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Applications of the Schrödinger equation in nonperiodic semiconductor structures

7.1 The infinite square-shaped quantum well

The **infinite** square-shaped well potential is the simplest of all possible potential wells. The infinite square well potential is illustrated in **Fig. 7.1(a)** and is defined as

$$U(x) = 0 \quad \left(-\frac{1}{2} L \leq x \leq \frac{1}{2} L \right) \quad (7.1)$$

$$U(x) = \infty \quad \left(|x| > \frac{1}{2} L \right). \quad (7.2)$$

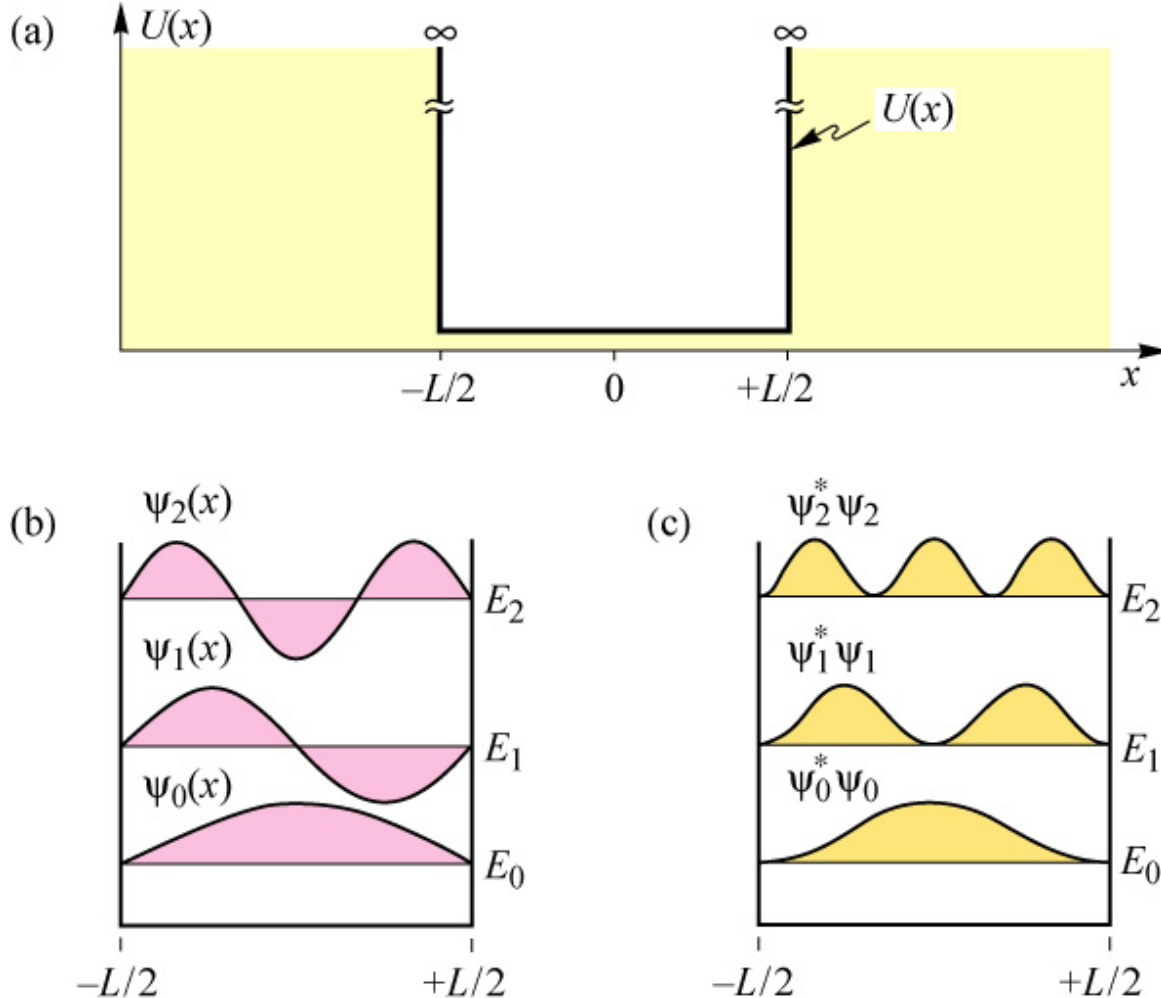


Fig. 7.1. (a) Schematic illustration of the infinite square well potential. The solutions of this potential well are shown in terms of (b) eigenfunctions $\psi_n(x)$, (b) eigenstate energies E_n , and (c) probability densities $\psi_n^* \psi_n$.

To find the stationary solutions for $\psi_n(x)$ and E_n we must find functions for $\psi_n(x)$, which satisfy the Schrödinger equation. The time-independent

Schrödinger equation contains only the differential operator d/dx , whose eigenfunctions are exponential or sinusoidal functions. Since the Schrödinger equation has the form of an eigenvalue equation, it is reasonable to try only eigenfunctions of the differential operator. Furthermore, we assume that $\psi_n(x) = 0$ for $|x| > L/2$, because the potential energy is infinitely high in the barrier regions. Since the 3rd Postulate requires that the wave function be continuous, the wave function must have zero amplitude at the two potential discontinuities, that is $\psi_n(x = \pm L/2) = 0$. We therefore employ sinusoidal functions and differentiate between states of **even** and **odd symmetry**. We write for even-symmetry states

$$\psi_n(x) = A \cos \frac{(n+1)\pi x}{L} \quad \left(n = 0, 2, 4, \dots \quad \text{and} \quad |x| \leq \frac{L}{2} \right) \quad (7.3)$$

and for odd-symmetry states

$$\psi_n(x) = A \sin \frac{(n+1)\pi x}{L} \quad \left(n = 1, 3, 5, \dots \quad \text{and} \quad |x| \leq \frac{L}{2} \right). \quad (7.4)$$

Both functions have a finite amplitude in the well-region ($|x| \leq L/2$) and they have zero amplitude in the barriers, that is

$$\psi_n(x) = 0 \quad \left(n = 0, 1, 2, \dots \quad \text{and} \quad |x| > \frac{L}{2} \right) \quad (7.5)$$

The shapes of the three lowest wave functions ($n = 0, 1, 2 \dots$) are shown in **Fig. 7.1(b)**. In order to normalize the wave functions, the constant A must be determined. The condition $\langle \psi | \psi \rangle = 1$ yields

$$A = \sqrt{2/L} . \quad (7.6)$$

One can verify that Eqs. (7.3) and (7.4) are solutions of the infinite square well by inserting the normalized wave functions into the Schrödinger equation. Insertion of the ground-state wave function ($n = 0$) into the Schrödinger equation yields

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right) = E_0 \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right) . \quad (7.7)$$

Calculating the derivative on the left-hand side of the equation yields the **ground state energy** of the infinite square well

$$E_0 = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2. \quad (7.8)$$

The **excited state energies** ($n = 1, 2, 3 \dots$) can be evaluated analogously. One obtains the eigenstate energies in the infinite square well according to

$$E_n = \frac{\hbar^2}{2m} \left[\frac{(n+1)\pi}{L} \right]^2 \quad (n = 0, 1, 2, 3 \dots). \quad (7.9)$$

The spacing between two adjacent energy levels, that is $E_n - E_{n-1}$, is proportional to n . Thus, the energetic spacing between states *increases* with energy. The energy levels are schematically shown in **Fig. 7.1(b)** for the infinite square well.

The probability density of a particle described by the wave function ψ is given by $\psi^* \psi$ (2nd Postulate). The probability densities of the three lowest states are shown in **Fig. 7.1(c)**.

The eigenstate energies are, as already mentioned, *expectation values of the total energy* of the respective state. It is therefore interesting to know if the eigenstate energies are purely kinetic, purely potential, or a mixture of both. The expectation value of the kinetic energy of the ground state is calculated according to the 5th Postulate:

$$\langle E_{\text{kin},0} \rangle = \left\langle \psi_0 \left| \frac{p^2}{2m} \right| \psi_0 \right\rangle . \quad (7.10)$$

Using the momentum operator $p = (\hbar/i) (d/dx)$ one obtains the expectation value of the kinetic energy of the ground state

$$\langle E_{\text{kin},0} \rangle = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 \quad (7.11)$$

which is identical to the total energy given in Eq. (7.8). Evaluation of kinetic energies of all other states yields

$$\langle E_{\text{kin},n} \rangle = \frac{\hbar^2}{2m} \left[\frac{(n+1)\pi}{L} \right]^2. \quad (7.12)$$

The kinetic energy coincides with the total energy given in Eq. (7.9). **Thus, the energy of a particle in an infinite square well is purely kinetic.** The particle has no potential energy.

We next turn to a second, more intuitive method to obtain the wave functions of the infinite potential well. This second method is based on the de Broglie wave concept. Recall that the de Broglie wave is defined for a constant momentum p , that is, for a particle in a *constant* potential. The energy of the wave is purely kinetic. In order to find solutions of the infinite square well, we match the de Broglie wavelength to the width of the quantum well according to the condition

$$\frac{1}{2} \lambda (n+1) = L \quad (n = 0, 1, 2 \dots) \quad (7.13)$$

In this equation, multiples of half of the de Broglie wavelength are matched to the width of the quantum well. Expressing the kinetic energy in terms of the de Broglie wavelength, that is

$$E = \frac{p^2}{2m} = \frac{1}{2m} \left(\frac{2\pi\hbar}{\lambda} \right)^2 \quad (7.14)$$

and inserting Eq. (7.13) into Eq. (7.14) yields

$$E_n = \frac{\hbar^2}{2m} \left[\frac{(n+1)\pi}{L} \right]^2 \quad (n = 0, 1, 2 \dots) . \quad (7.15)$$

This equation is identical to Eq. (7.12) which was obtained by the solution of the Schrödinger equation. The de Broglie wave concept yields the correct solution of the infinite potential well, because (i) the particle is confined to the constant potential of the well region, (ii) the energy of the particle is purely kinetic, and (iii) the wave function is sinusoidal.

The infinite square shaped quantum well is the simplest of all potential wells. The wave functions (eigenfunctions) and energies (eigenvalues) in an infinite square well are relatively simple. There is a large number of potential wells with other shapes, for example the square well with *finite* barriers, parabolic well, triangular well, or V-shaped well. The exact solutions of these wells are more complicated. Several methods have been developed to

calculate approximate solutions for arbitrary shaped potential wells. These methods will be discussed in the chapter on quantum wells in this book.

7.2 The asymmetric and symmetric finite square-shaped quantum well

In contrast to the infinite square well, the *finite square well* has barriers of finite height. The potential of a finite square well is shown in **Fig. 7.2**. The two barriers of the well have a different height and therefore, the structure is denoted *asymmetric* square well. The potential energy is constant within the three regions I, II, and III, as shown in **Fig. 7.2**. In order to obtain the solutions to the Schrödinger equation for the square well potential, the solutions in a *constant potential* will be considered first.

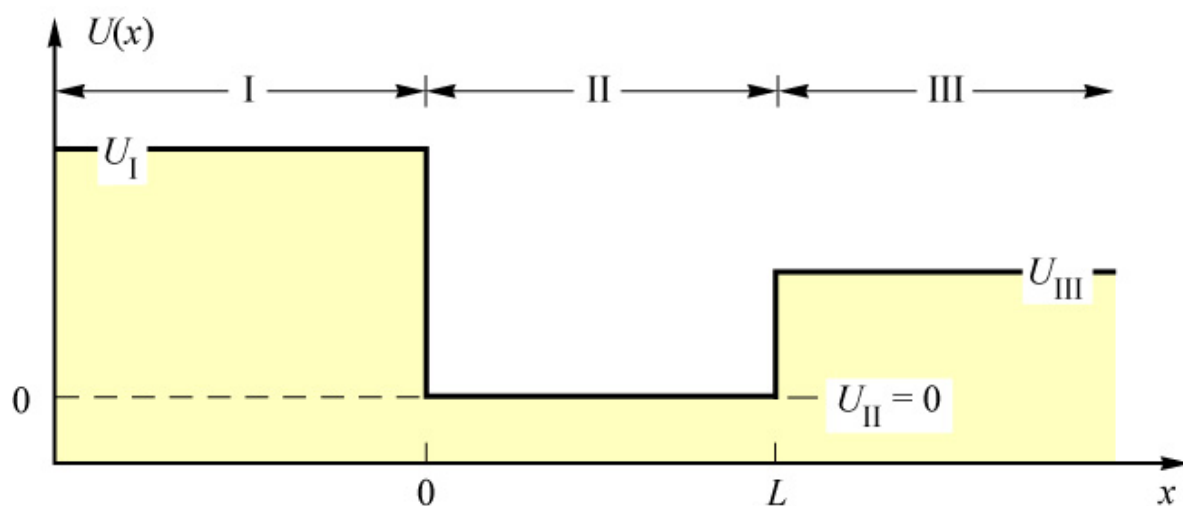


Fig. 7.2. Asymmetric square well potential with well width L and barrier heights U_I and U_{III} .

Assume that a particle with energy E is in a constant potential U . Then two cases can be distinguished, namely $E > U$ and $E < U$. In the **first case** ($E > U$) the general solution to the time-independent one-dimensional Schrödinger equation is given by

$$\psi(x) = A \cos kx + B \sin kx \quad (7.16)$$

where A and B are constants and

$$k = \sqrt{2mE / \hbar^2} . \quad (7.17)$$

Insertion of the solution into the Schrödinger equation proves that it is indeed a correct solution. Thus the wave function is an *oscillatory sinusoidal function* in a constant potential with $E > U$. In the **second case** ($E < U$), the solution of the time-independent one-dimensional Schrödinger equation is given by

$$\psi(x) = C e^{\kappa x} + D e^{-\kappa x} \quad (7.18)$$

where C and D are constants and

$$\begin{aligned}\kappa &= \sqrt{2 m (U - E) / \hbar^2} \\ &= \sqrt{\frac{2 m U}{\hbar^2} - k^2} .\end{aligned}\tag{7.19}$$

Again, the insertion of the solution into the Schrödinger equation proves that it is indeed a correct solution. Thus the wave function is an *exponentially growing or decaying* function in a constant potential with $E < U$.

Next, the solutions of an asymmetric and symmetric square well will be calculated. The potential energy of the well is piecewise constant, as shown in **Fig. 7.2**. Having shown that the wave functions in a constant potential are either sinusoidal or exponential, the wave functions in the three regions I ($x \leq 0$), II ($0 < x < L$), and III ($x \geq L$), can be written as

$$\psi_{\text{I}}(x) = A e^{\kappa_{\text{I}} x}\tag{7.20}$$

$$\psi_{\text{II}}(x) = A \cos k x + B \sin k x\tag{7.21}$$

$$\psi_{\text{III}}(x) = (A \cos kL + B \sin kL) e^{-\kappa_{\text{III}}(x-L)} \quad (7.22)$$

In this solution, the first boundary condition of the 3rd Postulate, *i. e.* $\psi_{\text{I}}(0) = \psi_{\text{II}}(0)$ and $\psi_{\text{II}}(L) = \psi_{\text{III}}(L)$, is already satisfied. From the second boundary condition of the 3rd Postulate, *i. e.* $\psi_{\text{I}}'(0) = \psi_{\text{II}}'(0)$ and $\psi_{\text{II}}'(L) = \psi_{\text{III}}'(L)$, the following two equations are obtained

$$A \kappa_{\text{I}} - B k = 0 \quad (7.23)$$

$$A (\kappa_{\text{III}} \cos kL - k \sin kL) + B (\kappa_{\text{III}} \sin kL + k \cos kL) = 0 . \quad (7.24)$$

This homogeneous system of equations has solutions, only if the determinant of the system vanishes. From this condition, one obtains

$$\tan kL = \frac{kL (\kappa_{\text{I}}L + \kappa_{\text{III}}L)}{k^2L^2 - \kappa_{\text{I}}L\kappa_{\text{III}}L} \quad (7.25)$$

which is the **eigenvalue equation** of the *finite asymmetric square well*.

For the *finite symmetric square well*, which is of great practical relevance, the **eigenvalue equation** is given by

$$\tan kL = \frac{2 kL \kappa L}{k^2 L^2 - \kappa^2 L^2} \quad (7.26)$$

where $\kappa = \kappa_I = \kappa_{III}$. If κ is expressed as a function of k (see Eq. 7.19), then Eq. (7.26) depends only on a single variable, *i. e.*, k . Solving the eigenvalue equation yields the eigenvalues of k and, by using Eqs. (7.17) and (7.19), the allowed energies E and decay constants κ , respectively. The allowed energies are also called the ***eigenstate energies*** of the potential.

Inspection of Eq. (7.26) yields that the eigenvalue equation has a ***trivial solution*** $kL = 0$ (and thus $E = 0$) which possesses no practical relevance. Non-trivial solutions of the eigenvalue equation can be obtained by a graphical method. **Figure 7.3** shows the graph of the left-hand and right-hand side of the eigenvalue equation. The dashed curve represents the right-hand side of the eigenvalue equation. The intersections of the dashed curve with the periodic tangent function are the solutions of the eigenvalue equation. The quantum state with the lowest non-trivial solution is called the ***ground state*** of the well. States of higher energy are referred to as ***excited states***.

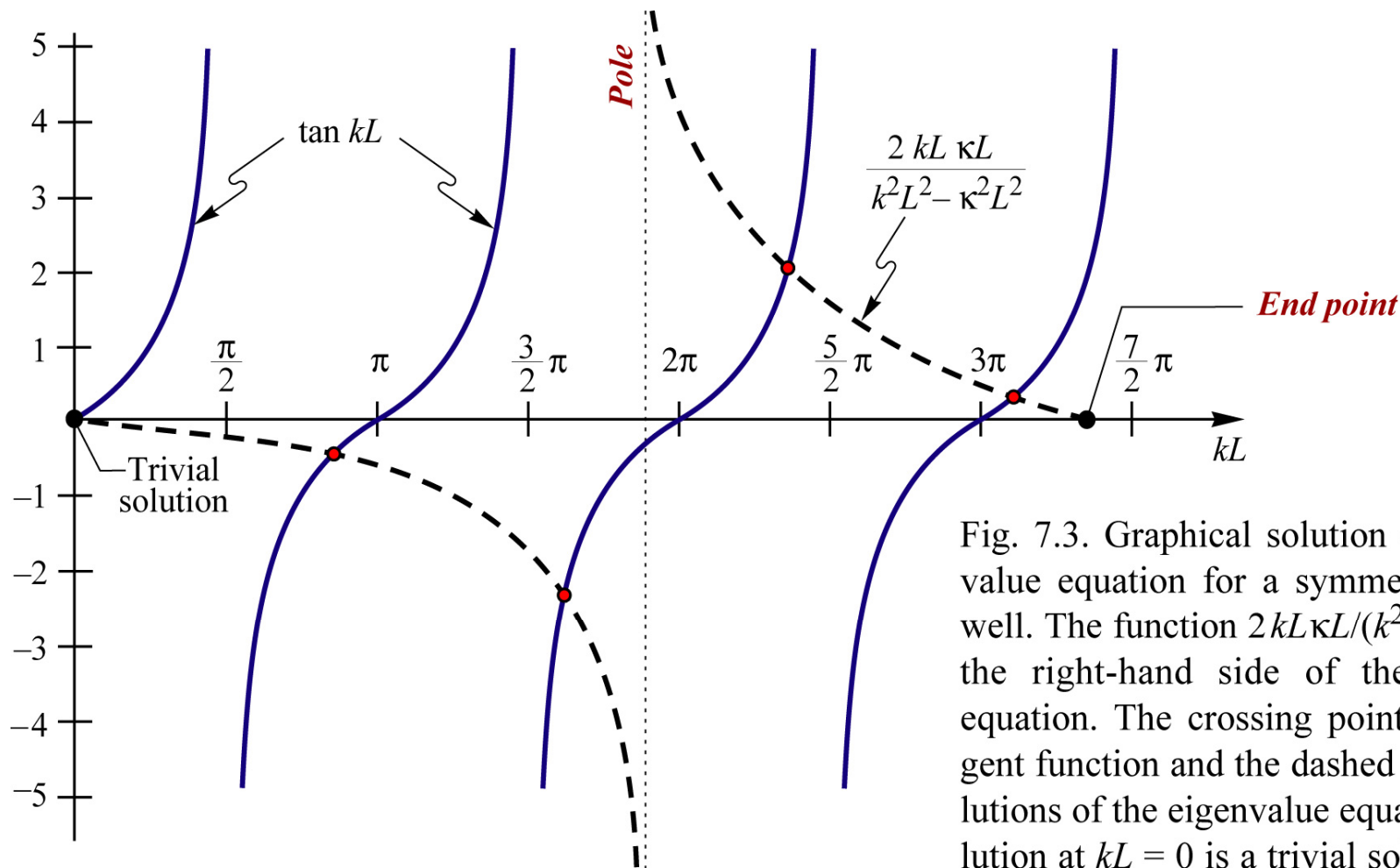


Fig. 7.3. Graphical solution of the eigenvalue equation for a symmetric quantum well. The function $\frac{2kL\kappa L}{k^2L^2 - \kappa^2L^2}$ is the right-hand side of the eigenvalue equation. The crossing points of the tangent function and the dashed curve are solutions of the eigenvalue equation. The solution at $kL = 0$ is a trivial solution having no practical relevance.

The dashed curve shown in **Fig. 7.3** has two significant points, namely a **pole** and an **end point**. The dashed curve has a **pole** when the denominator of

the right-hand side of the eigenvalue equation vanishes, *i. e.*, when $kL = \kappa L$. Using Eq. (7.19), it is given by

Pole:
$$k L|_{\text{Pole}} = \sqrt{m U / \hbar^2} L \quad (7.27)$$

The dashed curve *ends* when $k = (2mU / \hbar^2)^{1/2}$. If k exceeds this value, the square root in Eq. (7.19) becomes imaginary. The **end point** of the dashed curve is thus given by

End point:
$$k L|_{\text{End point}} = \sqrt{2 m U / \hbar^2} L \quad (7.28)$$

There are no further bound state solutions to the eigenvalue equation beyond the end point.

Now that the eigenvalues of k and κ are known, they are inserted into Eqs. (7.23) and (7.24); this allows for the determination of the constants A and B and the wave functions. Thus the allowed energies and the wave functions of the square well have been determined.

It is possible to show that all states with even quantum numbers ($n = 0, 1, 2 \dots$) are of **even symmetry** with respect to the center of the well, *i. e.* **$\psi(x) = \psi(-x)$** . All states with odd quantum numbers ($n = 1, 3, 5 \dots$) are of

odd symmetry with respect to the center of the well, i. e. $\psi(x) = -\psi(-x)$. The even and odd state wave functions in the well are thus of the form

$$\psi_{\text{II}}(x) = A_{\text{II}} \cos \left[k_n \left(x - \frac{L}{2} \right) \right] \quad (\text{for } n = 0, 2, 4 \dots) \quad (7.29)$$

and

$$\psi_{\text{II}}(x) = A_{\text{II}} \sin \left[k_n \left(x - \frac{L}{2} \right) \right] \quad (\text{for } n = 1, 3, 5 \dots) . \quad (7.30)$$

The proof of these equations is left to the reader. The three lowest wave functions of a symmetric square well are shown in **Fig. 7.4**.

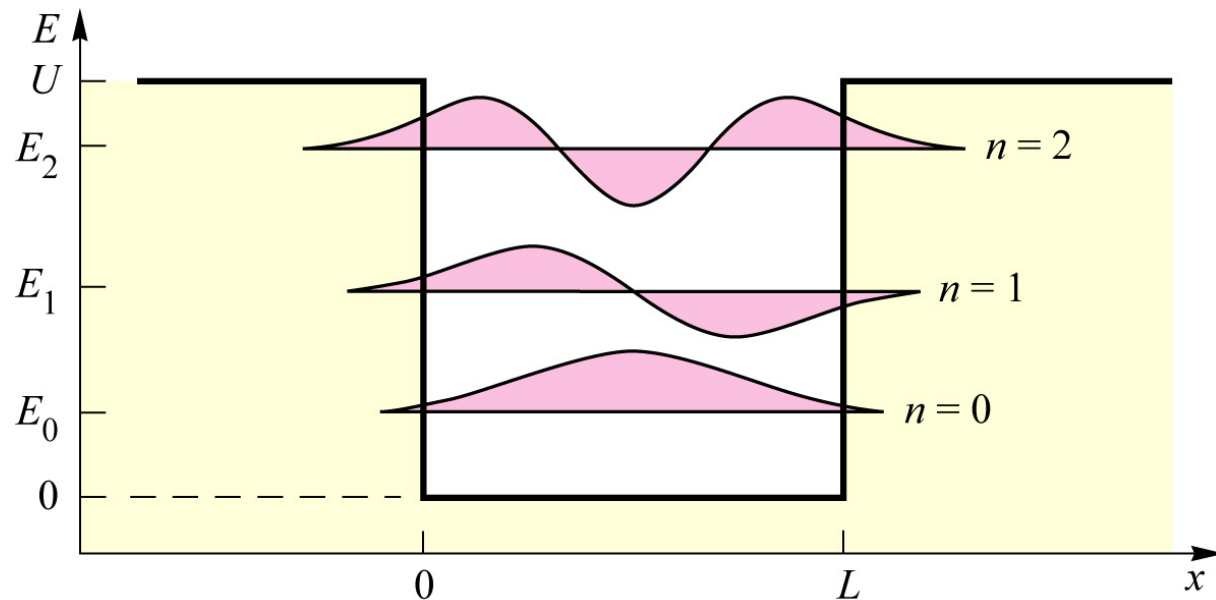


Fig. 7.4. Schematic illustration of the three lowest wave functions of the symmetric quantum well.

Exercise: *Boundary condition in semiconductor quantum wells.* The boundary conditions for the wave function at an interface between two media I and II are given by $\psi_I(x) = \psi_{II}(x)$ and $\psi_I'(x) = \psi_{II}'(x)$ as stated in the 3rd Postulate. These boundary conditions apply to situations common in particle physics, in which the particle mass m *does not change* when going from a Medium I across a boundary to a Medium II. However, the effective mass (m^*) *changes* as electrons transfer from one semiconductor to another. This change in effective mass requires a modification of the second boundary condition and the ***modified second boundary condition*** is given by

$$\boxed{\frac{1}{m_{\text{I}}^*} \frac{d\psi_{\text{I}}(x)}{dx} = \frac{1}{m_{\text{II}}^*} \frac{d\psi_{\text{II}}(x)}{dx}} \quad (7.31)$$

The first boundary condition, namely $\psi_{\text{I}}(x) = \psi_{\text{II}}(x)$, is still valid and this condition does not need to be modified.

The modified second boundary condition can be derived from the requirement of a *constant current density* at the boundary. The current density of an electron moving with constant velocity v across an interface is given by $J = eV^{-1}v$, where V is the unit volume. Expressing the current density in terms of the electron momentum yields $J = eV^{-1}p/m^*$. Using the 4th Postulate, a corresponding quantum mechanical expression is found, *i. e.*

Classical	Quantum mechanical
$eV^{-1} \frac{p}{m^*}$	$eV^{-1} \frac{1}{m^*} \frac{\hbar}{i} \frac{d\psi(x)}{dx}$

The quantum mechanical expression elucidates that the current density at an interface is constant, only if $(m^*)^{-1} [d\psi(x)/dx]$ is constant across the interface.

A rigorous derivation of the quantum mechanical current density was given by Flügge (1971). It is given by

$$J = \frac{e \hbar}{2 m i} \left(\psi^* \nabla \psi - \psi \nabla \psi^* \right) \quad (7.32)$$

Bastard (1981) first showed that the second boundary condition must be modified in semiconductor heterostructures according to Eq. (7.31).

Apply the modified boundary condition to an asymmetric semiconductor quantum well structure and derive the eigenvalue equation. Assume that the effective masses are m_I^* , m_{II}^* , and m_{III}^* in the first barrier, well, and second barrier region, respectively.

Result:

$$\tan k L = \frac{\frac{k L}{m_{II}^*} \left(\frac{\kappa_I L}{m_I^*} + \frac{\kappa_{III} L}{m_{III}^*} \right)}{\frac{k^2 L^2}{m_{II}^{*2}} - \frac{\kappa_I L}{m_I^*} - \frac{\kappa_{III} L}{m_{III}^*}} \quad (7.33)$$

What is the eigenvalue equation for the symmetric semiconductor quantum well with $\kappa = \kappa_I = \kappa_{III}$ and $m_I^* = m_{III}^*$?

Result:
$$\tan kL = \frac{2 \frac{kL}{m_{II}^*} \frac{\kappa L}{m_I^*}}{\frac{k^2 L^2}{m_{II}^{*2}} - \frac{\kappa^2 L^2}{m_I^{*2}}} \quad (7.34)$$

What is the maximum value for kL , *i. e.*, *end point* of the dashed curve?

Result:
$$kL|_{\text{Endpoint}} = \sqrt{2 m_{II}^* U / \hbar^2} L \quad (7.35)$$

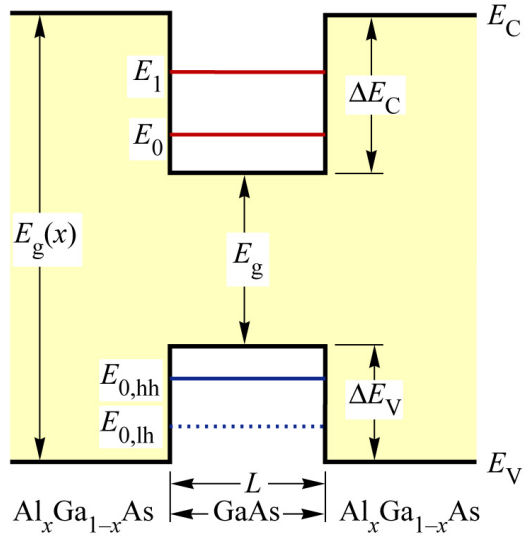
Use the location of the end point to determine a condition for the quantum wells thickness under which a symmetric quantum well structure has *only* one bound state.

Result:
$$L < \frac{\pi \hbar}{\sqrt{2 m_{II}^* U}} \quad (7.36)$$

Is it possible for asymmetric or symmetric square well structures to have no bound states at all?

Answer: A symmetric square well always has at least one bound state. An asymmetric square well has no bound state for sufficiently small values of L .

Figure 7.5 shows the numerical solutions for bound states in the conduction band and valence band of an $\text{Al}_{0.30}\text{Ga}_{0.70}\text{As} / \text{GaAs}$ square-shaped quantum well. The graph reveals that there is only one bound state in the conduction band well for well widths smaller than approximately 50 \AA . Does this agree with the analytic result of Eq. (7.36)?



$$E_{g, \text{Al}_x\text{Ga}_{1-x}\text{As}} = (1.424 + 1.247 \times x) \text{ eV}$$

$$\Delta E_C = (2/3) \Delta E_g$$

$$\Delta E_V = (1/3) \Delta E_g$$

$$m_{e, \text{Al}_x\text{Ga}_{1-x}\text{As}}^* = (0.067 + 0.083 \times x) m_0$$

$$m_{hh, \text{Al}_x\text{Ga}_{1-x}\text{As}}^* = (0.45 + 0.30 \times x) m_0$$

$$m_{lh, \text{Al}_x\text{Ga}_{1-x}\text{As}}^* = (0.08 + 0.057 \times x) m_0$$

Fig. 7.5. Quantized energies of subbands in the conduction band and valence band of an Al_xGa_{1-x}As/GaAs single quantum well structure at room temperature. There are different subbands for heavy holes (hh) and light holes (lh) in the valence band.

