Quantum mechanics in 1D

Note Title 2/22/2017

Time dependent Schrödinger equation

[my discussions here will not follow exactly Taylor et al. but still cover similar content]

The de Broglie wave $\psi(\vec{r},t)$ is governed by Schrödinger's equation (SE)

$$i\hbar \frac{\partial}{\partial t}\Psi(\vec{r},t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t) + V(\vec{r},t)\,\Psi(\vec{r},t) \qquad \text{(Time-dependent SE)}$$

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

Laplacian

potential (which we will mostly consider to be independent of time i.e. $V(\vec{r})$).

In one dimension:

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

which you may want to compare with the usual wave equation

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\xi(x,t) = \frac{\partial^2}{\partial x^2}\xi(x,t) \qquad \text{e.g. } \xi(x,t) = A\sin(kx-\omega t)$$

plug in

$$\frac{1}{c^2}(-\omega^2)\,A\sin(kx-\omega t) = -k^2 A\sin(kx-\omega t)$$

$$c^2 = \frac{\omega^2}{k^2} \Leftarrow$$

As in the wave phenomena, the superposition principle allows to construct many solutions [Recall a standing wave from two counter propagating waves $\rightarrow$ $\leftarrow$]

If $\Psi_1(x,t)$ & $\Psi_2(x,t)$ are each solutions to TDSE, then $a\Psi_1(x,t) + b\Psi_2(x,t)$ is another valid solution.

Mathematical trick: Separation of variable

1D TDSE is an equation of 2 variables, one can first try simple solution $\Psi(x,t) = \phi(t)\,\psi(x)$

and if we find many such solutions $\phi_i(t)\,\psi_i(x)$, then $\sum_i c_i\,\phi_i(t)\,\psi_i(x)$ is also a solution

Time Independent SE :

Applying the above strategy, let's plug $\underset{\phi(t)\,\psi(x)}{\underset{\shortparallel}{\Psi(x,t)}}$ in TDSE

$$i\hbar \frac{d\phi(t)}{dt}\,\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)\,\phi(t) + V(x)\,\psi(x)\,\phi(t)$$

$\overline{\phi(t)\,\psi(x)}$

$$i\hbar \frac{d\phi(t)}{dt}\,\frac{1}{\phi(t)} = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}\psi(x)\right)\frac{1}{\psi(x)} + V(x) \underset{\text{a constant}}{\overset{\text{must be}}{\equiv}} E$$

(eigen/stationary) energy

① $\phi(t) = e^{-i\frac{E}{\hbar}t}$ is a solution

② Then we arrive at the time independent SE (TISE)

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

The solution $\Psi(x,t) = \psi(x)\,e^{-i\frac{E}{\hbar}t}$ $\qquad \omega = \frac{E}{\hbar}$ (one of de Broglie's relations)

The other de Broglie relation is $\lambda = \frac{h}{p}$ or $k = \frac{2\pi}{\lambda} = \frac{p\cdot 2\pi}{h} = \frac{p}{\hbar}$

From simple sinusoidal wave $A\sin(kx-\omega t)$, we expect that a wave function $\Psi(x,t) = A\,e^{i(kx-\omega t)}$ may represent a free particle :

[i.e. $\psi(x) = A e^{ikx}$

$$-\frac{\hbar^2}{2m}(-k^2)\,e^{ikx} + V(x)\,e^{ikx} = E\,e^{ikx}$$

i.e. $V(x) = V_0$ const.

$$\boxed{\underset{\hbar\omega}{\underset{\shortparallel}{E}} = \frac{\hbar^2k^2}{2m} + V_0 = \frac{p^2}{2m} + V_0}$$

Note that the form $\Psi(x,t) = e^{-i\omega t}\psi(x)$ has probability density $|\Psi(x,t)|^2 = |\psi(x)|^2$ independent of time, this is also called a stationary solution.

We also note that a free particle wavefunction

$\psi(x) = A e^{ikx}$ has $|\psi(x)|^2 = |A|^2$ probability being constant everywhere, it is infinitely extended and is not very physical as $|\psi(x)|^2$ is not normalizable if it is regarded as a probability density $\int dx\, |\psi(x)|^2 = 1$ but $\int_{-\infty}^{\infty} dx |A|^2 = \infty$!

As you may also expect from our discussion of a wavepacket we need a range of k $(k-\Delta k, k+\Delta k)$ involved in order to localize the particle to $(x-\Delta x, x+\Delta x)$ but we will have $\Delta k\, \Delta x \gtrsim \frac{1}{2}$.

✡ Since $E = \frac{p^2}{2m} + V(x)$, in QM p becomes an operator $p = \frac{\hbar}{i}\frac{d}{dx}$, so $p^2 = -\hbar^2 \frac{d^2}{dx^2}$

Normalization : According to Max Born, $|\Psi|^2$ is probability density $\Rightarrow$

$$\int_{-\infty}^{\infty} dx\, |\Psi(x,t)|^2 = 1 \quad \text{for any wavefn } \Psi(x,t).$$

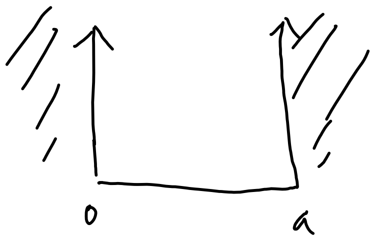
in particular for stationary solution $\psi(x)$: $\int_{-\infty}^{\infty} dx\, |\psi(x)| = 1$

In the above we have seen the example of a free particle (i.e. $V(x) = V_0$ constant potential, i.e. no force is applied).

In the following, we will discuss cases for different potential $V(x)$.

(Our goal is to understand the case of a Coulomb potential $V(r) = -\frac{kqe}{r}$ so we can understand properties of an atom.)

Infinite square well / Rigid box



$$V(x) = \begin{cases} 0 & \text{if} \quad x \in (0, a) \\ \infty & \text{otherwise} \end{cases}$$

is a potential that describe a rigid box.

Recall that for a particle confined in such a region, the uncertainty principle predicts a minimum energy $\langle K \rangle \gtrsim \frac{\hbar^2}{2ma^2}$ $\quad \Delta k \geq \frac{1}{2\Delta x} = \frac{1}{a}$ $\quad \frac{\hbar^2}{2m}\frac{1}{a^2}$

Let us find out what QM really predicts.

First we expect $\psi(x) = 0$ outside $x \in (0, a)$, so we only need to focus in the region $(0, a)$, for which the TISE is

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

For convenience, we define $E = \frac{\hbar^2 k^2}{2m}$, then

$$-\frac{d^2\psi(x)}{dx^2} = k^2\,\psi(x)$$

This is a second-order differential equation, we will either guess solutions or employ mathematics. We know free particle $e^{\pm ikx}$ satisfies the equation (by inspection) and since $e^{\pm ikx} = \cos kx \pm i \sin kx$, this means we may as well use $\sin kx$ and $\cos kx$.

So we conclude that $\psi(x) = A \sin kx + B \cos kx$

but there are two unknowns A & B!

To determine A & B, we need two boundary conditions,
i.e. we need to know $\psi(x)$ at two different places.

At the walls, $\psi(x)\Big|_{x=0,a} = 0$ just like a string fixed at both ends.

So ① $\psi(0) = 0, \Rightarrow \quad A \cdot 0 + B \cdot 1 = 0 \Rightarrow B = 0$

② $\psi(a) = 0 \quad A \sin ka = 0$ [we cannot find A. (which cannot be zero)

but find $\sin ka = 0 \Rightarrow ka = n\pi$ (n = integer $\neq 0$ can take +)

$\Rightarrow k_n = \frac{n\pi}{a}$

thus $\psi_n(x) = A_n \sin k_n x = A_n \sin \frac{n\pi x}{a}$ [negative n does not give new solutions & n cannot be zero $\Rightarrow$ otherwise $\psi_0 = 0$]

The energy associated with the stationary solution $\psi_n(x)$ is $E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n\hbar^2\pi^2}{2ma^2}$

Since the smallest is $E_1 = \frac{\hbar^2\pi^2}{2ma^2}$ cf. $\langle K \rangle_{min} = \frac{\hbar^2}{2ma^2}$ from uncertainty principle.

$\Rightarrow$ energy is quantized

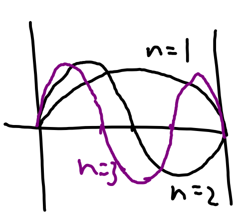
Normalization: A_n can be found from $\int_0^a dx \, |\psi_n(x)|^2 = 1$

$$|A_n|^2 \int_0^a dx \, \underbrace{\sin^2 \frac{n\pi x}{a}}_{\frac{1-\cos 2n\pi x}{2}} = |A_n|^2 \, a \cdot \frac{1}{2} = 1 \quad \text{take } A_n = \sqrt{\frac{2}{a}}$$

$$\frac{1}{4n\pi} \sin 2\pi n x \Big|_0^a = 0$$

$$\Downarrow$$

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$



classical analogy: standing wave $a = n \cdot \frac{\lambda}{2} \Rightarrow \lambda = \frac{2a}{n} \Rightarrow k_n = \frac{2\pi}{\lambda} = \frac{\pi n}{a}$

$\Psi_n(x,t) = \psi_n(x) e^{-i\omega_n t}$ $\qquad \omega_n = \frac{E_n}{\hbar}$

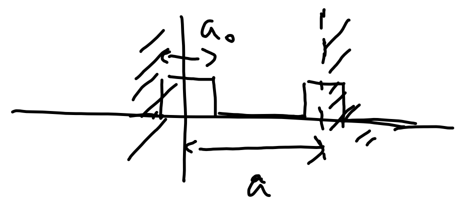
The most general solution for Time-dependent SE is

$$\Psi(x,t) = \sum_n c_n \Psi_n(x,t) = \sum_n c_n \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}\, e^{-i\frac{n\hbar\pi^2}{2ma^2}t}$$

If we are given an initial wavefunction $\Psi(x,0)$ then we can find c_n

$$\Psi(x,0) = \sum_n c_n \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a} \qquad \text{via Fourier series}$$

$$c_n = \sqrt{\frac{2}{a}} \int_0^a dx\, \sin\frac{n\pi x}{a}\, \Psi(x,0) \qquad \text{e.g.}$$



Similar to what we have analyzed before

Example 7.1

Verify explicitly that the function (7.52) is a solution of the Schrödinger equation (7.51) for any values of the constants A and B. [This illustrates part of the theorem stated in connection with (7.49).]

To verify that a given function satisfies an equation, one must substitute the function into one side of the equation and then manipulate it until one arrives at the other side. Thus, for the proposed solution (7.52),

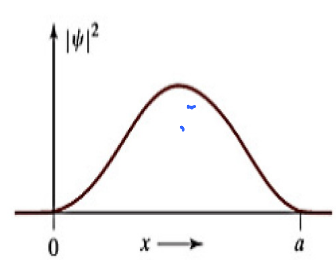
$$\psi''(x) = \frac{d^2}{dx^2}(A\sin kx + B\cos kx)$$

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

(7.51) $\psi''(x) = -k^2\psi(x)$

Example 7.2

Consider a particle in the ground state of a rigid box of length a. **(a)** Find the probability density $|\psi|^2$. **(b)** Where is the particle most likely to be found? **(c)** What is the probability of finding the particle in the interval between $x = 0.50a$ and $x = 0.51a$? **(d)** What is it for the interval $[0.75a, 0.76a]$? **(e)** What would be the average result if the position of a particle in the ground state were measured many times?



(a) GS. $\psi_1(x) = \sqrt{\frac{2}{a}} \sin\frac{\pi x}{a}$, $P(x) = |\psi_1(x)|^2 = \frac{2}{a}\sin^2\frac{\pi x}{a} = \frac{1}{a}\left(1 - \cos\frac{2\pi x}{a}\right)$

(b) maximal at $\frac{\pi x}{a} = \frac{\pi}{2} \Rightarrow x = \frac{a}{2}$, $P(x) = \frac{2}{a}$

(c)

$$P_{[0.5a,\,0.51a]} = \int_{0.5a}^{0.51a} dx\ \frac{1}{a}\left[1-\cos\frac{2\pi x}{a}\right] = 0.01 - \frac{1}{2\pi}\sin\frac{2\pi x}{a}\Big|_{0.5a}^{0.51a} = 0.01 - \frac{1}{2\pi}\left(\sin 2\pi\cdot 0.51 - 0\right]$$

$\sin 1.02\pi \approx -\sin 0.02\pi \approx -0.02\pi$

But can do $P_{[0.5a,\,0.51a]} \approx |\psi(0.5a)|^2 \Delta x = \frac{2}{a}\cdot 0.01a \approx 0.02$

(d)

$$P_{[0.75a,\,0.76a]} = \int_{0.75a}^{0.76a} dx\ \frac{1}{a}\left[1-\cos\frac{2\pi x}{a}\right] = 0.01 - \frac{1}{2\pi}\sin\frac{2\pi x}{a}\Big|_{0.75a}^{0.76a}$$

$$= 0.01 - \frac{1}{2\pi}\left[\sin 2\pi\cdot 0.76 - \sin 2\pi\cdot 0.75\right]$$

Can do $P \approx |\psi(0.75a)|^2 \Delta x \approx \frac{1}{a}\cdot 0.01a \approx 0.01$

(e)

$$\bar{x} = \int_0^a dx\ x\cdot P(x) = \frac{1}{a}\int_0^a dx\ x\left[1-\cos\frac{2\pi x}{a}\right] = \frac{1}{a}\frac{a^2}{2} - \frac{1}{a}\int_0^a dx\ x\ \frac{a}{2\pi}\left(\sin\frac{2\pi x}{a}\right)'$$

$$= \frac{a}{2} - \frac{1}{a}\left[x\,\frac{a}{2\pi}\sin\frac{2\pi x}{a}\Big|_0^a - \int_0^a dx\ \frac{a}{2\pi}\sin\frac{2\pi x}{a}\right] = \frac{a}{2}$$

by inspection, $|\psi(x)|^2$ symmetric w.r.t. $x = a/2$ $\Rightarrow$ $\langle x\rangle = a/2$

The meaning of the average $\langle x\rangle$ or other variables is that if repeat the same measurement on identically prepared state $\psi(x)$ many times, n_i times obtaining x_i results and thus the average

$$\langle x\rangle = \frac{\sum_i n_i x_i}{\sum_i n_i} \longrightarrow \text{in the infinite measurement samples}$$

$$\langle x\rangle = \int dx\ x\ P(x)$$

$$\langle f(x)\rangle = \int dx\ f(x)\ P(x).$$

momentum

$\hat{p} = i\hbar\frac{d}{dx}$

$\langle\hat{p}\rangle = \int dx\ \psi^*\ i\hbar\frac{d}{dx}\psi$

✱ It is important to know that if one were to measure energy of an eigenstate (stationary state) ψ_n, the energy will always be $E_n \overset{\text{rigid box}}{=} \frac{n^2\pi^2\hbar^2}{2ma^2}$!

Example 7.3

Answer the same questions as in Example 7.2 but for the first excited state of the rigid box.

The wave function is given by (7.60) with $n = 2$, so

$$|\psi(x)|^2 = \frac{2}{a}\sin^2\left(\frac{2\pi x}{a}\right)$$

This is plotted in Fig. 7.7, where it is clear that $|\psi(x)|^2$ has two equal maxima at

$$x_{mp} = \frac{a}{4} \quad \text{and} \quad \frac{3a}{4}$$

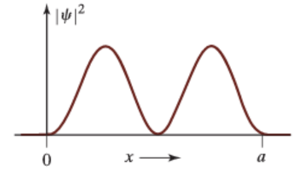


FIGURE 7.7
The probability density $|\psi(x)|^2$ for a particle in the first excited state ($n = 2$) of a rigid box.

$\langle x \rangle = \frac{a}{2}$ by inspection

$P_{(x, x+\Delta x)} \approx |\psi(x)|^2 \Delta x$.

* Free particle again

If we set $V(x) = 0$

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

when there is no potential we expect $E \geq 0$

we can prove this by contradiction. Assume $E < 0$

$$\psi''(x) = \underbrace{-\frac{2mE}{\hbar^2}}\psi(x) = \left(\sqrt{-\frac{2mE}{\hbar^2}}\right)^2\psi(x) = \alpha^2\psi(x) \qquad \alpha \equiv \sqrt{\frac{-2mE}{\hbar^2}} > 0$$

Then $\psi(x) = A e^{\alpha x} + B e^{-\alpha x}$, but since x is the real axis it blows up at either $x = \pm\infty$

When $E \geq 0$, we can set $E = \frac{\hbar^2 k^2}{2m}$ and take $k \geq 0$

and thus $\psi''(x) = -k^2\psi(x) \Rightarrow \psi(x) = a\,e^{ikx} + b\,e^{-ikx}$

But this is equivalent to $\psi(x) = A\cos kx + B\sin kx$

that we showed earlier.

Under TDSE. $\quad i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t)$

$$\psi(x,t) = e^{-i\omega t}\psi(x), \quad \omega = \frac{E}{\hbar} = \frac{\hbar k^2}{2m}$$

$$\underset{\text{in terms of } a,b}{=} a\,e^{i(kx-\omega t)} + b\,e^{-i(kx+\omega t)}$$

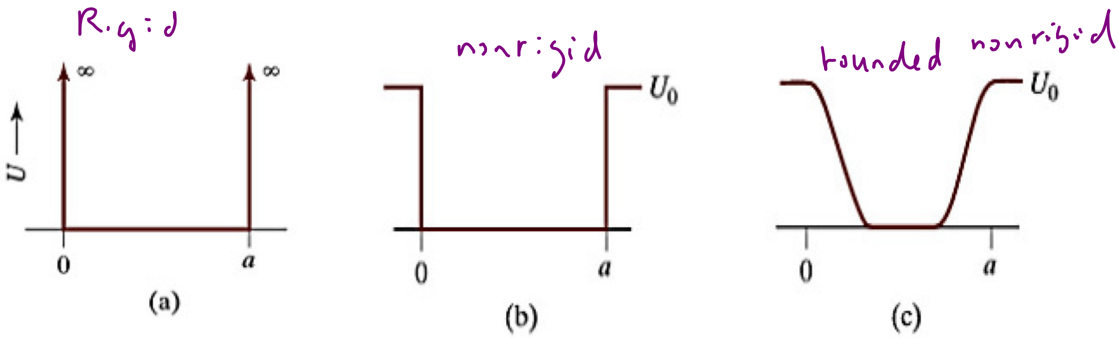
moving to right $\qquad$ moving to left.

separately $e^{i(kx-\omega t)}$ & $e^{-i(kx+\omega t)}$ are "degenerate"

i.e. having the same energy E.

Nonrigid box / finite square well

We will begin with qualitative discussions on the solutions of TISE, which will give us some intuitions to the solutions of nonrigid box and more general potential, building on what we learned from rigid box case. Then we will be more quantitative.



First lowest potential energy is zero in (a) – (b). $\min U(x) = 0$

We explained earlier that no solution for $E < 0 = \min U(x)$

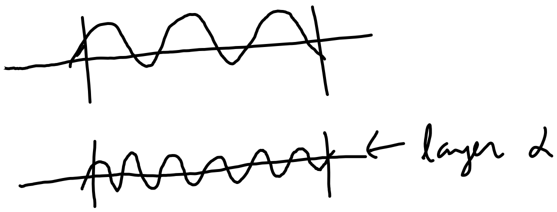
For rigid box, the solutions E_n are discrete or quantized, and their wavefunctions are, of course, bounded in region $(0, a)$.

These are called bound states.

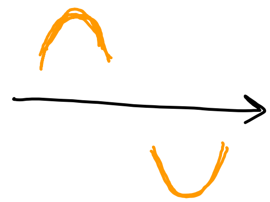
In the nonrigid case if $E \ll U_0$, we will expect the solutions are similar. In $x \in (0, a)$ as ① $\frac{d^2}{dx^2}\psi(x) = \frac{2m(U(x)-E)}{\hbar^2}\psi$

$$\frac{d^2}{dx^2}\psi(x) = -\frac{2mE}{\hbar^2}\psi(x) = \underbrace{-}_{}\alpha^2\psi(x) \Rightarrow \psi(x) = A\sin\alpha x + B\cos\alpha x$$

oscillatory behavior if $\frac{d^2}{dx^2}\psi(x) = \boxed{\frac{2m(U(x)-E)}{\hbar^2}}\psi(x)$ has negative "coefficient" and the large α (or $\frac{2m(U(x)-E)}{\hbar^2}$) the faster the oscillation in space.

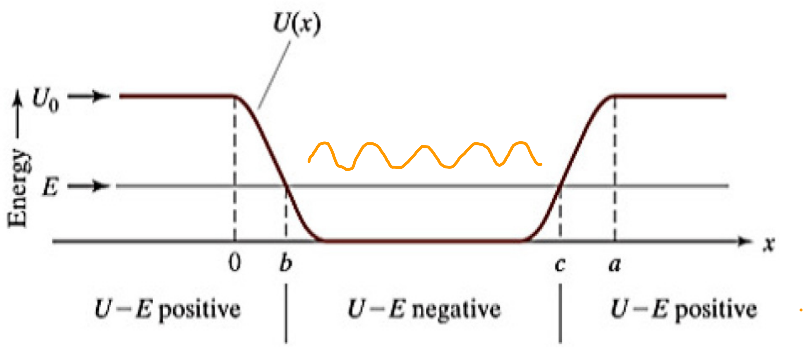


$\psi'' < 0$ if $\psi > 0$

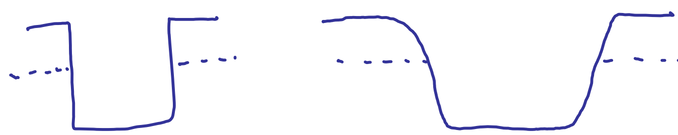


$\psi'' > 0$ if $\psi < 0$

so we expect oscillatory in (b, c) of the rounded box

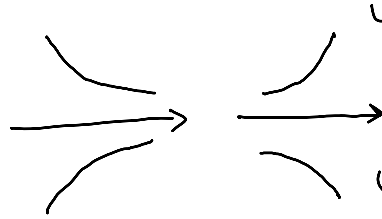


Outside the box



we have $$\psi''(x) = \underbrace{\frac{2m(U(x)-E)}{\hbar^2}}_{>0}\psi = \alpha^2\psi$$

From functional analysis

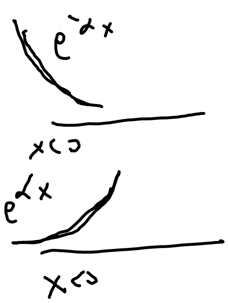


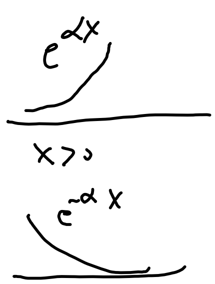
$\psi > 0$; $\psi'' > 0 \Rightarrow$ ∪

$\psi < 0$, $\psi'' < 0 \Rightarrow$ ∩

e.g. α const. solutions

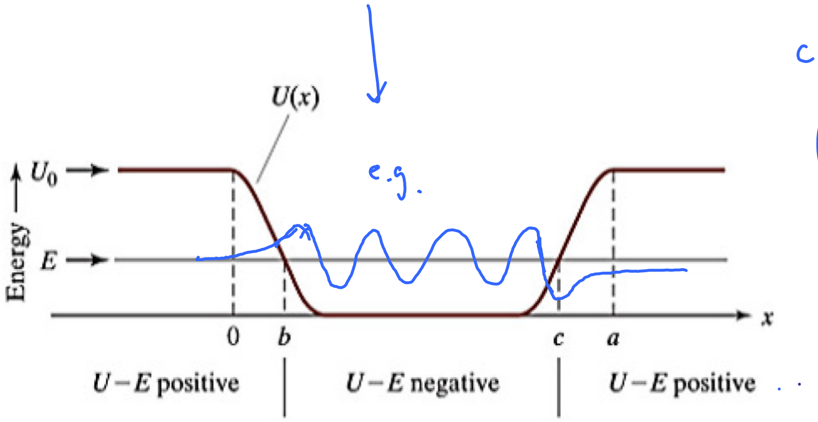
$e^{\alpha x}$ $e^{-\alpha x}$





In order for wave function not to blow up, we need to have

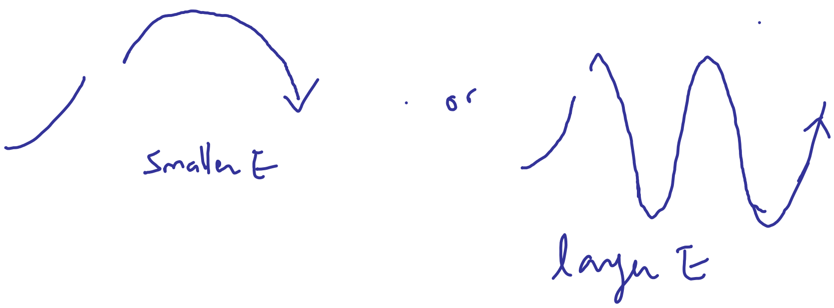
So we expect that wave function will leak out to the classically forbidden region ($E < U$)



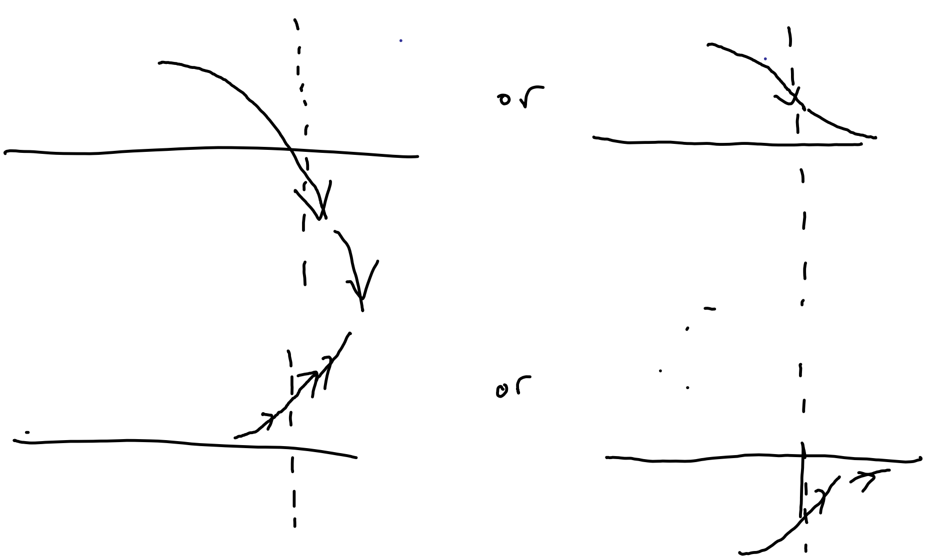
But not all energy E will have $\psi(x) \to 0$ at $x = \pm\infty$

$\Rightarrow$ valid solutions have quantized energy E.

To get the last conclusion. We can imagine start with a wave function $\psi = 0$ at $x = -\infty$ and increases, then as it enters the classically allowed region, the wavefunction begins to oscillate



Dependent on how it exists to the other side of classically forbidden region, it may grow indefinitely.



As we can see that it is rare to have case 3 below; it needs to

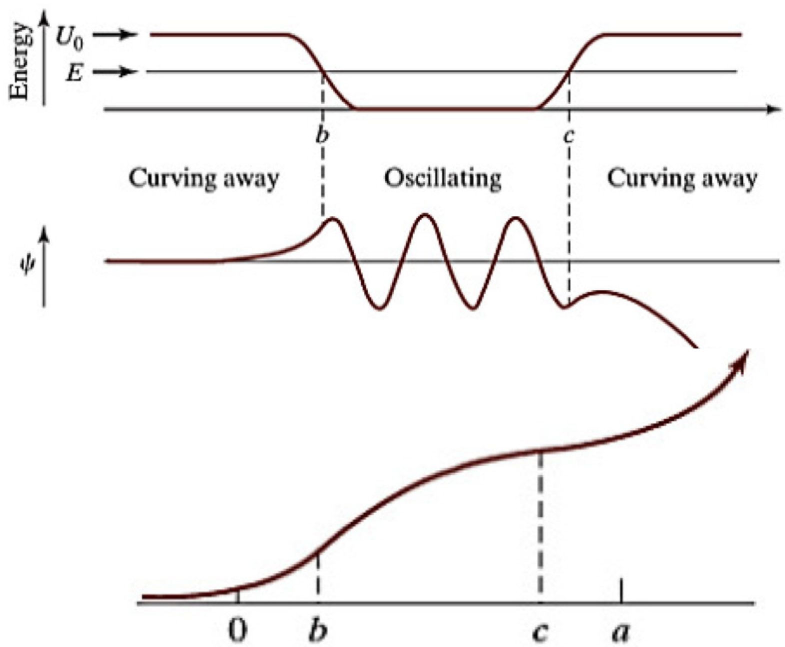
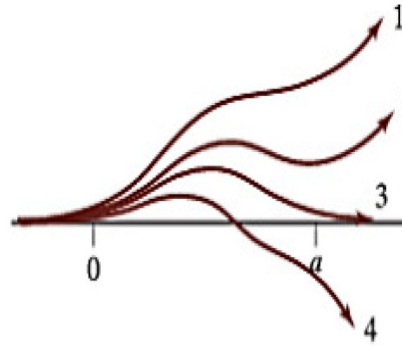


FIGURE 7.14

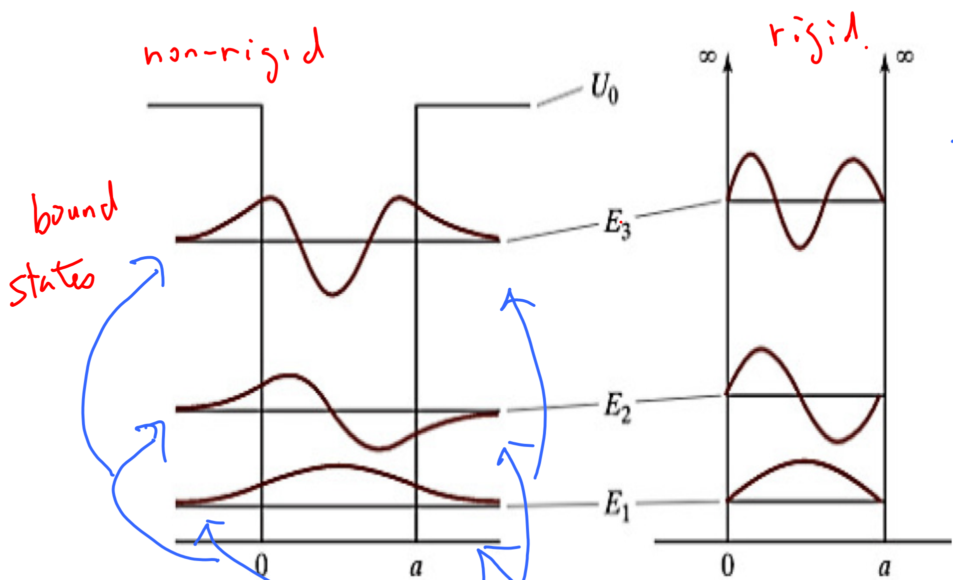
When E is very small, the wave function bends too slowly inside the well. The function that has the form $Ae^{\alpha x}$ when $x < 0$ blows up as $x \longrightarrow +\infty$.



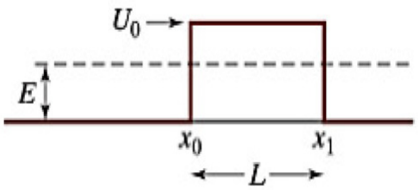
fine tune energy E.

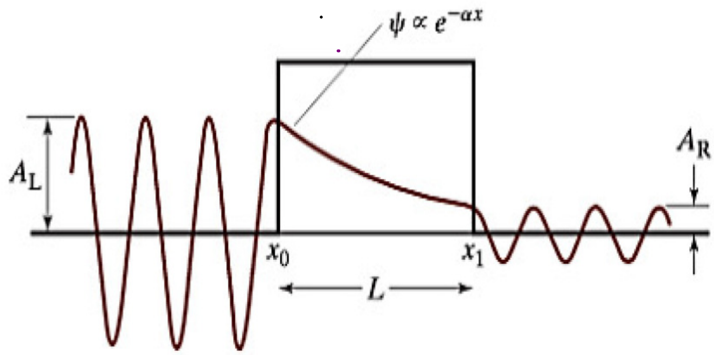
$\Rightarrow$ Thus quantization.

Thus we arrive at the following qualitative feature of lowest energy eigenstates (stationary solutions). One interesting feature different from the regid case is the "leakage" of wave function into the classically forbidden region. Such a leakage can lead to tunneling!



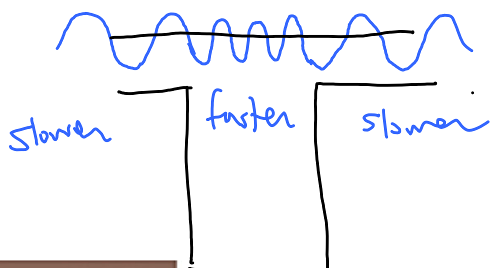
Tunneling





$$\frac{A_R}{A_L} \approx \frac{e^{-\alpha x_1}}{e^{-\alpha x_0}} = e^{-\alpha L} \qquad P = \left(\frac{A_R}{A_L}\right)^2 \approx e^{-2\alpha L} \qquad \alpha = \frac{\sqrt{2m(U_0 - E)}}{\hbar}$$

We have discussed that case $E < U_0$. When $E > U_0$, we expect oscillatory behavior in all regions.



Example 7.5

Consider two identical conducting wires, lying on the x axis and separated by an air gap of thickness $L = 1$ nm (that is, a few atomic diameters). An electron that is moving inside either conductor has potential energy zero, whereas in the gap its potential energy is $U_0 > 0$. Thus the gap is a barrier of the type illustrated in Fig. 7.21. The electron approaches the barrier from the left with energy E such that $U_0 - E = 1$ eV; that is, the electron is 1 eV below the top of the barrier. What is the probability that the electron will emerge on the other side of the barrier? How different would this be if the barrier were twice as wide?

$$\alpha = \frac{\sqrt{2m(U_0-E)}}{\hbar} = \frac{\sqrt{2mc^2(U_0-E)}}{\hbar c}$$

use $\hbar c = 197\,\text{eV}\cdot\text{nm}$

$$\approx \frac{\sqrt{2\cdot 0.511\times10^6\,\text{eV}\cdot 1\,\text{eV}}}{197\,\text{eV}\cdot\text{nm}}$$

$$\approx 5.1\ \text{nm}^{-1}$$

$L = 1\,\text{nm}$

$$P = e^{-2\alpha L} = e^{-10.2} \sim 3.7\times10^{-5}$$

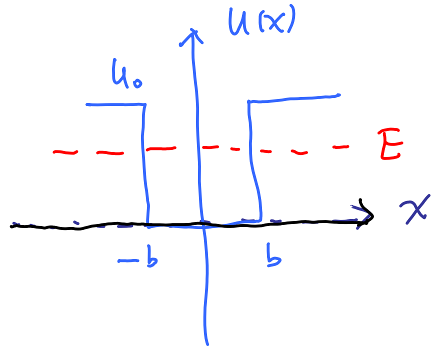
small but not negligible

$L = 2\,\text{nm}$

$$P = e^{-20.4} \sim 1.4\times10^{-9}$$

negligible!

Finite square well again: More quantitative discussion



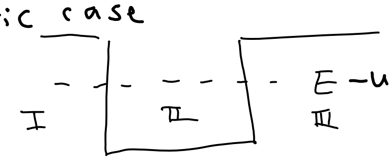
Finite square well

$$U(x) = \begin{cases} U_0 & -b < x < b \\ 0 & |x| > b \end{cases}, \quad U_0 > 0$$

Different from the infinite square well, the wave fcn @ the well boundary $\pm b$ DOES NOT vanish.

This potential well supports both bound and scattering states.

Bound states : symmetric case



$\boxed{x < -b}$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = (E - U_0)\psi, \quad E - U_0 \equiv -\frac{\hbar^2}{2m}\alpha^2$$

$$\alpha \equiv \sqrt{-\frac{2m(E-U_0)}{\hbar^2}} > 0$$

i.e. $\dfrac{d^2\psi}{dx^2} = \alpha^2\psi$

$$\boxed{\psi_I(x) = Be^{\alpha x}} \qquad (e^{-\alpha x} \to \infty \text{ as } x \to -\infty)$$

$\boxed{x > b}$

$$\psi_{III}(x) = Fe^{-\alpha x}$$

(focus on symmetric solution $\Rightarrow F = B$), $\boxed{\psi_{III} = Be^{-\alpha x}}$

$-b < x < b$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi, \quad E = U_0 - \frac{\hbar^2\alpha^2}{2m} \equiv \frac{\hbar^2 k^2}{2m} > 0$$

$$\frac{d^2}{dx^2}\psi = \frac{2m}{\hbar^2}\psi = k^2\psi \quad ;$$

$$\psi_{II}(x) = \underbrace{C \sin kx}_{\text{antisymmetric}} + \underbrace{D \cos kx}_{\text{symmetric}}$$

Will focus on symmetric solution : so set $C = 0$

$$\boxed{\psi_{II}(x) = D\cos kx}$$

Boundary conditions: wavefunction and its derivative should be continuous (unless the potential is ∞ at the point)

So at $x = b$

$$\psi_{II}(b) = D\cos kb = \psi_{III}(b) = B e^{-\alpha b} \quad \text{— ①}$$

$$\psi_{II}'(x) = -kD\sin kx, \quad \psi_{III}'(x) = -\alpha B e^{-\alpha x}$$

So at $x = b$:

$$\psi_{II}'(b) = -kD\sin kb = \psi_{III}'(b) = -\alpha B e^{-\alpha b} \quad \text{— ②}$$

B, D, & α (as $\frac{\hbar^2 k^2}{2m} = U_0 - \frac{\hbar^2\alpha^2}{2m}$) are unknowns.

If we can solve for α, then we get the energy

Take: $\frac{②}{①}$: $(bk)\tan(kb) = (b\alpha)$

$$E = U_0 - \frac{\hbar^2\alpha^2}{2m} \equiv \frac{\hbar^2 k^2}{2m} > 0$$

We can set $z \equiv kb$

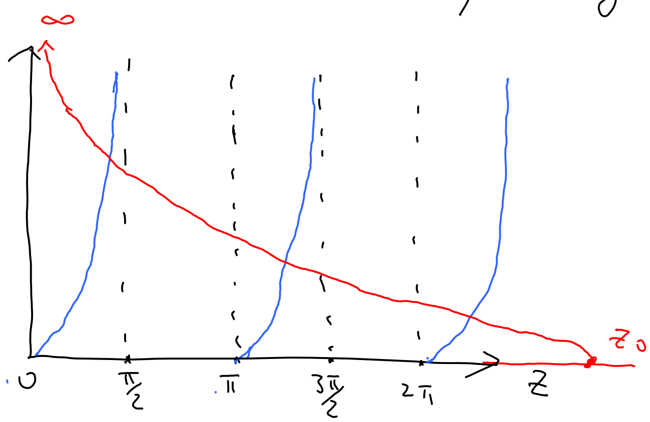
$$\frac{\hbar^2 k^2}{2m} + \frac{\hbar^2\alpha^2}{2m} \equiv U_0$$

$$\alpha b = \sqrt{\frac{2mU_0 b^2}{\hbar^2} - z^2} \equiv \sqrt{z_0^2 - z^2}$$

$$z_0^2 = \frac{2mU_0 b^2}{\hbar^2}$$

$$z\tan z = \sqrt{z_0^2 - z^2} \quad \text{or} \quad \tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$$

Q: How to solve this? by "drawing" curves & finding intersections.



① For $0 < z_0 < \pi$: one solution

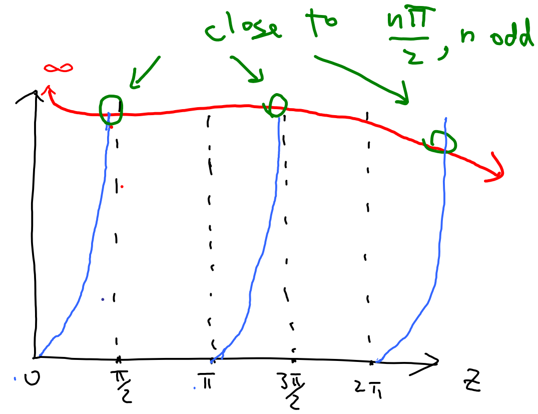
For $\pi \le z_0 < 2\pi$: two solutions

⋮

$(n-1)\pi \le z_0 < n\pi$: n solutions

$\Rightarrow$ always $\exists$ a bound state (even sol)

Let us examine two limiting cases



1. Wide, deep well.

If z_0 very large $\left[z_0 \equiv \frac{b}{\hbar}\sqrt{2mU_0} \text{ large} \right]$

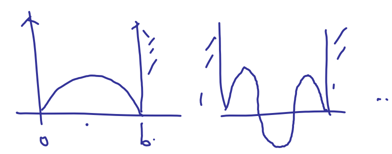
intersections occur close to

$$z_n = n\pi/2 \qquad n \text{ odd}:$$

i.e. $\frac{n^2\pi^2}{4} = k^2 b^2 = \frac{2m}{\hbar^2}(E_n)\, b^2$

$$\Rightarrow E_n \cong \frac{n^2\pi^2\hbar^2}{2m(2b)^2} \qquad a \equiv 2b$$

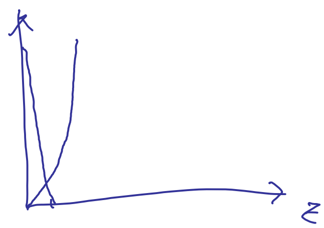
[cf.

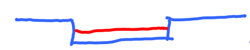


Compare to inf. square well $\longrightarrow$ $E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$ (n odd) (symmetric)

2. Shallow, narrow well.

z_0 very small



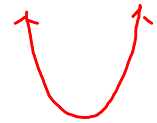


(For $z_0 < \pi/2$ lowest odd state disappears) $\Rightarrow$ only one solution of bound state,

No matter how weak the potential

verify this!

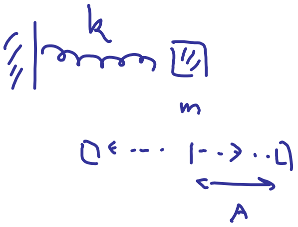
Simple Harmonic oscillator



has potential $U(x) = \frac{1}{2}k(x-x_0)^2$ which may come from expansion of force

near x_0 equilibrium $\quad F(x) = \underbrace{F(x_0)}_{=0} + \underbrace{F'(x_0)}_{=-k}(x-x_0) + \cdots \approx -k\,(x-x_0)$

Hooke's law



We know that $\quad x(t) = A\cos(\omega_c t + \varphi)$

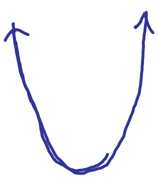
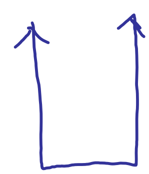
$\uparrow$ Amplitude

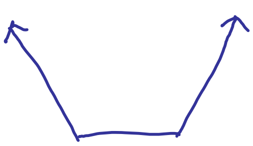
$\omega_c = \sqrt{\frac{k}{m}}$ or freq. $f = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$. period $T = 2\pi\sqrt{\frac{m}{k}}$

at extreme points $\quad U_{max} = \frac{1}{2}kA^2 \Rightarrow A = \sqrt{\frac{2U_{max}}{k}}$

The above is a review of what you have learned.

Quantum mechanical behavior?

 can be qualitatively regarded as 

or  so we expect some similar

feature as the rigid box. Of course quantitatively, they are different.

Solving the SE:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \underbrace{\frac{1}{2}k}_{\frac{1}{2}m\omega_c^2}x^2\,\psi(x) = E\,\psi(x)$$

will require knowledge of some special function or technique of series expansion, so we will not do it here. Instead we will just write down some solutions.

First in contrast to the rigid box $E_n = n^2 E_1$, the simple harmonic oscillator has energy levels $E_n = \hbar\omega_c(n+\frac{1}{2})$, $n=0,1,2,\dots$

Their eigenstates or wavefcns

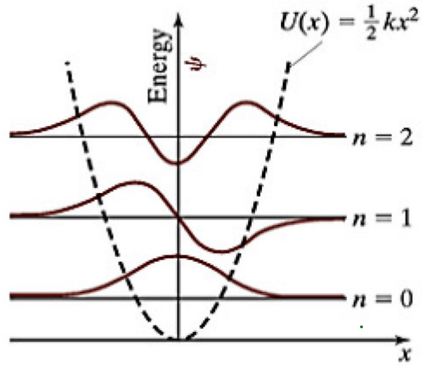


TABLE 7.1

The energies and wave functions of the first three levels of a quantum harmonic oscillator. The length b is defined as $\sqrt{\hbar/m\omega_c}$.

n	E_n	$\psi(x)$
0	$\frac{1}{2}\hbar\omega_c$	$A_0 e^{-x^2/2b^2}$
1	$\frac{3}{2}\hbar\omega_c$	$A_1 \frac{x}{b} e^{-x^2/2b^2}$
2	$\frac{5}{2}\hbar\omega_c$	$A_2\left(1 - 2\frac{x^2}{b^2}\right)e^{-x^2/2b^2}$

This is the simplest way to understand Planck's quantization $E = \hbar\omega = hf$ except we have zero point energy $E_0 = \frac{1}{2}hf$

"n" may be regarded as the number of photons.

Example 7.4

Verify that the $n = 1$ wave function given in Table 7.1 is a solution of the Schrödinger equation with $E = \frac{3}{2}\hbar\omega_c$. (For the cases $n = 0$ and $n = 2$, see Problems 7.49 and 7.52.)

$$\frac{3}{b^2}\psi = \frac{3m\omega_c}{\hbar}\psi = \frac{2mE}{\hbar^2}\psi$$

$$\frac{1}{b^4} = \frac{m^2\omega_c^2}{\hbar^2}$$

$$\psi_1(x) = A_1\frac{x}{b}e^{-x^2/2b^2} \qquad b = \sqrt{\frac{\hbar}{m\omega_c}}$$

SE: $$-\frac{\hbar^2}{2m}\psi''(x) + \frac{1}{2}m\omega_c^2 x^2\psi(x) = E\psi(x) \Rightarrow -\psi''(x) + \frac{m^2\omega_c^2}{\hbar^2}x^2\psi = \frac{2mE}{\hbar^2}\psi$$

$E = E_1 = \frac{3}{2}\hbar\omega_c$.

$$\psi_1'(x) = A_1\frac{1}{b}e^{-x^2/2b^2} - A_1\frac{x^2}{b^3}e^{-\frac{x^2}{2b^2}}$$

$$\psi_1''(x) = -A_1\frac{x}{b^3}e^{-\frac{x^2}{2b^2}} - 2A_1\frac{x}{b^3}e^{-\frac{x^2}{2b^2}} + A_1\frac{x^3}{b^5}e^{-\frac{x^2}{2b^2}}$$

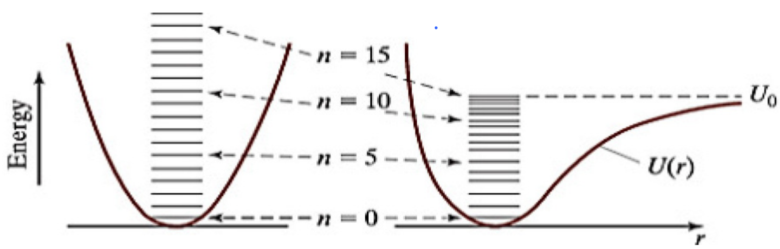
$$= e^{-\frac{x^2}{2b^2}}A_1\left(\frac{x^3}{b^5} - 3\frac{x}{b^3}\right)$$

$$-\frac{x^2}{b^4}\psi = -A_1 \frac{x^3}{b^5} e^{-x^2/2b^2}$$

$$\text{l.h.s} = -\psi'' + \frac{x^2}{b^4}\psi = 3A_1 \frac{x}{b^3} e^{-x^2/2b^2}, \qquad \text{r.h.s} = \frac{3}{b^2}\psi = 3A_1 \frac{x}{b} e^{-x^2/2b^2}$$

so. l.h.s = r.h.s.

One can also use S.H.O solutions as a starting point to understand vibrational spectrum:



the real potential widens more than the simple harmonic potential, causing the spectrum to become denser near one end.

Plus there will be a continuum of energy $E > U_0$

e.g.

H_2 molecule emits infrared photons of frequency 1.2×10^{14} Hz when it drops from one vibrational level to the next. This radiation is used by astronomers to locate clouds of H_2 molecules in our galaxy.

Further comments on TDSE

$\psi_1(x)$ solution of TISE with energy E_1
$\psi_2(x)$ " , E_2

$$\Rightarrow \begin{cases} \Psi_1(x,t) = \psi_1(x)\, e^{-i\omega_1 t} & \omega_1 = \frac{E_1}{\hbar} \\ \Psi_2(x,t) = \psi_2(x)\, e^{-i\omega_2 t} & \omega_2 = \frac{E_2}{\hbar} \end{cases}$$

are two stationary states that satisfy TDSE

Then their superposition is also a solution of TDSE:

$$\Psi(x,t) = \alpha\, \Psi_1(x,t) + \beta\, \Psi_2(x,t) \qquad \text{for any } \alpha \,\&\, \beta$$

* Even though Ψ_1 & Ψ_2 are "stationary": $|\Psi_1|$ & $|\Psi_2|$ indep of time.
$|\Psi(x,t)|^2$ will not be stationary, that is it will change in time

$$\Psi(x,t) = e^{-i\omega_1 t}\left(\alpha\,\psi_1(x) + \beta\,\psi_2(x)\,e^{-i\omega_{21}t}\right) \qquad \omega_{21} \equiv \omega_2 - \omega_1$$

$$|\Psi(x,t)|^2 = \left|\alpha\,\psi_1(x) + \beta\,\psi_2(x)\,e^{-i\omega_{21}t}\right|^2$$

$$= |\alpha|^2|\psi_1(x)|^2 + |\beta|^2|\psi_2(x)|^2 + \alpha\beta^*\psi_1(x)\psi_2^*(x)\,e^{i\omega_{21}t} + \alpha^*\beta\,\psi_1^*(x)\,\psi_2(x)\,e^{-i\omega_{21}t}$$

Example 7.6

For a particle in a rigid box, consider the nonstationary state with wave function (7.112) for the special case that $\alpha = \beta = 1/\sqrt{2}$. (The particular value $1/\sqrt{2}$ is chosen to guarantee that Ψ is normalized — see Problem 7.58.) Evaluate $|\Psi(x,t)|^2$ and plot it for several different times.

$$\tau = \frac{2\pi}{\omega_{21}}$$

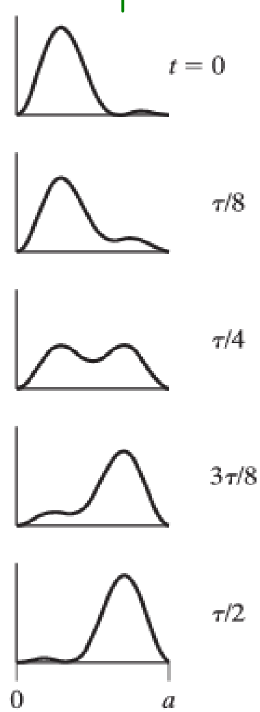
$$\hbar\,\omega_{21} = \frac{\hbar^2\pi^2}{2ma^2}(2^2 - 1^2)$$

$$\psi_1(x) = \sqrt{\frac{2}{a}}\,\sin\frac{\pi x}{a}, \qquad \psi_2(x) = \sqrt{\frac{2}{a}}\,\sin\frac{2\pi x}{a}$$

$$\Psi(x,t) = \frac{1}{\sqrt{2}}\,\psi_1(x)\,e^{-\frac{iE_1 t}{\hbar}} + \frac{1}{\sqrt{2}}\,\psi_2(x)\,e^{-\frac{iE_2}{\hbar}t}$$

$$|\Psi(x,t)|^2 = \tfrac{1}{2}[\psi_1(x)^2 + \psi_2(x)^2 + 2\psi_1(x)\psi_2(x)\cos(\omega_{21}t)]$$

$$= \frac{1}{2}\,\frac{2}{a}\left[\sin^2\frac{\pi x}{a} + \sin^2\frac{2\pi x}{a} + 2\sin\frac{\pi x}{a}\sin\frac{2\pi x}{a}\cos\frac{3\hbar\pi^2}{2ma^2}t\right]$$



See mathematica file for animations

Addiontional examples

7.32 •• If a particle has wave function $\psi(x)$, the probability of finding the particle between any two points b and c is

$$P(b \le x \le c) = \int_b^c |\psi(x)|^2\, dx \qquad (7.122)$$

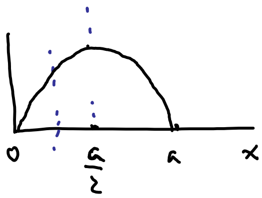
For a particle in the ground state of a rigid box, calculate the probability of finding it between $x = 0$ and $x = a/3$ (where a is the width of the box). Use the hint in Problem 7.29.

7.29 •• Show that the integral which appears in the normalization condition for a particle in a rigid box has the value

$$\int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{a}{2}$$

[*Hint:* Use the identity for $\sin^2\theta$ in terms of $\cos 2\theta$

$$|\psi(x)|^2 = \frac{2}{a}\sin^2\frac{\pi x}{a}$$



$$P(0 \le x \le \tfrac{a}{3}) = \int_0^{\frac{a}{3}} \frac{2}{a}\sin^2\frac{\pi x}{a}\, dx = \frac{2}{a}\int_0^{\frac{a}{3}} \frac{1-\cos\frac{2\pi x}{a}}{2}\, dx$$

$$= \frac{1}{a}\left(\frac{a}{3} - \frac{a}{2\pi}\sin\frac{2\pi x}{a}\Big|_0^{\frac{a}{3}}\right) = \frac{1}{3} - \frac{1}{2\pi}\sin\frac{2\pi}{3}$$

$$= \frac{1}{3} - \frac{1}{2\pi}\frac{\sqrt{3}}{2} \approx 0.196$$

7.35 ••• Consider a particle in the ground state of a rigid box of length a. **(a)** Evaluate the integral (7.122) to give the probability of finding the particle between $x = 0$ and $x = c$ for any $c \le a$. **(b)** What does your result give when $c = a$? Explain. **(c)** What if $c = a/2$? **(d)** What if $c = a/4$? **(e)** The answer to part (*c*) is half that for part (*b*), whereas that to part (*d*) is *not* half that for part (*c*). Explain.

Similar to Prob 7.32

(a) $$P(0 \le x \le c) = \frac{2}{a}\int_0^c \frac{1-\cos\frac{2\pi x}{a}}{2}\, dx$$

$$= \frac{1}{a}\left(c - \frac{a}{2\pi}\sin\frac{2\pi x}{a}\Big|_0^c\right)$$

$$= \frac{c}{a} - \frac{1}{2\pi}\sin\frac{2\pi c}{a}$$

(b) $c = a$, $P_{(0,a)} = 1$

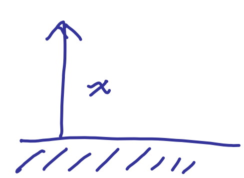
(c) $c = a/2$, $P_{(0,\frac{a}{2})} = \frac{1}{2}$

(d) $c = a/4$ $P_{(0,\frac{a}{4})} = \frac{1}{4} - \frac{1}{2\pi}\sin\frac{\pi}{2} = \frac{1}{4} - \frac{1}{2\pi} < \frac{1}{2}P_{(0,\frac{a}{2})}$

(e) see areas above

7.44 •• Consider the infinitely deep potential well shown in Fig. 7.29. **(a)** Argue that this is the potential energy of a particle of mass m above a hard surface in a uniform gravitational field with x measured vertically up. **(b)** Sketch the wave functions for the ground state and the first two excited states of this well.

(a) P.S. $U(x) = mgx$



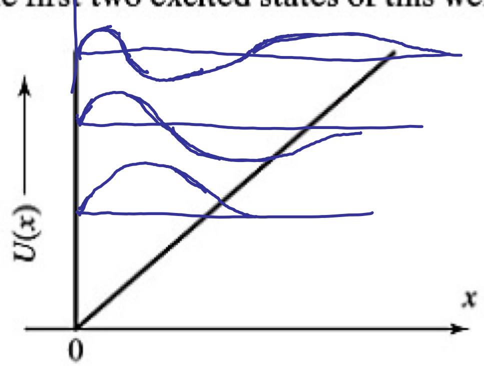


FIGURE 7.29

7.50 • The wave function $\psi_0(x)$ for the ground state of a harmonic oscillator is given in Table 7.1. Show that its normalization constant A_0 is

$$A_0 = (\pi b^2)^{-1/4} \qquad (7.123)$$

You will need to know the integral $\int_{-\infty}^{\infty} e^{-\lambda x^2}\,dx$, which can be found in Appendix B.

$$\psi_0(x) = A_0\, e^{-\frac{x^2}{2b^2}}$$

$$1 = \int_{-\infty}^{\infty} dx\,|\psi_0(x)|^2 = |A_0|^2 \cdot \underbrace{\int_{-\infty}^{\infty} dx\, e^{-\frac{x^2}{b^2}}}_{\sqrt{\pi b^2}}$$

$$\Downarrow$$

$$A_0 = (\pi b^2)^{-\frac{1}{4}}$$

7.53 ••• The wave functions of the harmonic oscillator, like those of a particle in a finite well, are nonzero in the classically forbidden regions, outside the classical turning points. In this question you will find the probability that a quantum particle which is in the ground state of an SHO will be found outside its classical turning points. The wave function for this state is in Table 7.1, and its normalization constant A_0 is given in Problem 7.50. **(a)** What are the turning points for a classical particle with the ground-state energy $\frac{1}{2}\hbar\omega_c$ in an SHO with $U = \frac{1}{2}kx^2$? Relate your answer to the constant b in Eq. (7.99). **(b)** For a quantum particle in the ground state, write down the integral that gives the total probability for finding the particle between the two classical turning points. The form of the required integral is given in Problem 7.32, Eq. (7.122).

To evaluate it, change variables until you get an integral of the form $\int_{-1}^{1} e^{-y^2}\,dy$; this is a standard integral of mathematical physics (called the *error function*) with the known value 1.49. What is the probability of finding the particle between the classical turning points? **(c)** What is the probability of finding it *outside* the classical turning points?

(a) classical turning points

$$U = \frac{1}{2}kx^2 = \frac{1}{2}\hbar w_c$$

$$x_0 = \pm\sqrt{\frac{\hbar w_c}{k}} \qquad k = m w_c^2$$

$$= \pm\sqrt{\frac{\hbar}{m w_c}} = \pm b$$

(b)

$$P_{[-b,b]} = \int_{-b}^{b} |\psi_0(x)|^2\,dx$$

$$= |A_0|^2 \int_{-b}^{b} e^{-\frac{x^2}{b^2}}\,dx$$

$$y = \frac{x}{b}. \quad dx = b\,dy$$

$$= |A_0|^2 b \int_{-1}^{1} e^{-y^2}\,dy$$

$$\simeq \frac{b}{\sqrt{\pi b^2}} \cdot 1{,}49 = \frac{1{,}49}{\sqrt{\pi}} \simeq 0{,}841$$

(c) $P_{\text{outside}} \approx 0{,}159$