Quantum Mechanics

Lecture 2

Recall from the previous lecture: the Schrödinger equation for a particle of mass m in a 1D potential $V(x)$ is

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t) \qquad (2.1)$$

and its bound state wave function is square integrable and normalisable:

$$\int_{all\,space} |\psi|^2 \, dV = 1 \qquad (2.2)$$

We shall now derive the time independent Schrödinger equation and then apply it to particular cases.

Time independent Schrödinger equation (TiSE).

When the Hamiltonian has no explicit time dependence, the Schrödinger eqn can be separated by the substitution

$$\psi(x,t) = u(x)e^{-iEt/\hbar}$$

hence

$$\frac{\partial}{\partial t}\psi(x,t) = -i\frac{E}{\hbar}u(x)e^{-iEt/\hbar}$$

and after cancellation of the exponential factor we have

$$\boxed{\hat{H}u(x) = Eu(x)} \qquad (2.3)$$

where the function $u(x)$ is called the ***spatial*** wave function.

This is the time independent Schrödinger eqn. Mathematically speaking it is an ***eigenvalue equation:*** the solutions $u(x)$ are the ***eigenfunctions*** and the corresponding values of E are the ***eigenvalues***.

A system that is described by the TiSE is said to be in a ***stationary state***.

Continuity of the wave function and of its derivative.

We shall for the time being consider only stationary states, and we shall say **"wave function"** meaning the spatial wfn $u(x)$.

The 1D TiSE for a particle of mass m in the potential $V(x)$ is

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

or

$$u''(x)=\frac{2m}{\hbar^2}\left[V(x)-E\right]u(x) \qquad (2.4)$$

where $u''(x)\equiv d^2u(x)/dx^2$

Let us integrate this eqn from x_0 to x:

$$u'(x) = u'(x_0) + \frac{2m}{\hbar^2}\int_{x_0}^{x}\left[V(t) - E\right]u(t)\,dt$$

Now we ***postulate*** that the wfn is continuous everywhere.

This is plausible since the probability of finding the electron at two points separated by an infinitesimal distance should not change discontinuously.

Then, if the ***P.E.*** is continuous in the interval $[x_0, x]$, we have

$$u'(x) = u'(x_0) + \frac{2m}{\hbar^2}\left[V(x_0 + \theta\,\Delta x) - E\right]u(x_0 + \theta\,\Delta x)\,\Delta x$$

where $\theta \in [0,1]$ and $\Delta x = x - x_0$

and taking the limit $x \to x_{0+}$ *i.e.* $\Delta x \to 0$ we get

$$\boxed{\lim_{x \to x_{0+}}\left[u'(x) - u'(x_0)\right] = 0}$$

i.e. the derivative of the wfn is also continuous.

The requirement of continuity of the *P.E.* fn $V(x)$ is actually too strong: continuity of the derivative of the wfn can be shown also for *P.E.* fs with finite discontinuity – Exercise!

Only at points of infinite discontinuity of the *P.E.* fn does the derivative of the wfn exhibit a discontinuity.

In the following examples we shall apply these general results to particular cases.

Particle in *infinite* 1D square well

Recall the TiSE (2.2):

$$u''(x) + \frac{2m}{\hbar^2}\left[E - V(x)\right]u(x) = 0$$

or

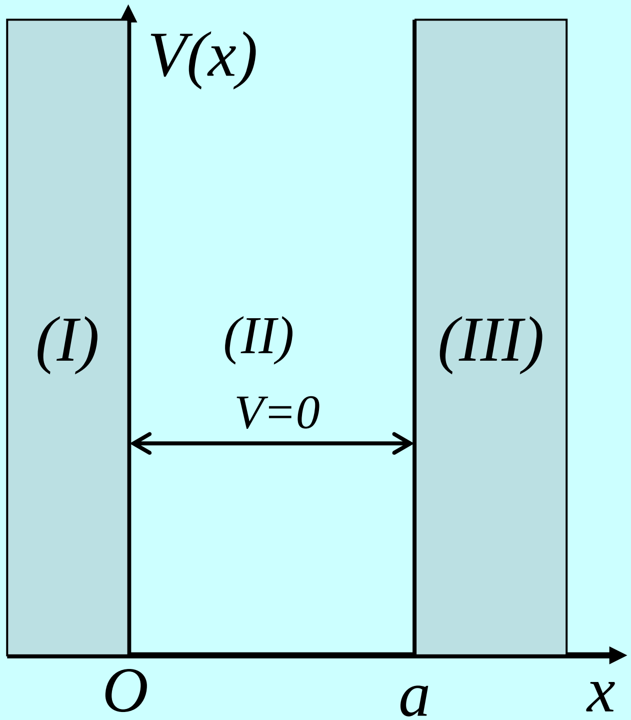
$$u''(x) + \left[\varepsilon - v(x)\right]u(x) = 0$$

where

$$\varepsilon = 2mE/\hbar^2, \quad v(x) = 2mV(x)/\hbar^2$$

For an infinite square well we have

$$v(x) = \begin{cases} 0 & \text{if} \quad 0 \le x \le a \\ \infty & \text{if} \quad x \le 0 \text{ or } x \ge a \end{cases}$$



In region *(I)* and *(III)*:

$$u_{I,III}(x) = 0$$

and in region *(II)* :

$$u''_{II}\left(x\right) + k^2 u_{II}\left(x\right) = 0$$

$$k^2 = \varepsilon = 2mE/\hbar^2 > 0$$

with general solution

$$u_{II}(x) = c_1 \cos kx + c_2 \sin kx$$

Continuity at $x=0$: $u_I\left(0\right) = u_{II}\left(0\right), \quad i.e. \quad 0 = c_1$

Continuity at $x=a$: $u_{II}\left(a\right) = u_{III}\left(a\right), \quad i.e. \quad 0 = c_2 \sin ka$

c_2=0 **?** **No:** if c_1=0 ***and*** c_2=0, then $u(x)=0$ identically, *i.e.* there is no physical state.

Therefore we must put

$$\sin ka = 0$$

hence

$$k_n a = n\pi, \quad n = 1, 2, 3, \cdots$$

and

$$E_n = \frac{\hbar^2}{2m} k_n^2 = n^2 \frac{\pi^2 \hbar^2}{2ma^2}, \quad n = 1, 2, 3, \cdots$$

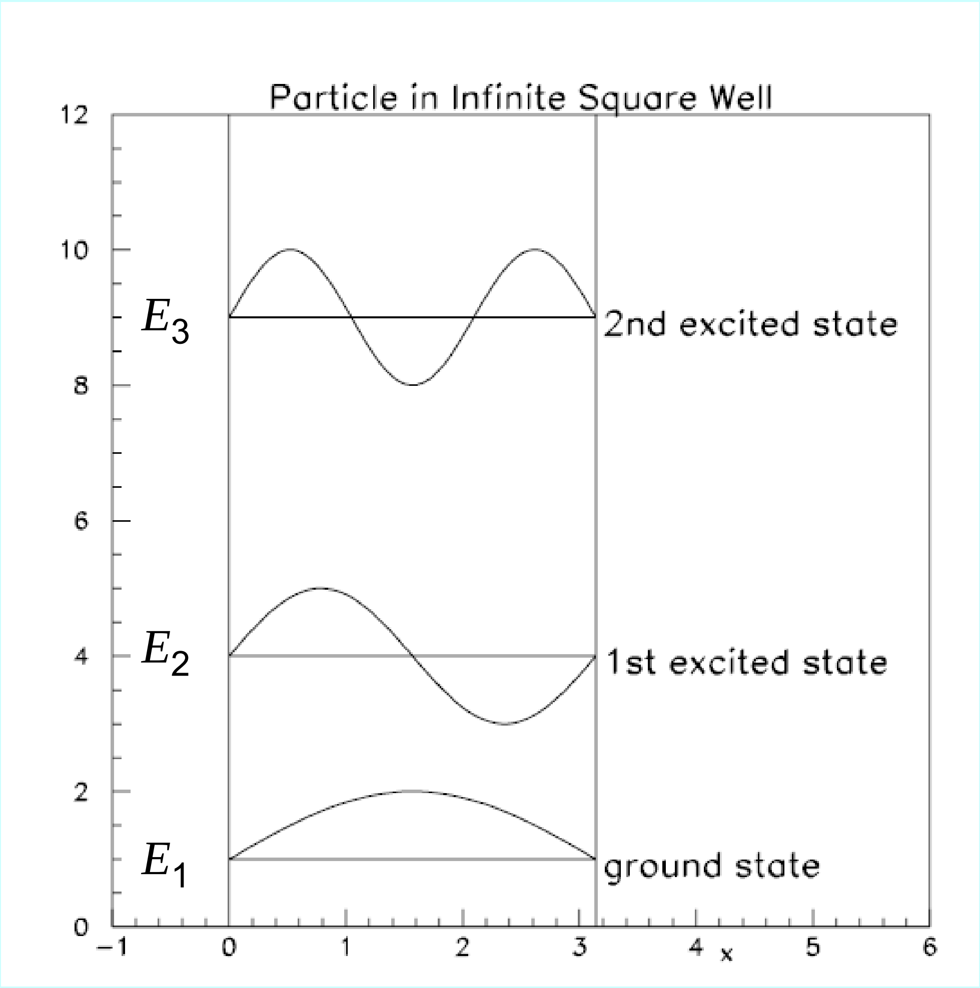
Example: electron in infinite sq well of atomic size

$m_e c^2$=0.5 MeV=0.5x10^6 eV, $\hbar c$=200 eV nm

hydrogen atom in its ground state (Bohr radius): a_B=0.05 nm

hence E_1=320 eV This is fairly large on an atomic scale

but not unreasonable, considering the artificial *P.E.* fn.



$$u_3(x) = \sin(3\pi x/a)$$

$$u_2(x) = \sin(2\pi x/a)$$

$$u_1(x) = \sin(\pi x/a)$$

Conclusions:

Continuity of the wave function, imposed on the general solution of the TiSE, has led to a set of ***discrete energy levels*** E_n.

The corresponding wave functions are square integrable and normalisable:

$$\int_{-\infty}^{\infty} u_n^2(x)\,dx = c_2^2 \int_0^a \sin^2(k_n x)\,dx = \frac{1}{2} a\, c_2^2 = 1$$

hence, with suitable choice of the phase of c_2:

$$c_2 = \sqrt{a/2}$$

We should note the difference with the behaviour of a classical particle in an infinite square well:

the energy of a classical particle is continuous!

Particle in finite *1D* square well

Consider the finite *1D* square well potential

$$V(x)=\begin{cases}0 & \text{if} \quad x\le -a & (I)\\ V_0 & \text{if} \quad -a\le x\le a & (II)\\ 0 & \text{if} \quad x\ge a & (III)\end{cases}$$

We are looking for solutions of the TiSE with $E<0$ (bound states).

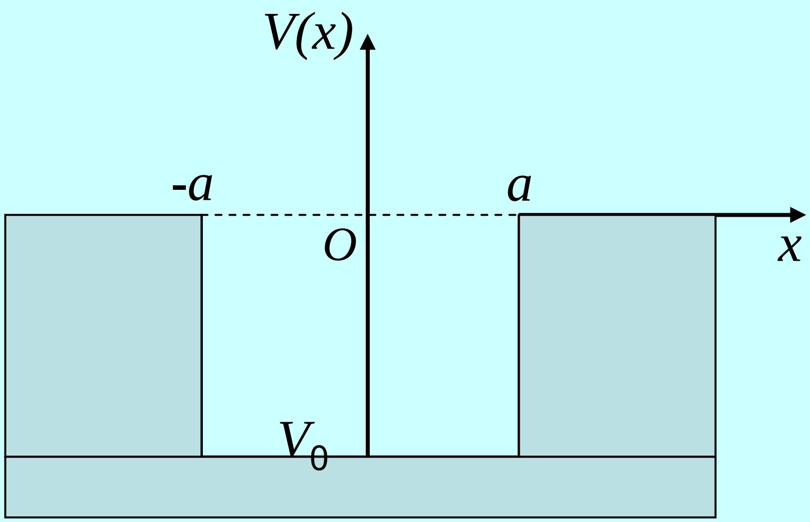
Because of the discontinuities of $V(x)$ we must write down the TiSE for the three regions separately:

$$u_I''(x)-\kappa^2 u_I(x)=0$$
$$u_{II}''(x)+k^2 u_{II}(x)=0$$
$$u_{III}''(x)-\kappa^2 u_{III}(x)=0$$

where

$$\kappa^2=-2mE/\hbar^2; \quad k^2=\left(2m/\hbar^2\right)\left[E-V_0\right]$$

Finite square well potential of width $2a$ and depth $V_0 < 0$



We make use of the symmetry of the *P.E.* fn: $V(-x)=V(x)$

(i) If $|x| \le a$ then we are in region II, and if we apply the transformation $x \to -x$ then we remain in region II. Therefore

$$u_{II}''(-x)+k^2 u_{II}(-x)=0$$

Now define

$$u_2^{(\pm)}(x)=\frac{1}{\sqrt{2}}\left(u_{II}(x)\pm u_{II}(-x)\right)$$

then

$$u_2^{(\pm)}(-x)=\pm u_2^{(\pm)}(x)$$

i.e. $u_2^{(+)}(x)$ is an even fn and $u_2^{(-)}(x)$ is an odd fn of x

and they satisfy the DEq.

$$u_2^{(\pm)\prime\prime}(x)+k^2 u_2^{(\pm)}(x)=0$$

with solutions

$$u_2^{(+)} = C^{(+)} \cos x; \quad u_2^{(-)}(x) = C^{(-)} \sin x$$

(ii) assume $x > a$, *i.e.* we are in region (III) and the wfn satisfies

$$u_{III}''(x) - \kappa^2 u_{III}(x) = 0$$

with the general solution

$$u_{III}(x) = Ae^{\kappa x} + Be^{-\kappa x}$$

But to be square integrable, the wfn must tend to zero for $x \to \infty$

hence $A=0$, *i.e.*

$$u_{III}(x) = Be^{-\kappa x}, \quad (x > a)$$

Similarly we find in region (I), $(x < -a)$

$$u_I(x) = De^{\kappa x}, \quad (x < -a)$$

Now we impose symmetry:

$$u_{III}^{(+)}(x) = u_{I}^{(+)}(-x)$$

hence

$$\boxed{B^{(+)} = D^{(+)}}$$

and if we impose antisymmetry:

$$u_{III}^{(-)}(x) = -u_{I}^{(-)}(-x)$$

then

$$\boxed{B^{(-)} = -D^{(-)}}$$

<u>Summary:</u>

$$\boxed{\begin{aligned} u_{I}^{(\pm)}(x) &= \pm B^{(\pm)} e^{\kappa x}, \quad (x < -a); \\ u_{III}^{(\pm)}(x) &= B^{(\pm)} e^{-\kappa x}, \quad (x > a); \end{aligned}}$$

The symmetric (antisymmetric) solutions are also called solutions of positive (negative) ***parity***.

To complete the calculation we must impose continuity of the wave functions at $x=-a$ and $x=a$

Let us do this first for the positive parity solutions.

$$u_I^{(+)}(-a) = u_2^{(+)}(-a)$$
$$\text{and} \quad u_I^{(+)\prime}(-a) = u_2^{(+)\prime}(-a)$$

$\rightarrow$

$$B^{(+)}e^{-\kappa a} = C^{(+)}\cos ka$$
$$\kappa B^{(+)}e^{-\kappa a} = kC^{(+)}\sin ka$$

and putting $\xi = ka; \eta = \kappa a$ and dividing the equations, we get

$$\eta = \xi \tan \xi \qquad (2.5)$$

Recall the definition of k and κ:

$$\kappa^2 = -2mE/\hbar^2; \quad k^2 = \left(2m/\hbar^2\right)\left[E - V_0\right]$$

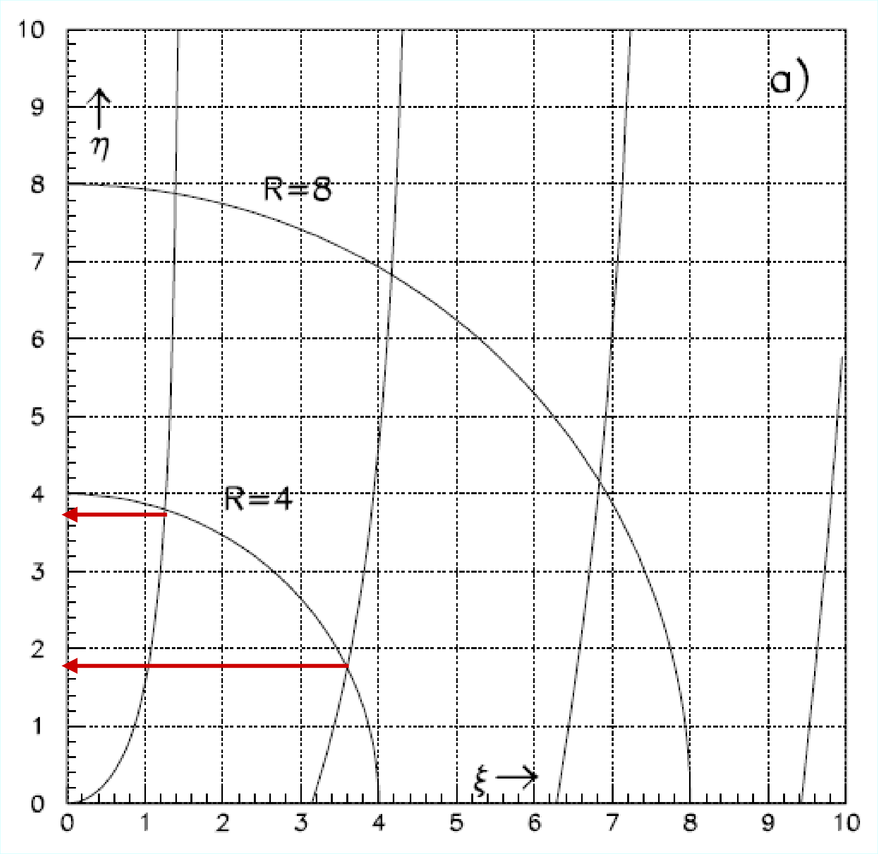
and since $V_0<0$:

$$k^2 + \kappa^2 = \left(2m/\hbar^2\right)\left|V_0\right|$$

$$\boxed{\xi^2 + \eta^2 = R^2} \qquad (2.6)$$

where $\quad R^2 = \left(2ma^2/\hbar^2\right)|V_0|$

The curves (2.5) and (2.6) are shown in the following figure:



The energy eigenvalues can be found from the intersections of the curves.

For example: for R=4 we find two roots, one near $\boldsymbol{\eta}$ = 1.8 and a second one near 3.7

and with

$$\eta^2 = \kappa^2 a \;\; = -2ma^2 E/\hbar^2$$

$$\boxed{\begin{aligned} E &= -\eta^2\,\hbar^2/2ma^2 \\ &= -|V_0|\left(\eta^2/R^2\right) \end{aligned}}$$

The greatest value of η corresponds to the lowest value of the energy, i.e. to the ***ground state energy***.

We see from the figure that there are two energy levels for R=4 and three levels for R=8.

Taking the approximate values of η which we have read off the figure for R=4, we find

$$E_1^{(+)} = -0.86|V_0|$$

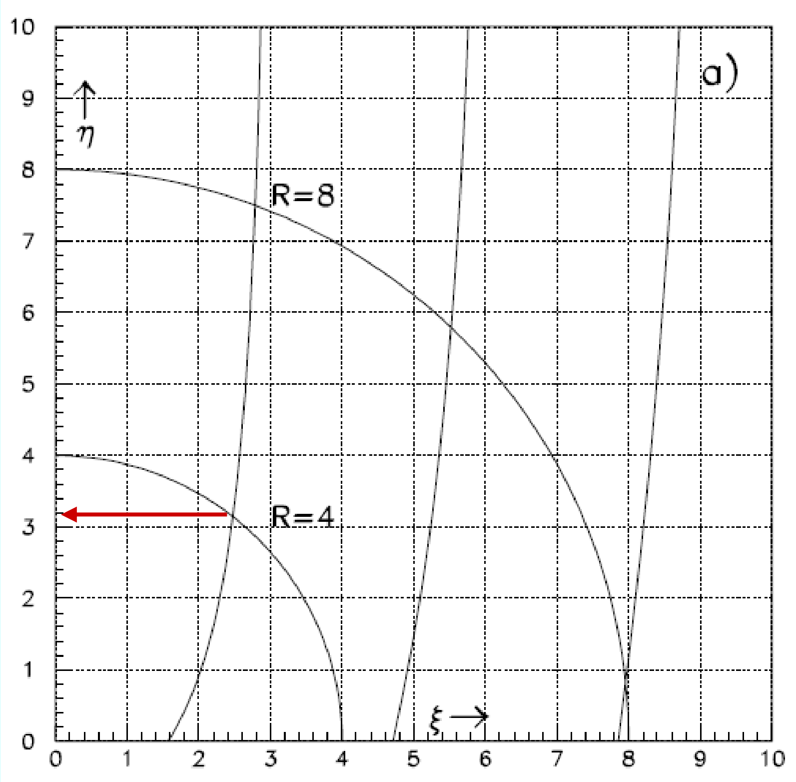
$$E_2^{(+)} = -0.20|V_0|$$

If more accurate values need to be found, then one has to resort to numerical methods to solve the equations (2.5) and (2.6).

Negative parity solutions.

The continuity conditions applied to the negative parity solutions give the following result (***Exercise!***):

$$\eta = -\xi \cot \xi \qquad (2.7)$$



This set of curves together with (2.6) is shown in the figure.

For R=4 there is only one negative parity level, corresponding to $\boldsymbol{\eta}$ = 3.2 (approximately).

The energy eigenvalue is

$$E_1^{(-)} = -0.64|V_0|$$

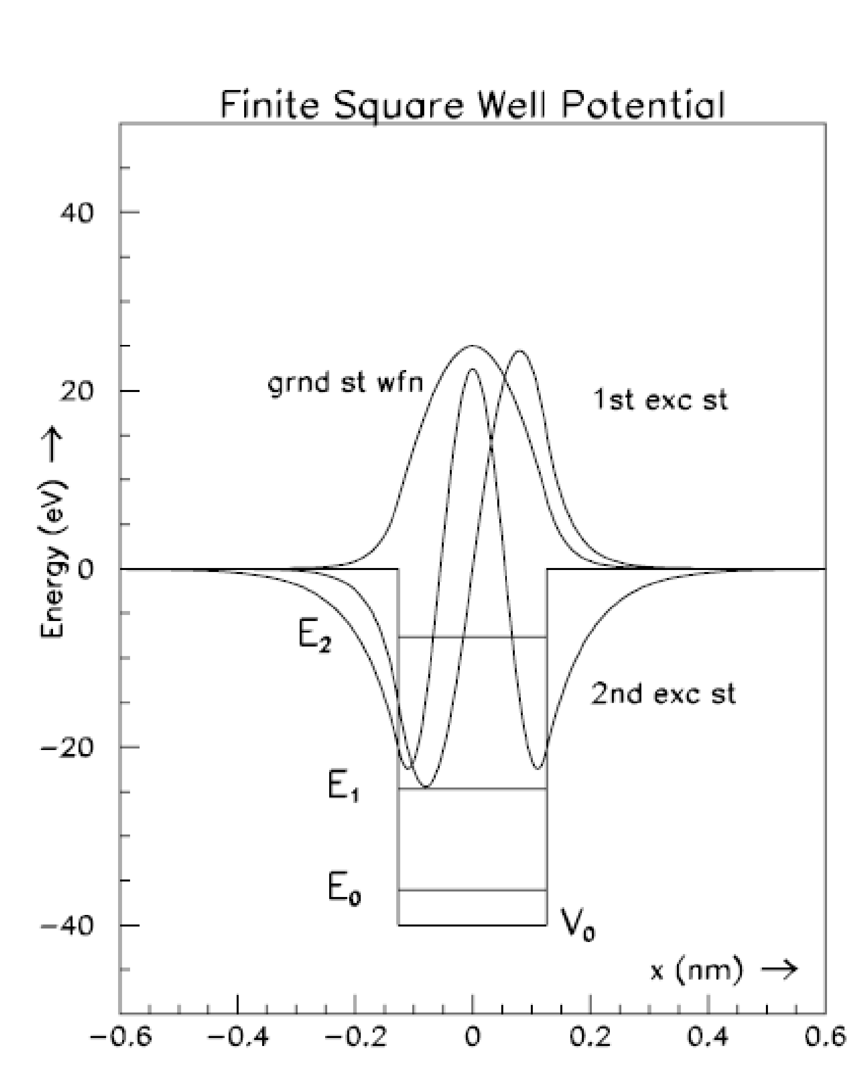
and we note that

$$E_1^{(+)} < E_1^{(-)} < E_2^{(+)}$$

Conclusions:

- In a finite square well there is at least one energy level.
- if the *P.E.* fn is symmetric, then the ground state has positive parity, the first excited state has negative parity, *etc*.

An example of a square well with three energy levels is shown in the next figure where I have also plotted the wave functions of the three states corresponding to these levels.



Energy levels and wave functions of an electron in a finite square well:

$$V_0 = -40\,\text{eV}$$

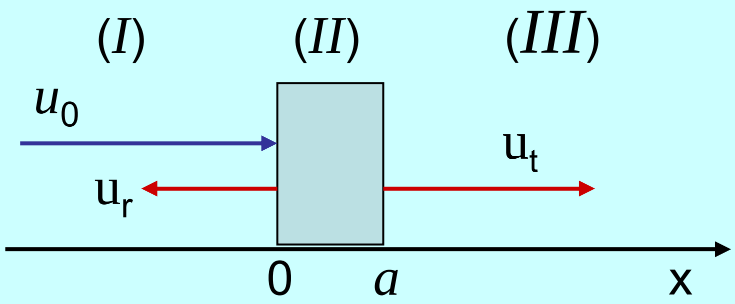
$$2\text{a} \simeq 2.5\,\text{nm}$$

The constants were taken with approximate values:

$$m_e = 0.5\,\text{MeV}/c^2$$

$$\hbar c = 200\,\text{eV nm}$$

Square Barrier Potential



$$V(x) = \begin{cases} 0 & \text{for} \quad x \leq 0 \qquad (I) \\ V_0 > 0 & \text{for} \quad 0 \leq x \leq a \; (II) \\ 0 & \text{for} \quad x \geq 0 \qquad (III) \end{cases}$$

u_0 is the incident wave

u_r is the reflected wave

u_t is the transmitted wave

Two cases are of interest:

(i) $E < V_0$

(ii) $E > V_0$

(i) Case 1: $E < V_0$

TiSE:

$$u_I''(x) + k^2 u_I(x) = 0, \quad k^2 = 2mE/\hbar^2$$

$$u_{II}''(x) - \kappa^2 u_{II}(x) = 0, \quad \kappa^2 = 2m(V_0 - E)/\hbar^2$$

$$u_{III}''(x) + k^2 u_{III}(x) = 0$$

General solution:

$$u_I(x) = Ae^{ikx} + Be^{-ikx}$$

$$u_{II}(x) = Ce^{\kappa x} + De^{-\kappa x}$$

$$u_{III}(x) = Fe^{ikx} + Ge^{-ikx}$$

No wave incident from the right: $G = 0$

Continuity at $x = 0$ and $x = a$:

$$u_I(0) = u_{II}(0)$$

$$u_I'(0) = u_{II}'(0)$$

$$u_{II}(a) = u_{III}(a)$$

$$u_{II}'(a) = u_{III}'(a)$$

$$A + B = C + D$$
$$ik(A - B) = \kappa(C + D)$$

$$Ce^{\kappa a} + De^{-\kappa a} = Fe^{ika}$$
$$\kappa\left(Ce^{\kappa a} - De^{-\kappa a}\right) = ikFe^{ika}$$

After a fairly lengthy calculation we get the following result:

$$R = \left|\frac{B}{A}\right|^2 = \frac{V_0^2 \sinh^2 \kappa a}{4E(V_0 - E) + V_0^2 \sinh^2 \kappa a}$$

$$T = \left|\frac{F}{A}\right|^2 = \frac{4E(V_0 - E)}{4E(V_0 - E) + V_0^2 \sinh^2 \kappa a}$$

R is the ***reflection coefficient***

T is the ***transmission coefficient***

$$T + R = 1$$

Discussion:

Contrary to classical expectation, the particle is not completely reflected by the barrier:

partly it is reflected and partly it is transmitted.

But part of an electron is never observed, so our result must have another meaning.

This lies in the probability interpretation proposed by Max Born and universally accepted:

R is the probability of the particle being reflected

T is the probability of the particle being transmitted

The result $R + T = 1$ means that the total probability of the particle being reflected ***or*** transmitted is ***certainty.***

Derivation: Recall the equation which express continuity of the wfn and its derivative:

Continuity at x=0

$$A+B=C+D \tag{3.1}$$

$$ik\left(A-B\right)=\kappa\left(C-D\right) \tag{3.2}$$

Continuity at $x=a$:

$$Ce^{\kappa a}+De^{-\kappa a}=Fe^{ika} \tag{3.3}$$

$$\kappa\left(Ce^{\kappa a}-De^{-\kappa a}\right)=ikFe^{ika} \tag{3.4}$$

i.e. we have 4 equations for 5 coefficients (amplitudes).

Our strategy will be to express B and F in terms of A:

B is the amplitude of the reflected wave,

F is the amplitude of the transmitted wave.

C and D are of no interest; we shall eliminate them

$$(3.2)/\kappa+(3.1): \quad C=\frac{1}{2}\left[A+B+i\lambda(A-B)\right] \qquad (3.5)$$

$$(3.2)/\kappa-(3.1): \quad D=\frac{1}{2}\left[A+B-i\lambda(A-B)\right] \qquad (3.6)$$

$$(3.4)/\kappa+(3.3): \qquad C=\frac{1}{2}Fe^{(ik-\kappa)a}(1+i\lambda) \qquad (3.7)$$

$$(3.4)/\kappa-(3.3): \qquad D=\frac{1}{2}Fe^{(ik+\kappa)a}(1-i\lambda) \qquad (3.8)$$

where $\lambda = k/\kappa$. Thus

$$Fe^{(ik-\kappa)a}(1+i\lambda)=\left[A+B+i\lambda(A-B)\right]=A(1+i\lambda)+B(1-i\lambda)$$

$$Fe^{(ik+\kappa)a}(1-i\lambda)=\left[A+B-i\lambda(A-B)\right]=A(1-i\lambda)+B(1+i\lambda)$$

Eliminate $\boldsymbol{F}e^{ika}$, hence

$$A\left(1+\lambda^2\right)\left(e^{\kappa a}-e^{-\kappa a}\right)=B\left[\left(1+i\lambda\right)^2 e^{-\kappa a}-\left(1-i\lambda\right)^2 e^{\kappa a}\right]$$

or

$$\frac{B}{A}=\frac{\left(1+\lambda^2\right)\left(e^{\kappa a}-e^{-\kappa a}\right)}{\left(1+i\lambda\right)^2 e^{-\kappa a}-\left(1-i\lambda\right)^2 e^{\kappa a}}$$

$$=\frac{\left(1+\lambda^2\right)\sinh\kappa a}{2i\lambda\cosh\kappa a-\left(1-\lambda^2\right)\sinh\kappa a}$$

and taking the mod-square we get

$$\left|\frac{B}{A}\right|^2=\frac{\left(1+\lambda^2\right)^2\sinh^2\kappa a}{4\lambda^2\cosh^2\kappa a+\left(1-\lambda^2\right)^2\sinh^2\kappa a}$$

and using the identity $\cosh^2 x - \sinh^2 x = 1$ we get

$$\left|\frac{B}{A}\right|^2 = \frac{\left(1+\lambda^2\right)^2 \sinh^2 \kappa a}{4\lambda^2 + \left(1+\lambda^2\right)^2 \sinh^2 \kappa a}$$

Now recall:

$$k^2 = 2mE/\hbar^2, \quad \kappa^2 = 2m\left(V_0 - E\right)/\hbar^2$$

hence

$$\lambda^2 = \frac{E}{V_0 - E}, \quad \text{and} \quad 1+\lambda^2 = \frac{V_0}{V_0 - E}$$

and thus finally

$$R = \left|\frac{B}{A}\right|^2 = \frac{V_0^2 \sinh^2 \kappa a}{4E\left(V_0 - E\right) + V_0^2 \sinh^2 \kappa a}$$

and similarly we get the formula for $T=|F/A|^2$

(ii) Case 2: $E > V_0$

For $E>V_0$ we can similarly find the formulae for R and T (**Exercise**):

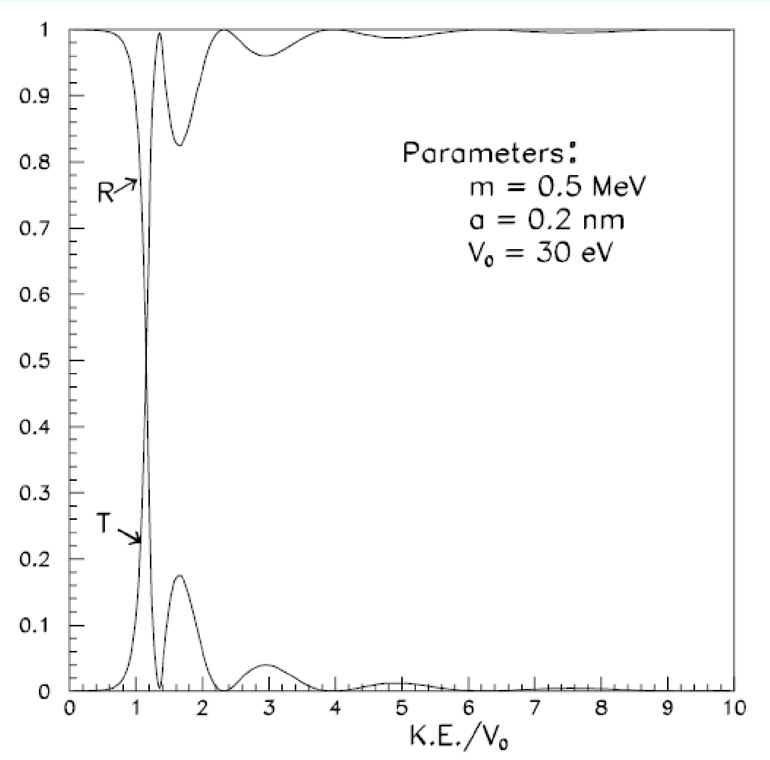
$$R = \left|\frac{B}{A}\right|^2 = \frac{V_0^2 \sin^2 \kappa a}{4E\left(E - V_0\right) + V_0^2 \sin^2 \kappa a}; \quad \kappa^2 = 2m\left(E - V_0\right)/\hbar^2$$

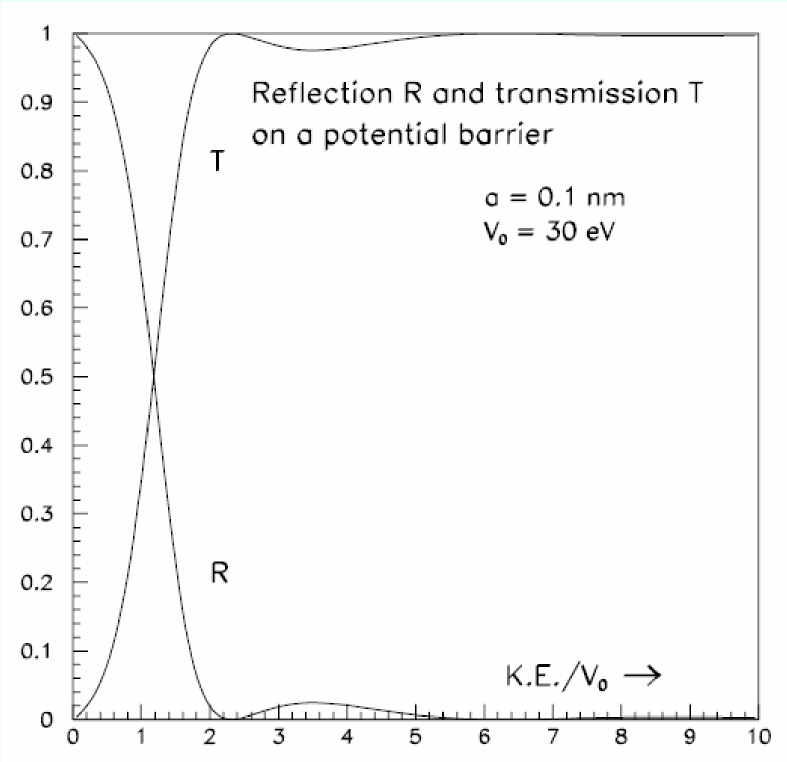
But we do not need to rederive the formulae: just note that they are related by the transformation $\kappa^2 \rightarrow -\kappa^2$

(iii) Case 3: $E = V_0$

Exercise: derive the formulae for this case (a) directly from the TiSE and (b) from the results of Cases 1 and 2 by taking the appropriate limit.

In the following figures I am showing two examples of curves of R and T for different choices of parameters.


Parameters:
m = 0.5 MeV
a = 0.2 nm
V_0 = 30 eV
R
T
K.E./V_0


Reflection R and transmission T
on a potential barrier
a = 0.1 nm
V_0 = 30 eV
T
R
K.E./V_0 →