Part I Fundamentals

Electron Theory : Matter Waves

Chap. 1 Introduction

Chap. 2 The Wave-Particle Duality

Chap. 3 The Schrödinger Equation

Chap. 4 Solution of the Schördinger Equation for Four Specific Problems

Chap. 5 Energy Bands in Crystals

Chap. 6 Electrons in a Crystal

4.1 Free Electrons

Suppose electrons propagating freely (i.e., in a potential-free space) to the positive x-direction.

Then $V = 0$ and thus

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

The solution for the above differential equation for an undamped vibration with spatial periodicity, (see Appendix 1)

$$\psi(x) = Ae^{i\alpha x}$$

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

Thus $\Psi(x) = Ae^{i\alpha x} \cdot e^{i\omega t}$

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

"energy continuum"

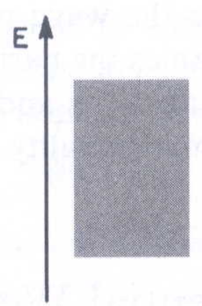


Figure 4.1. Energy continuum of a free electron (compare with Fig. 4.3).

4.2 Electron in a Potential Well (Bound Electron)

Consider an electron bound to its atomic nucleus. Suppose the electron can move freely between two infinitely high potential barriers

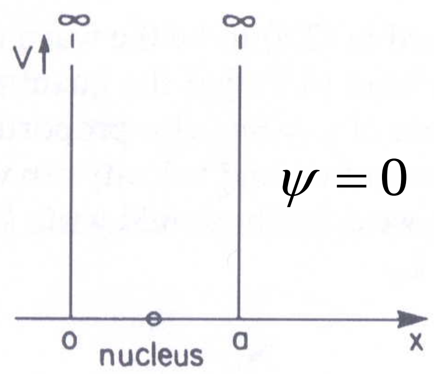


Figure 4.2. One-dimensional potential well. The walls consist of infinitely high potential barriers.

At first, treat 1-dim propagation along the *x*-axis inside the potential well

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

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

4.2 Electron in a Potential Well (Bound Electron)

Applying boundary conditions,

$$x = 0, \qquad \psi = 0 \qquad \longrightarrow \qquad B = -A$$

$$x = a \qquad \psi = 0 \qquad \longrightarrow \qquad 0 = Ae^{i\alpha a} + Be^{-i\alpha a} = A(e^{i\alpha a} - e^{-i\alpha a})$$

With Euler equation, $\sin\rho = \frac{1}{2i}(e^{i\rho} - e^{-i\rho})$

$$A[e^{i\alpha a} - e^{-i\alpha a}] = 2Ai \cdot \sin\alpha a = 0$$

$$\alpha a = n\pi, \qquad n = 0,1,2,3,....$$

"energy levels"

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

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

"energy quantization"

The solution $\psi = 2Ai \cdot \sin\alpha x$

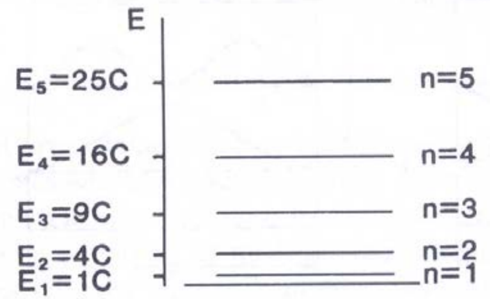


Figure 4.3. Allowed energy values of an electron that is bound to its atomic nucleus. E is the excitation energy in the present case. $C = \hbar^2\pi^2/2ma^2$, see (4.18). (E_1 is the zero-point energy.)

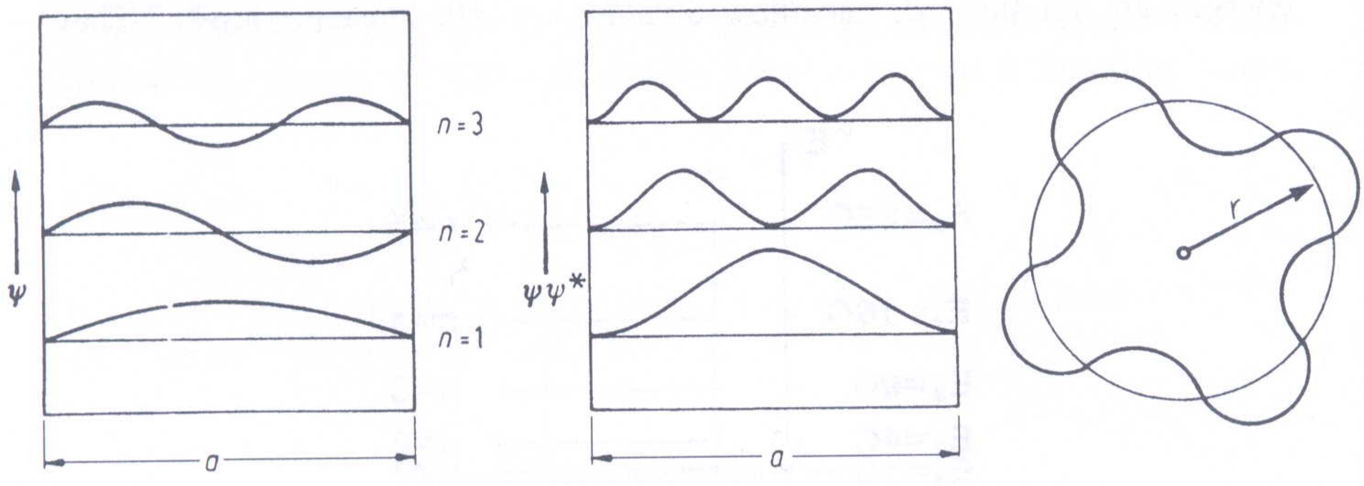
4.2 Electron in a Potential Well (Bound Electron)

Now discuss the wave function

$$\psi = 2Ai \cdot \sin \alpha x \quad \psi^* = -2Ai \cdot \sin \alpha x$$

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

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



(a) (b) (c)

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

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

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

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

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

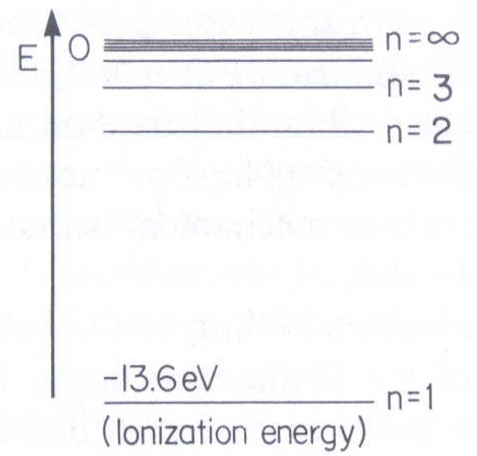


Figure 4.5. Energy levels of atomic hydrogen. *E* is the binding energy.

In 3-dim potential
$$E_n = \frac{\hbar^2\pi^2}{2ma^2}(n_x{}^2 + n_y{}^2 + n_z{}^2)$$

The same energy but different quantum numbers: "degenerate" states

4.3 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) $x > 0$

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

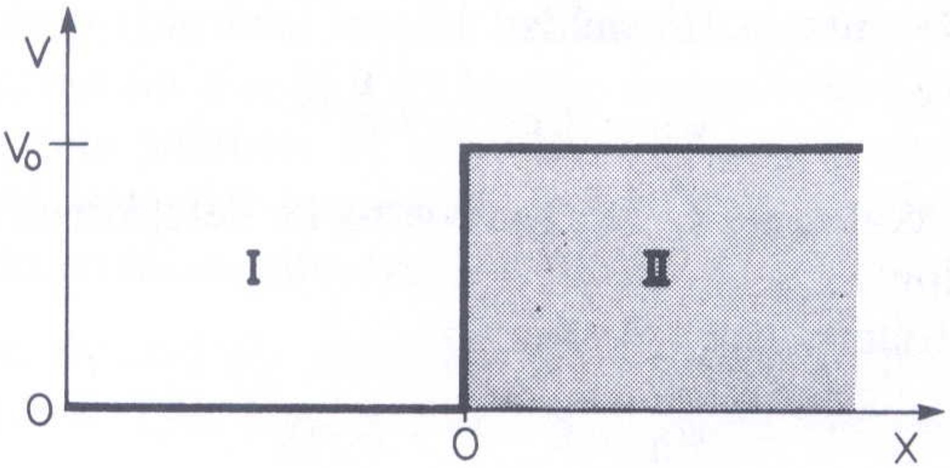


Figure 4.6. Finite potential barrier.

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 $x \to \infty$ $\psi_{II} = C \cdot \infty + D \cdot 0$

Since $\Psi\,\Psi^*$ can never be lager than 1, $\psi_{II} \to \infty$ is no solution, and thus $C \to 0$
, which reveals Ψ-function decreases in Region II

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

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

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

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

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

(2) At $x = 0$ $\quad \dfrac{d\psi_I}{dx} \equiv \dfrac{d\psi_{II}}{dx}$: 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,

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

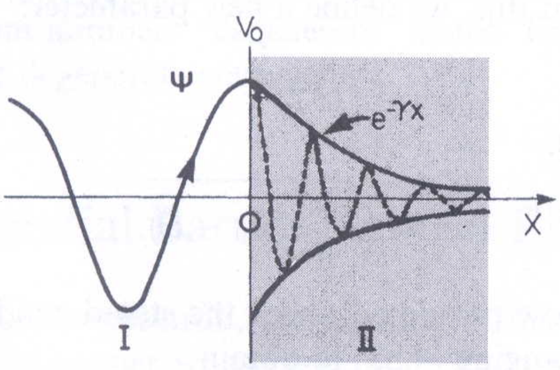


Figure 4.7. ψ-function (solid line) and electron wave (dashed line) meeting a finite potential barrier.

4.3 Finite Potential Barrier (Tunnel Effect)

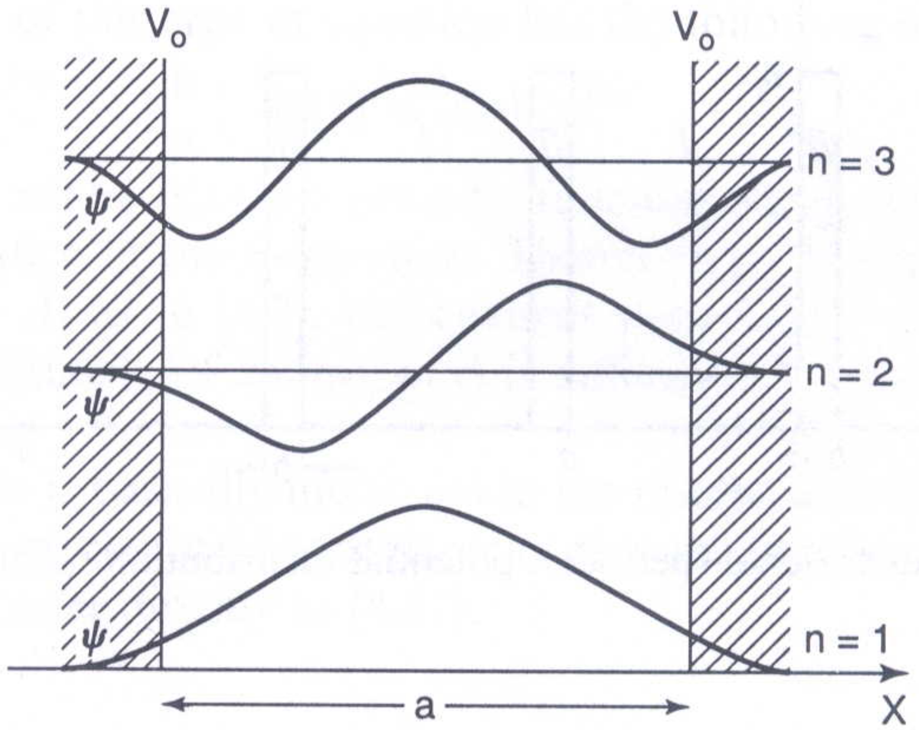


Figure 4.8. Square well with finite potential barriers. (The zero points on the vertical axis have been shifted for clarity.)

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

$E < V_0$

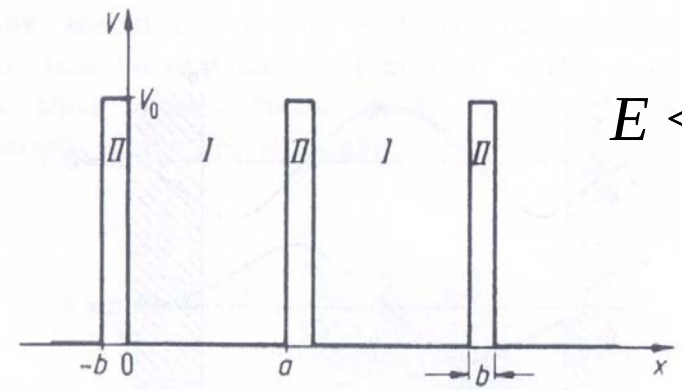


Figure 4.9. One-dimensional periodic potential distribution (simplified) (**Kronig-Penney model**).

Region (I)

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

Region (II)

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

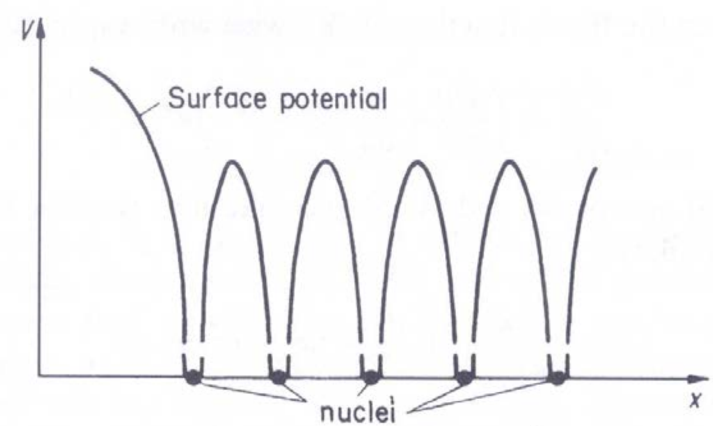


Figure 4.10. One-dimensional periodic potential distribution for a crystal (**muffin tin potential**).

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

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 complicated)

$$\psi(x) = u(x)\cdot e^{ikx} \qquad \textbf{(\textit{Bloch function})}$$

Where, $u(x)$ is a periodic function which possesses the periodicity of the lattice in the x-direction : $u(x) = u(x + a + b)$,

In 3-d, $u(\mathbf{r}) = u(\mathbf{r} + \mathbf{R})$, $\mathbf{R}$ = Bravais lattice vector

The final solution of the Schrödinger equations;

$$P\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka \quad \text{where} \quad P = \frac{maV_0 b}{\hbar^2}$$

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*

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

Insert 4.49 into 4.44 and take into account the abbreviation

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

The solutions of (I) and (II)

(I) $u = e^{-ikx}(Ae^{i\alpha x} + Be^{-i\alpha x})$ **(II)** $u = e^{-ikx}(Ce^{-\gamma x} + De^{\gamma x})$

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

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

$$A + B = C + D$$

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 $x = a + b$, Similarly, 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)

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

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

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

Since $V_0 b$ has to remain finite and $b \rightarrow 0$, 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 $\quad P = \dfrac{maV_0 b}{\hbar^2} \quad$, then $\quad P\dfrac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka$

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"

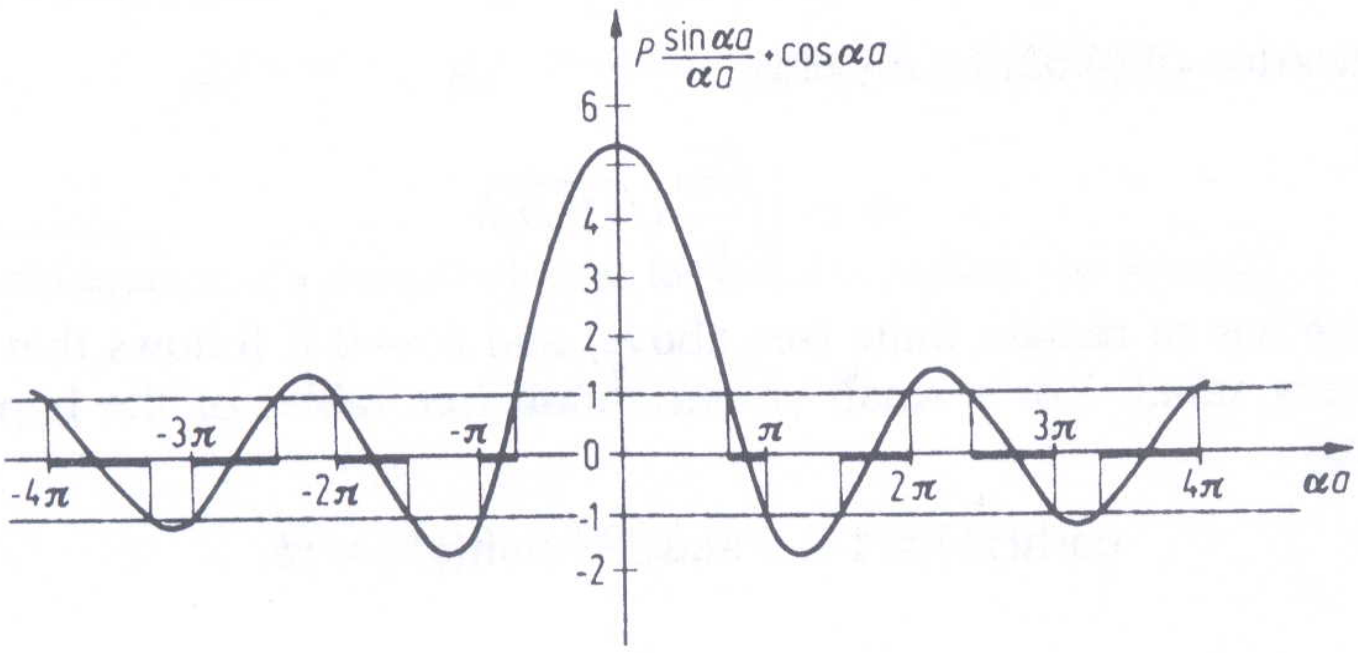


Figure 4.11. Function $P(\sin \alpha a/\alpha a) + \cos \alpha a$ versus αa. P was arbitrarily set to be $(3/2)\pi$.

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

- If **the potential barrier strength**, $\boldsymbol{V_0 b}$ is large, P is also large and the curve on Fig 4.11 steeper. The allowed band are narrow.
- $V_0 b$ and P are small, the allowed band becomes wider.
- If $V_0 b$ goes 0, thus, $P \to 0$

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

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

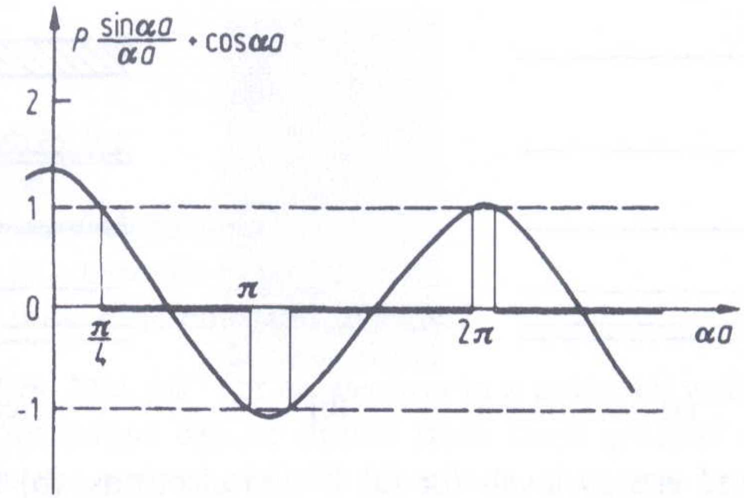


Figure 4.12. Function $P(\sin \alpha a/\alpha a) + \cos \alpha a$ with $P = \pi/10$.

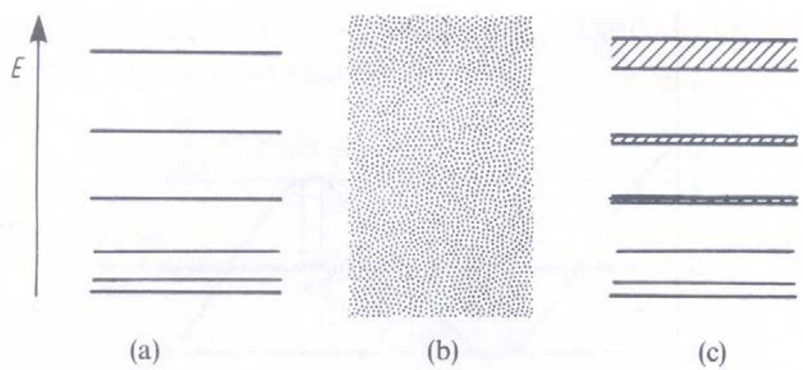


Figure 4.13. Allowed energy levels for (a) bound electrons, (b) free electrons, and (c) electrons in a solid.

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

See Fig. 7.2 of Bube

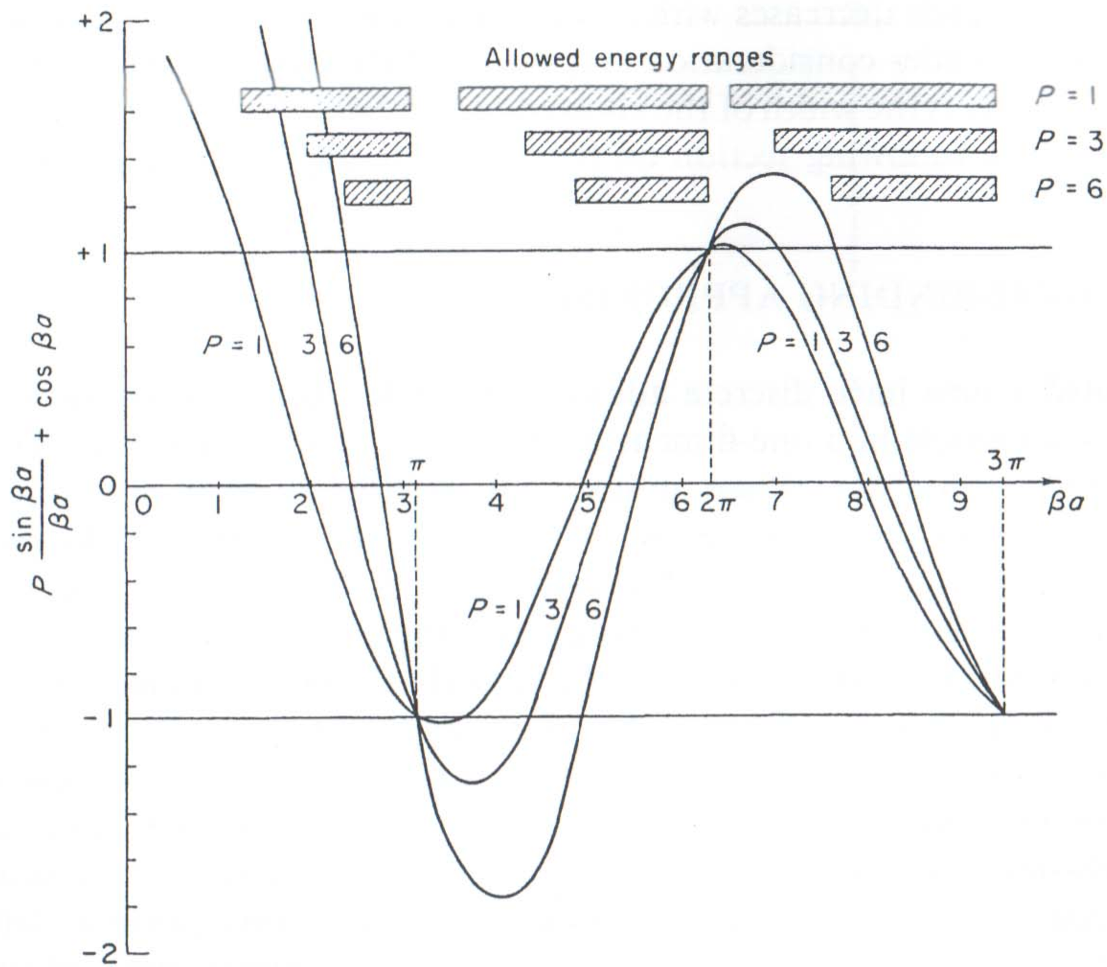


FIG. 7.2 Allowed and forbidden bands for the Kronig–Penney approximation to the periodic series of square-well potentials, for various values of the "strength of binding" parameter P.

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

- If the $V_0 b$ is very large, $P \rightarrow \infty$

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

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

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

Combining 4.46 and 4.69

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

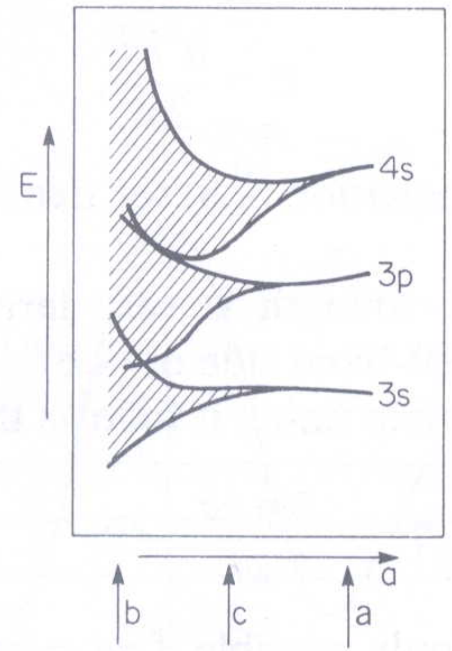


Figure 4.14. Widening of the sharp energy levels into bands and finally into a quasi-continuous energy region with decreasing interatomic distance, *a*, for a metal (after calculations of Slater). The quantum numbers are explained in Appendix 3.

Other model:

The tight-binding approximation

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

See Fig. 7.3 of Bube

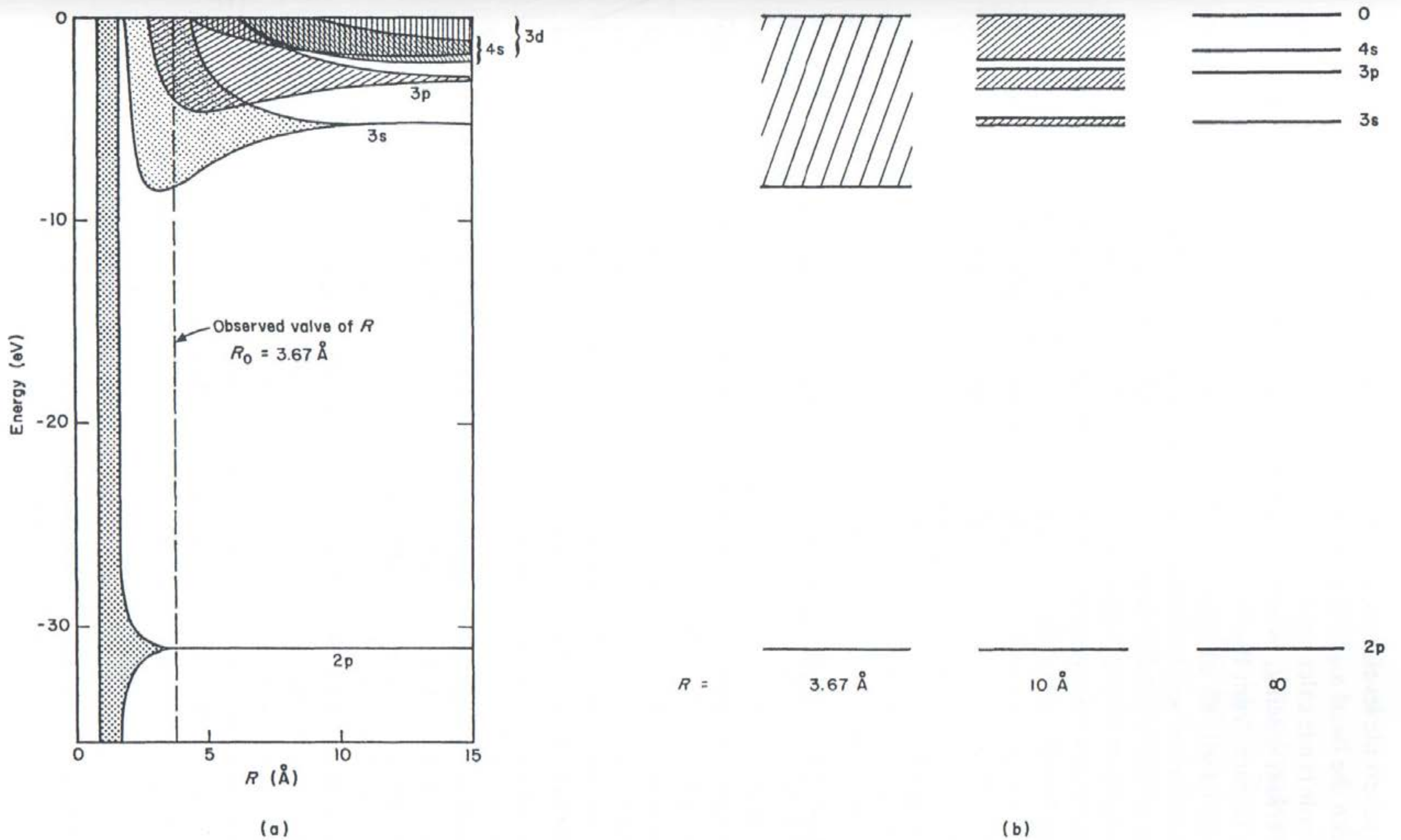


FIG. 7.3 (a) Energy bands developing in metallic sodium as a function of the interatomic distance R. (From J. C. Slater, *Phys. Rev.* **45**, 794 (1934).) (b) Specific energy-band formation for three values of R.