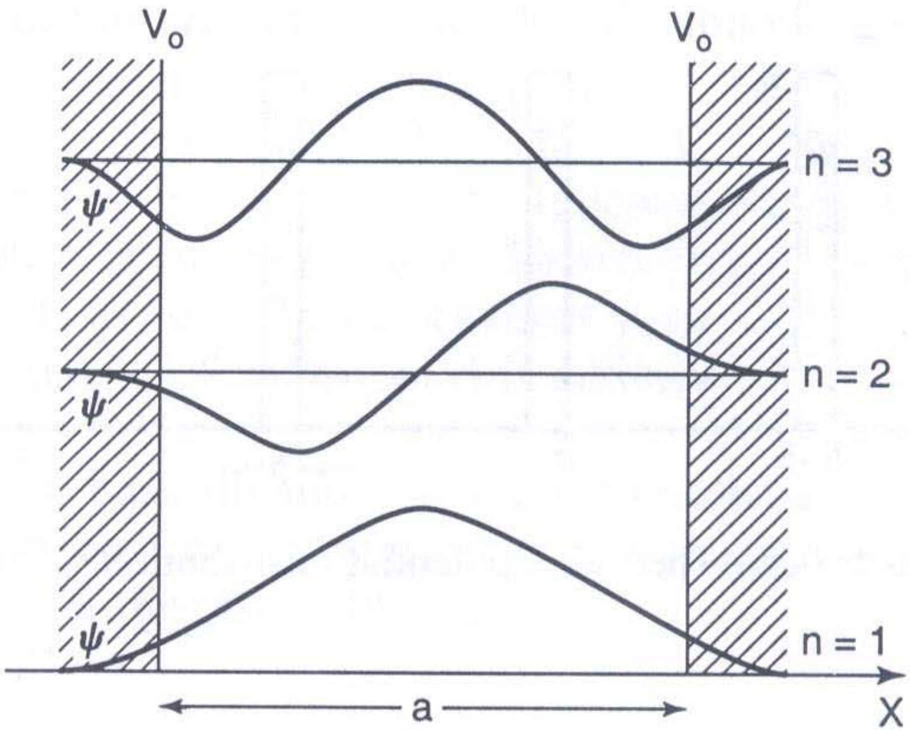


Figure 4.8. Square well with finite potential barriers. (The zero points on the vertical axis have been shifted for clarity.)

4.4 Electron in a Periodic Field of Crystal (the Solid State)

The behavior of an electron in a crystal → A motion through periodic repetition of potential well

well length : a

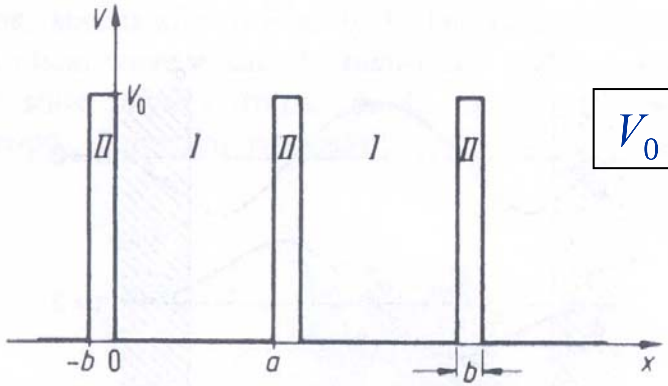
barrier height : V_0

barrier width : b

This model does not consider

i) the inner electrons are more strongly bound to core

ii) the individual potentials form each lattice overlap



$\boxed{V_0 > E}$

Figure 4.9. One-dimensional periodic potential distribution (simplified) (**Kronig-Penney model**).

Region (I)

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0$$

Region (II)

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V_0)\psi = 0$$

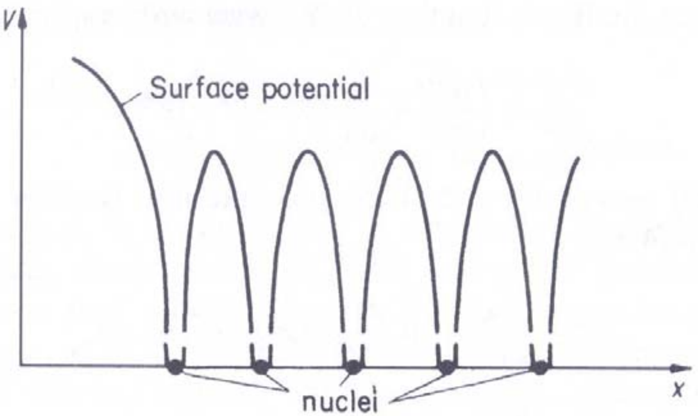


Figure 4.10. One-dimensional periodic potential distribution for a crystal (**muffin tin potential**).

4.4 Electron in a Periodic Field of Crystal (the Solid State)

(Continued) For abbreviation

$$\alpha^2 = \frac{2m}{\hbar^2}E \qquad \gamma^2 = \frac{2m}{\hbar^2}(V_0 - E)$$

The solution of this type equation (not simple but complicate)

$$\psi(x) = u(x)\cdot e^{ikx}$$

(*Bloch function*)

Where, u(x) is a periodic function which possesses the periodicity of the lattice in the x-direction

The final solution of the Schrödinger equations;

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

where $P = \dfrac{maV_0 b}{\hbar^2}$

4. Solution of Schrödinger Equation

4.4 Electron in a Periodic Field of Crystal (the Solid State)

Mathematical treatment for the solution : ***Bloch function***

$$\psi(x) = u(x) \cdot e^{ikx}$$

Differentiating the Bloch function twice with respect to x

$$\frac{d^2\psi}{dx^2} = \left(\frac{d^2u}{dx^2} + \frac{du}{dx}2ik - k^2u\right)e^{ikx}$$

Then the Schrödinger equations in two regions become *equations of damped vibrations*

$$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (k^2 - \alpha^2)u = 0 \quad \textbf{(I)}$$

$$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (k^2 + \gamma^2)u = 0 \quad \textbf{(II)}$$

The solutions of (I) and (II)

$$u = e^{-ikx}(Ae^{i\alpha x} + Be^{-i\alpha x}) \quad \textbf{(I)}$$

$$u = e^{-ikx}(Ce^{-\gamma x} + De^{\gamma x}) \quad \textbf{(II)}$$

4. Solution of Schrödinger Equation

4.4 Electron in a Periodic Field of Crystal (the Solid State)

(Continued) From continuity of the function ψ *and* $\dfrac{d\psi}{dx}$

$$A + B = C + D$$

du/dx values for equations (I) & (II) are identical at $x = 0$

$$A(i\alpha - ik) + B(-i\alpha - ik) = C(\gamma - ik) + D(\gamma - ik)$$

Further, ψ and u is continuous at $x = a + b \rightarrow$ Eq. (I) at $x = 0$ must be equal to Eq. (II) at $x = a + b$, more simply, Eq. (I) at $x = a$ is equal to Eq. (II) at $x = -b$

$$Ae^{(i\alpha - ik)a} + Be^{(-i\alpha - ik)a} = Ce^{(ik+\gamma)b} + De^{(ik-\gamma)b}$$

Finally, *du/dx* is periodic in $a + b$

$$Ai(\alpha - k)e^{ia(\alpha-k)} - Bi(\alpha + k)e^{-ia(\alpha+k)} = -C(\gamma + ik)e^{(ik+\gamma)b} + D(\gamma - ik)e^{(ik-\gamma)b}$$

limiting conditions : using 4.57- 4.60 in text and eliminating the four constant A-D, and using some Euler eq.(see Appendix 2)

$$\frac{\gamma^2 - \alpha^2}{2\alpha\gamma}\sin(\gamma b)\cdot\sin(\alpha a) + \cos(\gamma b)\cdot\cos(\alpha a) = \cos k(a+b)$$

4.4 Electron in a Periodic Field of Crystal (the Solid State)

If V_0 is very large, then E in 4.47 is very small compared to V_0 so that

$$\gamma = \sqrt{\frac{2m}{\hbar^2}}\sqrt{V_0} \quad \rightarrow \quad \gamma b = \sqrt{\frac{2m}{\hbar^2}}\sqrt{(V_0 b)b}$$

Since $V_0 b$ has to remain finite, and as $b \rightarrow 0$, γb becomes very small.

For a small γb, we obtain (see tables of the hyperbolic function)

$$\cosh(\gamma b) \approx 1 \quad and \quad \sinh(\gamma b) \approx \gamma b$$

Finally, neglect α^2 compared to γ^2 and, b compared to a so that 4.61 reads as follow

$$\frac{m}{\alpha\hbar^2} V_0 b \sin \alpha a + \cos \alpha a = \cos ka$$

Let $P = \dfrac{maV_0 b}{\hbar^2}$, then

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

4. Solution of Schrödinger Equation

4.4 Electron in a Periodic Field of Crystal (the Solid State)

“Electron that moves in a periodically varying potential field can only occupy certain allowed energy zone”

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

$$P = \frac{maV_0 b}{\hbar^2}$$

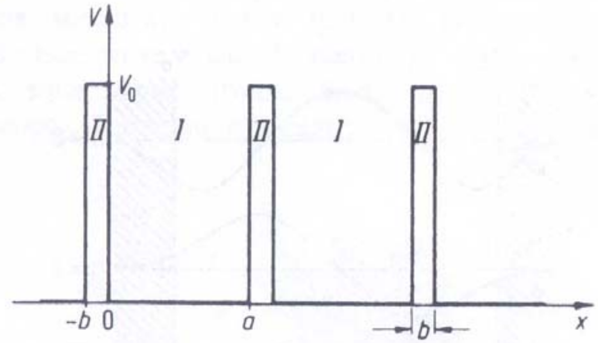
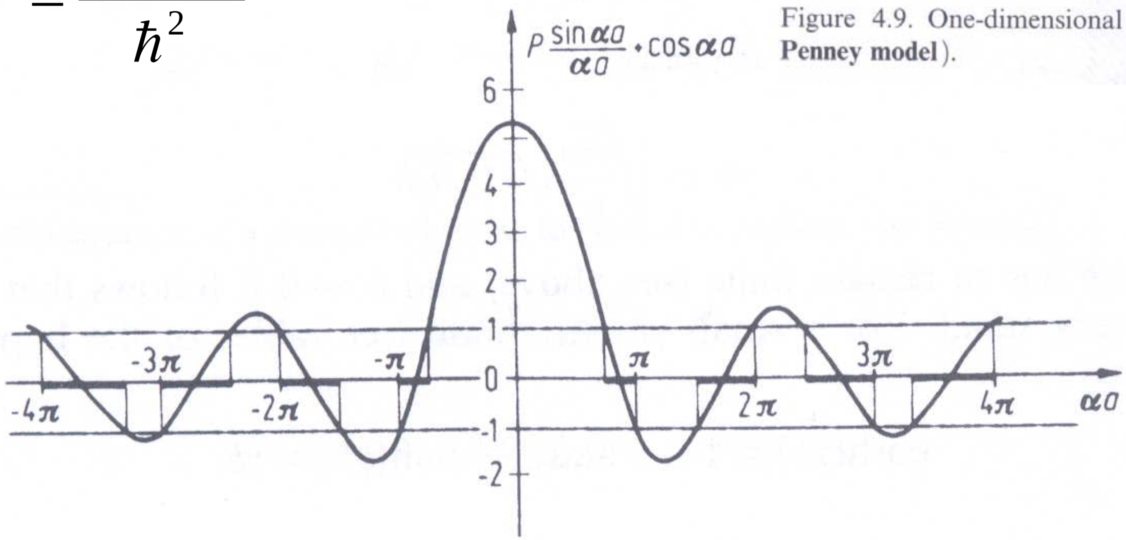


Figure 4.9. One-dimensional periodic potential distribution (simplified) (**Kronig-Penney model**).

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



With increasing αa, the disallowed (or forbidden) bands become narrower.

Figure 4.11. Function $P(\sin \alpha a/\alpha a) + \cos \alpha a$ versus αa. P was arbitrarily set to be $(3/2)\pi$.

4.4 Electron in a Periodic Field of Crystal (the Solid State)

The size of the allowed and forbidden energy bands varies with *P*.

For special cases, since $P = \dfrac{maV_0 b}{\hbar^2}$

(a) If the potential barrier strength, $V_0 b$ is large, *P* is also large and the curve on Fig 4.11 steeper. The allowed band are narrow.

(b) If $V_0 b$ and *P* are small, the allowed band becomes wider. (see Fig. 4.12)

(c) If $V_0 b$ goes 0, thus, $P \to 0$

From 4.67, $\cos \alpha a = \cos ka$

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

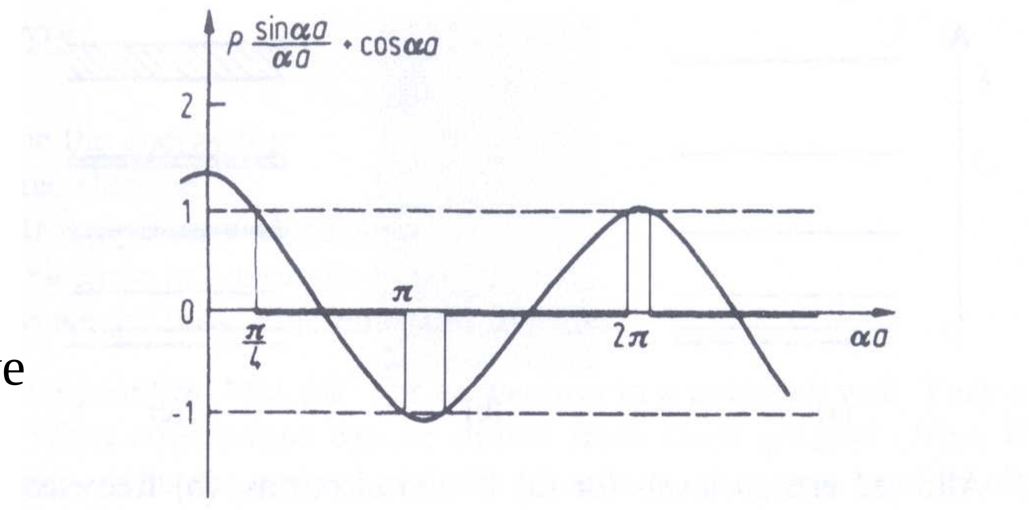


Figure 4.12. Function $P(\sin \alpha a/\alpha a) + \cos \alpha a$ with $P = \pi/10$.

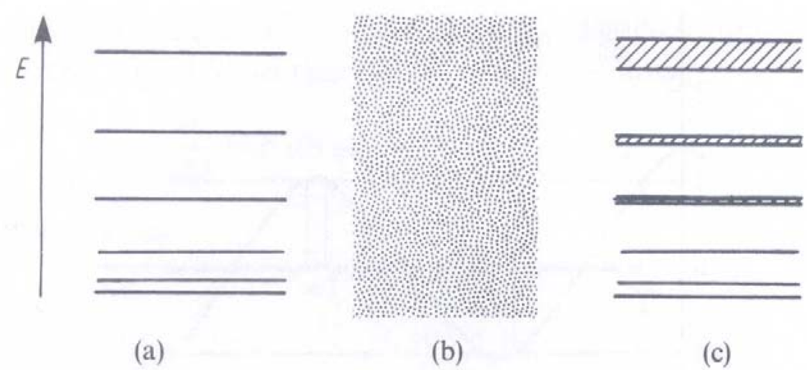


Figure 4.13. Allowed energy levels for (a) bound electrons, (b) free electrons, and (c) electrons in a solid.

4.4 Electron in a Periodic Field of Crystal (the Solid State)

(d) If the $V_0 b$ is very large, $P \to \infty$

$$\frac{\sin \alpha a}{\alpha a} \to 0$$

$$\sin \alpha a \to 0 \qquad \alpha a = n\pi$$

$$\alpha^2 = \frac{n^2 \pi^2}{a^2} \quad \text{for} \quad n = 1,2,3,....$$

Combining 4.46 and 4.69

$$E = \frac{\pi^2 \hbar^2}{2ma^2} \cdot n^2$$

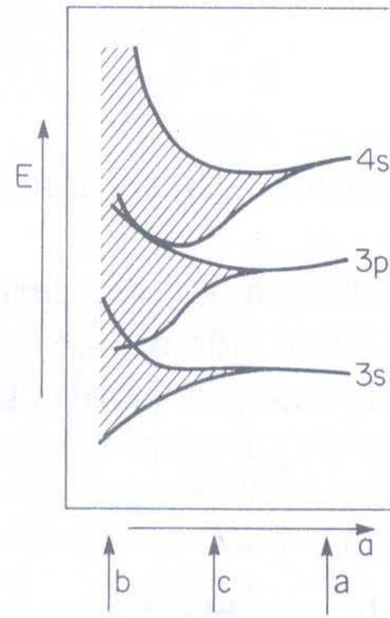


Figure 4.14. Widening of the sharp energy levels into bands and finally into a quasi-continuous energy region with decreasing interatomic distance, a, for a metal (after calculations of Slater). The quantum numbers are explained in Appendix 3.