ELEC4705 – Fall 2009

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LECTURE 5
Electron in a Well

Contents

5.1. Quantum Well

To understand the behaviour of an electron quantum mechanically we need to solve SCE for an appropriate potential. Previously, we looked at a free electron now we will look at some simple cases that bring out the crucial behaviour of wave-particle duality.

A large number of problems can be describe by simple potential wells. These examples come from atomic physics and more recently nano-technology.

We first consider an electron bounded to its atomic nucleus. For simplicity we assume that the electron can move freely between two infinitely high potential barriers. The potential barriers do not allow the electron to escape from this potential well (see the Figure 1). Because
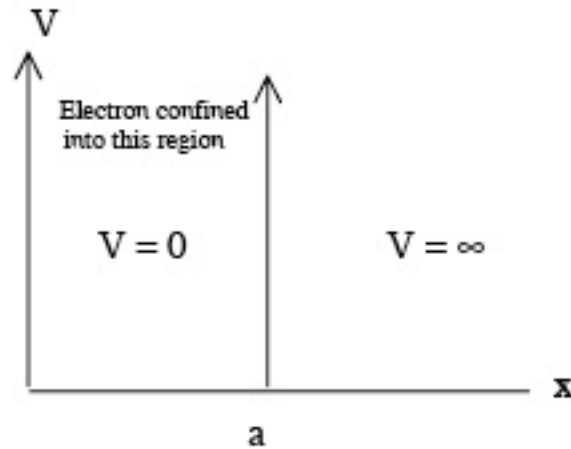

Figure 1. Quantum Well

of the infinite potential barriers, the wavefunction $\psi(x)$ vanishes outside the well, hence the domain Ω is given by

$$\Omega : \quad 0 \leq x \leq a \tag{5.1}$$

For which we have the Schrodinger equation as:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{5.2}$$

To represent the infinite barriers we apply the Dirichlet boundary conditions as follows:

$$\psi(0) = \psi(a) = 0 \tag{5.3}$$

i.e. we expect $\psi(x) = 0$ except for $0 \leq x \leq a$ (no chance of finding electron outside box as $V = \infty$).

Note*: that in general the potential energy is a function of the position of the particle and is a result of the forces exerted by other charged particles but here for simplicity we assume $V = 0$.*

Defining $k = \sqrt{\frac{2mE}{\hbar^2}}$ and replacing $V(x)$ by 0, the Schrodinger equation inside the well is as follows.

$$\frac{\partial^2 \psi(x)}{\partial x^2} + k\psi(x) = 0 \tag{5.4}$$

which is the same as we had for the free electron and the solution is therefore the same an oscillating wave.

The general solution to equation 5.4 is given by

$$\psi(x) = A \exp(jkx) + B \exp(-jkx) \tag{5.5}$$

For the free electron we assumed that the wave was only going in the +ive x direction. Now we allow both directions.

Using equation 5.3 we have

$$\psi(0) = A + B = 0 \quad \Rightarrow \quad B = -A \tag{5.6}$$

and

$$\begin{aligned}\psi(a) &= A \exp(ika) + B \exp(-ika) = 0 \\ &\Rightarrow A \sin(ka) = 0\end{aligned}$$

$$\tag{5.7}$$

This is very interesting condition as it has *a set of solutions*. There are a infinite number of k that satisfy the equation as given by:

$$ka = n\pi$$

$$\Rightarrow \quad \sqrt{\frac{2m}{\hbar^2}} a = n\pi$$

$$\Rightarrow \quad E_n = \frac{\hbar^2\pi^2}{2ma^2} n^2 \qquad n = 1, 2, \cdots \tag{5.8}$$

And so we have a set of solutions denoted by n which give different electron energies and waver functions.

From previous lectures we have the normalization condition as:

$$\int_{-\infty}^{+\infty} \psi(x)\,\psi^*(x)\,dx = 1 \tag{5.9}$$

The amplitude of the wavefunction is obtained by satisfying the normalization condition 5.9 as below:

$$\int_{-\infty}^{+\infty} 4A^2 \sin^2(kx)\, dx = 1$$

$$\int_{-\infty}^{+\infty} 4A^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

$$A = \sqrt{\frac{1}{2a}}$$

$$\psi(x) = \sqrt{\frac{2}{a}}\, \sin\left(\frac{n\pi}{a}x\right) \qquad for\ n = 1, 2, \cdots \qquad (5.10)$$

$$k = \frac{\pi n}{a} \qquad (5.11)$$

> **Note**: *Only certain values of k and certain energies E_n are allowed. This condition known as the "quantization condition" is forced on the solution by setting Ψ to zero at the well edges! n is known as the quantum number or quantum state the electron is in.*

Table 1 shows a few examples of wavenumbers and the corresponding set of wavefunction and energy values (eigenstates) which are illustrated in figure 2.

Table 1. sets of eigenstates

Level # n	k	ψ_n	E_n
1	$k_1 = \pi/a$	$\psi_1 = \sqrt{\frac{2}{a}} \sin \pi x/a$	$E_1 = \hbar^2\pi^2/2ma^2$
2	$k_2 = 2\pi/a$	$\psi_2 = \sqrt{\frac{2}{a}} \sin 2\pi x/a$	$E_2 = 4\hbar^2\pi^2/2ma^2$
3	$k_3 = \pi/a$	$\psi_3 = \sqrt{\frac{2}{a}} \sin 3\pi x/a$	$E_3 = 9\hbar^2\pi^2/2ma^2$
$\vdots$	$\vdots$	$\vdots$	$\vdots$

In the classical case the electron would travel back and forth between the walls and the probability density would therefore be equally distributed along the whole length of the well. However, as can be seen for QM the "electron" is unevenly distributed in the well and the
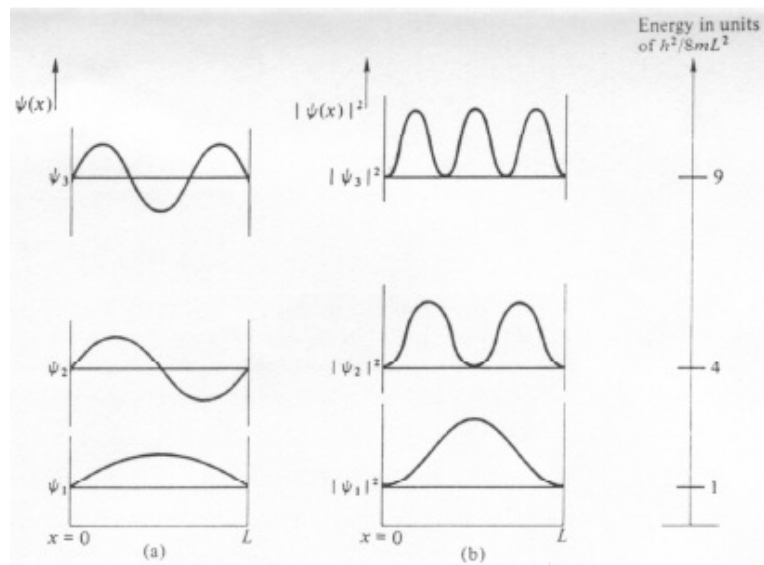
Figure 2. Quantum Well eigenstates

distribution is determined by the "state" of the electron – i.e. what E energy it has.

5.2. Quantum Well with Finite barriers

Now lets take a slightly more realistic example with finite "walls". Suppose we have a potential energy as shown in figure 3. We have two cases to consider 1) $E < V_0$ and 2) $E \geq V_0$ The well is best defined as
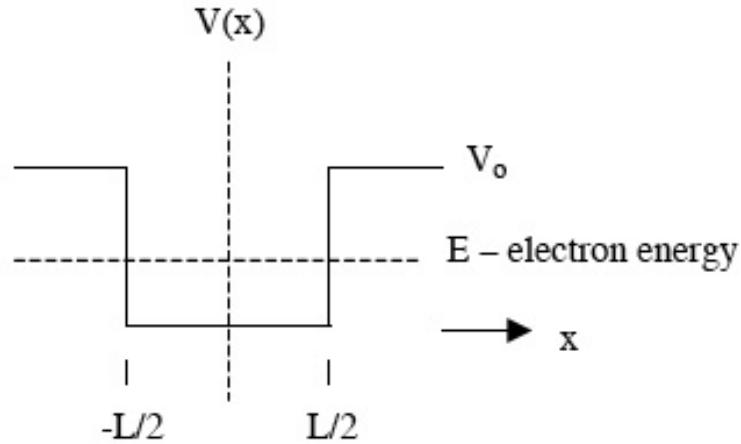

Figure 3. Potential energy for a QW with finite barriers
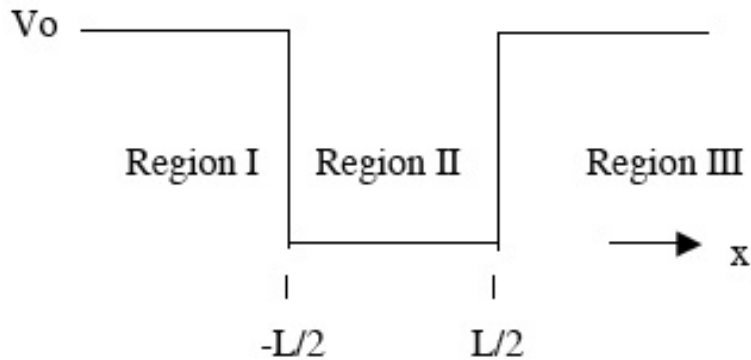
having three regions as in Fig. 4

Figure 4. the three regions in a finite QW

5.2.1. Bound States

First we study the bound states which is the case with $E < V_0$.

(a) $-L/2 < x < L/2$:

$$V(x) = 0$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{5.12}$$

$$\psi(x) = A\cos kx + B\sin kx \tag{5.13}$$

$$k = \frac{\sqrt{2mE}}{\hbar} \tag{5.14}$$

(b) $x < -L/2$:

$$V(x) = V_0$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V_0\psi(x) = E\psi(x) \tag{5.15}$$

$$\psi(x) = Ce^{\gamma x} + De^{-\gamma x} \tag{5.16}$$

$$\gamma = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \tag{5.17}$$

(c) $x > L/2$:

$$V(x) = V_0$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V_0\psi(x) = E\psi(x) \tag{5.18}$$

$$\psi(x) = Ee^{-\gamma x} + Fe^{\gamma x} \tag{5.19}$$

$$\gamma = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \tag{5.20}$$

The last two cases are very instructive. The solution to the SCE (a wave equation) is a the sum of two (decaying/increasing) exponentials as the $V_0 - E$ is negative not an oscillating function (a sin or cosine). This is referred to as an evanescent wave or non-propagating wave.

As the wavefunction must be finite everywhere even at $x = \pm\infty$ we have

$$\psi(x) \quad = Ce^{\gamma x} \qquad x < -L/2 \tag{5.21}$$

$$\psi(x) \quad = Ee^{-\gamma x} \qquad x > L/2 \tag{5.22}$$

At the boundaries, $x = \pm L/2$ the wavefunction and its derivatives must be continuous which results in:

(a) $x = -L/2$

$$A \cos k\frac{L}{2} - B \sin k\frac{L}{2} = Ce^{-\gamma L/2} \tag{5.23}$$

$$Ak \sin k\frac{L}{2} + Bk \cos k\frac{L}{2} = C\gamma e^{-\gamma L/2} \tag{5.24}$$

(b) $x = L/2$

$$A \cos k\frac{L}{2} + B \sin k\frac{L}{2} = Ee^{-\gamma L/2} \tag{5.25}$$

$$-Ak \sin k\frac{L}{2} + Bk \cos k\frac{L}{2} = -E\gamma e^{-\gamma L/2} \tag{5.26}$$

The solution will give us a set of discrete k's, E's and γ's, similar to the infinite barrier condition.

> **Note:** *To find the unknown coefficients we will use the normalization condition (see 5.5) and some math operations which you can work out.*

The first few wave functions (corresponding to the lowest energy states) of the finite potential well are illustrated in figure 5. As we see the trail of the wavefunctions extend outside the well which is because of tunneling. Having said that classically since $E < V_0$ the particle would not pass the barrier. The corresponding probability densities for each of the wavefunctions in figure 5 are shown in figure 6

These quantum states are similar to the bound ones found for the infinite well. But, the electron is "leaking out" into the barrier. Very strange as the electron energy is less than the barrier height. Energy is not conserved! However, this turns out to be true for only very short times! Usually, the electron is found in the well.
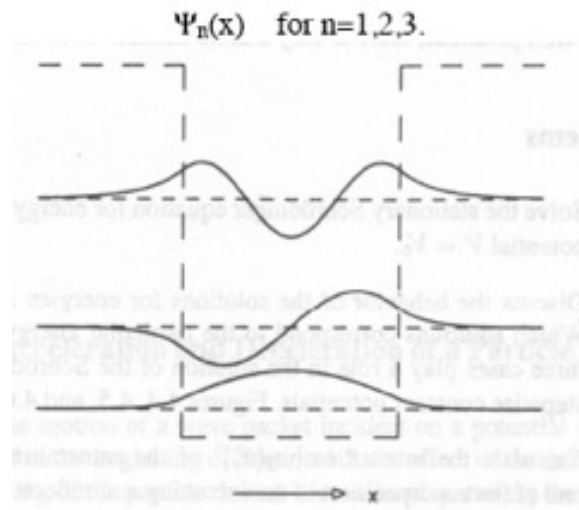
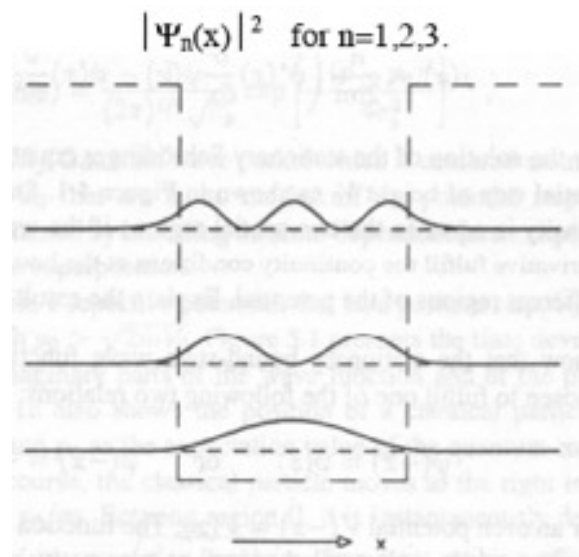**Figure 5.** First few wavefunction of a finite QW

Figure 6. Probabilities of the wavefunctions in figure 5

5.2.2. Unbound States

In case of $E > V_0$, the electron is no longer bounded and we have:

(a) $-L/2 < x < L/2$:

$$V(x) = 0$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{5.27}$$

$$\psi(x) = Ae^{jk_1x} + Be^{-jk_1x} \tag{5.28}$$

$$k_1 = \frac{\sqrt{2mE}}{\hbar} \tag{5.29}$$

Note that here we have continuos E's and k's.

(b) $x < -L/2$ or $x > L/2$:

$$V(x) = V_0$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V_0\psi(x) = E\psi(x) \tag{5.30}$$

$$\psi(x) = Ce^{jk_2x} + De^{-jk_2x} \tag{5.31}$$

$$k_2 = \frac{\sqrt{2m(E - V_0)}}{\hbar} \tag{5.32}$$

This is a similar to free electron case and so results in continuous E and k_2. However different values of energy gives us different continuous functions as k_2, see figure 7. We see that if the energy of the particle is close to that of the potential well, the particle "feels" the presence of the well, however, as the particles energy increases $E > V_0$, the effect of the potential well on the particle becomes negligible and the particle becomes completely free (unbound).
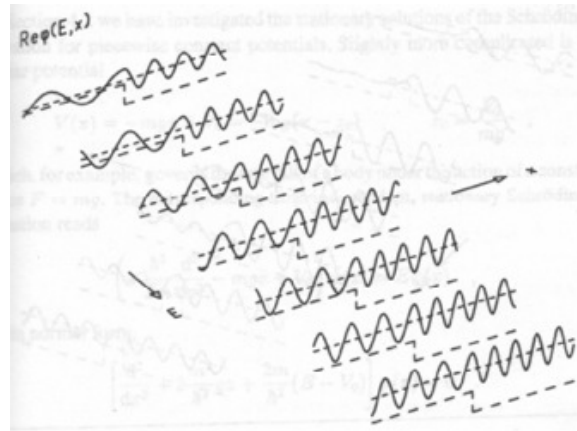
Figure 7. Unbound eigenstates

In summary, the allowed energy levels for a finite potential well has the following distribution as shown in figure 8.
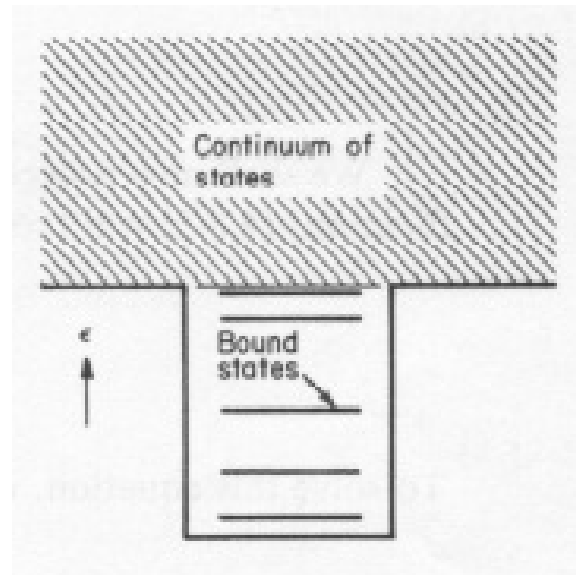

Figure 8. Energy levels in a finite QW

Note:*As a general rule in any region with a potential V_0; if $E > V_0$ we have oscillatory solutions (complex exponential) whereas if $E < V_0$ we have evanescent (real exponential) solutions.*

5.3. The Hydrogen Atom- Spherical Symmetry

A special and 3D case of the bound electron in a well is an atom. For an isolated Hydrogen atom, has one electron bounded to its nucleus by coulomb force as shown in figure 9. The potential energy is given by equation 5.33.
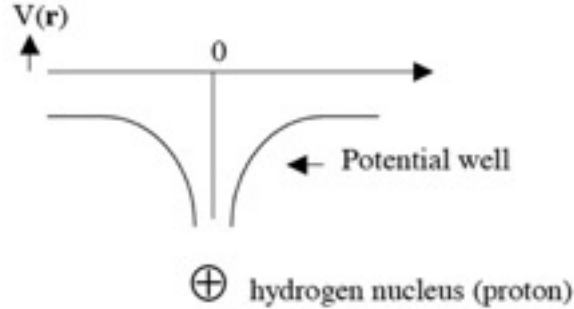

Figure 9. Hydrogen model

$$V(r) = \frac{-q^2}{4\pi\varepsilon_0 r} \tag{5.33}$$

Using equation 5.33 in Schrodinger equation we can analytically find the eigenstates for the Hydrogen atom. Since the mathematics is complicated we will only have the results in equations 5.34 and 5.35.

$$E_n = \frac{-m_0 q^4}{8\varepsilon_0^2 h^2 n^2} = \frac{-13.6}{n^2} \quad ev \qquad\qquad n = 1, 2, \cdots \tag{5.34}$$
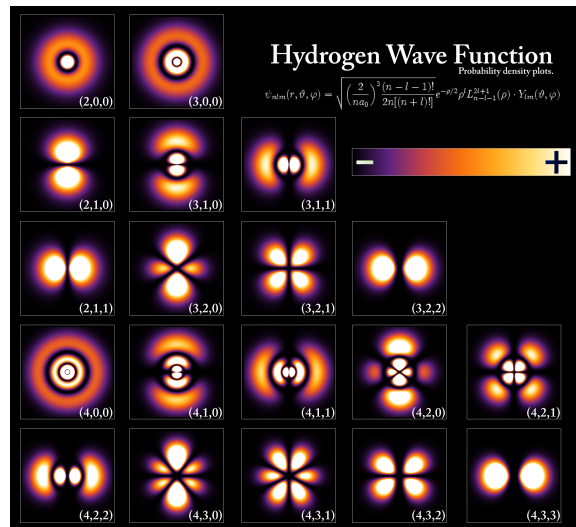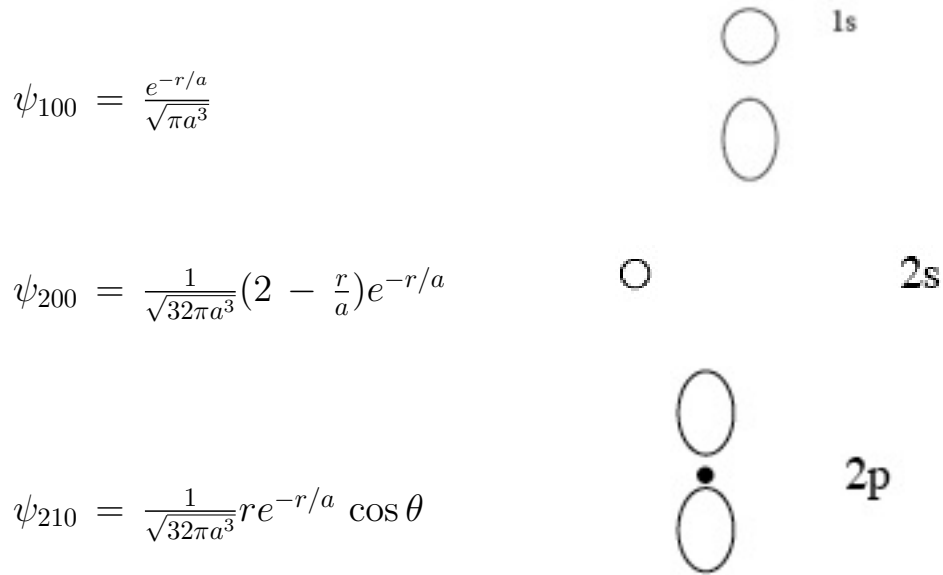
$$\psi_{nlm} = \sqrt{(\frac{2}{ma_0})^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-\rho/2} \rho^l \, L_{n-l-1}^{2l+1}(\rho).Y_l^m(\theta,\phi) \tag{5.35}$$

where we have

- Principle quantum number: $n = 1, 2, \cdots$
- Orbital quantum number: $l = 0, 1, 2, \cdots$
- Magnetic quantum number: $m = -l, -l+1, \cdots, l-1, l$
- $\rho = 2r/na_0$
- a_0:   Bohr radius
- $L_{n-l-1}^{2l+1}(\rho)$:   the laguerrer polynomials
- $Y_l^m(\theta,\phi)$:   spherical harmonic function

Table 2 shows few examples of the wavefunctions that describe the chemical states (orbitals):

Table 2. example orbitals

$$\psi_{100} = \frac{e^{-r/a}}{\sqrt{\pi a^3}}$$

1s

$$\psi_{200} = \frac{1}{\sqrt{32\pi a^3}}\left(2 - \frac{r}{a}\right)e^{-r/a}$$

2s

$$\psi_{210} = \frac{1}{\sqrt{32\pi a^3}}re^{-r/a}\cos\theta$$

2p

5.4. Implications of Quantized states

Because of the fact that the electron of an isolated atom can assume only certain energy levels, it follows that the energies which are excited or absorbed also posses only discrete values. The discrete E's produce spectral lines. if we have a transition from E_n to E_m then we will have a light at a particular frequency with energy $E_p = E_n - E_m$. (see figure 10)
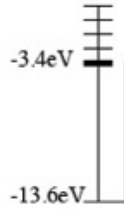
Figure 10. Characteristic photon energy

Application of quantum (discrete) energy:
- Semiconductor, Photonics, Laser
- Memory storage by storing information as excited states in molecules
- Input/Output signals using excitation and stimulated emission
- Quantum Computers; ground state $= 0$, 1_{st} excited state $= 1$. Use photons to switch states.

5.5. Appendix
Normalization the Wavefunction

As we said earlier the probability of finding the electron over all space must be 1 so we have the normalization condition defined as below.

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi.\Psi^* dr \; = \; 1 \qquad\qquad dr = dxdydz \qquad (5.36)$$

For the finite QW we have the wavefunctions in three regions as shown in figure 4 and so the normalization condition will be as below.

$$\int_{-\infty}^{\infty} \psi.\psi^* dx \; = \; \int_{-\infty}^{-L/2} \psi_I.\psi_I^* dx + \int_{-L/2}^{L/2} \psi_{II}.\psi_{II}^* dx + \int_{L/2}^{-\infty} \psi_{III}.\psi_{III}^* dx \; = \; 1$$

$$(5.37)$$