5. Quantum mechanics in one dimension

Schrödinger's equation is the analogue to the wave equation of sound, light, water, $\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2}$, which works for all classical waves, that have either a photon associated with it or a pseudo-particle (such as a phonon)

harmonic wave, plane wave is solution to this equation *moving to the right*

$y(x,t) = y_0 \cos 2\, p\, ({}^{x}/_{?} - {}^{t}/_{T}) = y_0 \cos {}^{2p}/_{?}\, (x - vt)$ where $v = {}^{?}/_{T}$

these functions describe something with physical significance, e.g. the E vector, the amplitude on a water wave, the air pressure in a sound wave

the square of that function **$y(x,t)^2$ ~ ? energy per unit volume, intensity (I) of waves is energy density times wave speed, so I ~ $y(x,t)^2$ ~ ? can be put down to number of photons (or pseudo-particles) at anyone place at a certain time, is also the likelihood of finding a photon (or pseudo-particle) there (x) and then (t)**

what we need is something altogether different but mathematically similar - **a wave equation for matter wave, the solutions to which, i.e. ? (x,t) -**

the matter waves - will be a valid description of how “small” things move – and the square of which ? (x,t)^2 will give us the probability of finding the particle of the matter wave there (x) and then (t)

? (x,t) contains everything that is and can be know about the particle, to get the probability of finding the particle at some specific (x,t) we have to calculate ? (x,t)^2 **<u>Born’s interpretation</u>**

call the probability that particle will be found in the infinitesimal small interval dx about the point x P(x), probability density as it is per length unit, then Born’s interpretation is

P(x) dx = ? (x,t)^2 dx will be a number = 1 (at time t)

it is not possible to specify with certainty the position of a particle (x) - ***Heisenberg’s uncertainty principle*** **– but it is possible to assign definitive values of probabilities for observing it at any place we care to calculate the square function for (at a given time)**

? (x,t)^2 is intensity of matter wave, a measurable quantity, while ? (x,t) is only a mathematical model for the matter wave, a non physical thing, can’t be measured

Schrödinger’s equation equivalent to Newton’s second law, (Solutions to Newton’s second law described how things move at the macroscopic scale!!! Newton’ second law contained the solution of Newton’s first law, Schrödinger equation will contain equivalent to Newton’s firs law a free particle, plane wave, harmonic wave and superpositions of plane waves describing a pulse)

Schrödinger developed his equation after his prior attempts to explain with de Broglie’s relation the Bohr model at a more fundamental level failed, a colleague told him one does need a wave equation to make progress with waves, so Schrödinger boned up on the maths and found the one that works for all matter waves !!!

Partial derivates and complex numbers

suppose we have a function f(x,y) of two variables and want to know how this function varies with one variable only, say x

we treat the other variable y as a constant and differentiate f(x,y) with respect to x

result is called a partial derivate and written as

$$\frac{\partial f}{\partial x} = [\frac{df}{dx}]_{y=cons}$$

rules of ordinary differentiation apply

e.g. f = f(x,y) = yx^2 $\frac{\partial f}{\partial x} = y \cdot 2x$ as y is a constant

on the other hand $\frac{\partial f}{\partial y} = x^2$ as x is now a constant

second order partial derivates $\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}[\frac{\partial f}{\partial x}]$ are calculated by repeating the procedure

e.g. f = f(x,y) = yx^2 $\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}[y \cdot 2x] = y \cdot 2$ as y is again a constant

application on something more challenging

classical wave equation is $\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2}$

for electromagnetic wave, sound wave, standing wave on a guitar, water wave, wave on a very long string free to travel

solutions of classical wave equation for monochromatic (? = constant) undamped (A = constant) wave traveling the right is

$y(x,t) = Ae^{-i?(t-x/v)}$

now show that y = $Ae^{-i? (t-x/v)}$ is a solution to the classical wave equation

first partial derivate of y with respect to x

$$\frac{\partial y}{\partial x} = \frac{iw}{v} y$$

second derivate $$\frac{\partial^2 y}{\partial x^2} = \frac{i^2 w^2}{v^2} y = -\frac{w^2}{v^2} y$$

first partial derivate with respect to t

$$\frac{\partial y}{\partial t} = -iwy$$

second derivate $$\frac{\partial^2 y}{\partial t^2} = i^2 w^2 y = -w^2 y$$

comparing the second derivates, difference is just $\frac{1}{v^2}$ otherwise they are identical so

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2}$$ which is the wave equation,

so y(x,t) = $Ae^{-i? (t-x/v)}$ must be a solution to this equation

complex wave functions / just like complex numbers

$? = A + iB$,   A real part of function
B imaginary part

then $? * = A - iB$,

(i is replace everywhere by – i and one has the conjugate complex function)

$?^{2} =$ $? * ? = ? \; ? * = A^2 - i^2 B^2 = A^2 + B^2$ is all real
$i^2 = -1$

the fundamental problem of quantum mechanics

given the wave function at some instant, say t = 0, i.e. ? (x,0), find the wave function at some or all other times t - when there are forces acting on the particle

? (x,0) is the initial information on the particle,

Newton’s mechanics analogue was initial position (x) and momentum (p) of a classical particle,

now it is an infinite set of numbers a set of values, for all points x one value of **? (x,0)** in Newton’s mechanics we obtain x(t) and p(t) by solving Newton’s second law $\sum \vec{F}dt = d\vec{p}, \sum \vec{F} = \frac{md\vec{v}}{dt} = m\vec{a}$, an net force acting on the particle changed it’s momentum, change in position over kinematics

Schrödinger’s equation (SE) propagates ? (x,0) forward in time,

that’s what we want to know, given (within Heisenberg’s uncertainty) we know where a particle is and what its momentum there is, we want to calculate were will be at some time (t) and what will it’s momentum be at that time

i.e. the initial **? (x,0) changes into ? (x,t)**

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

F = $-\frac{dU}{dx}$ is the force acting on the particle
U(x) is the potential energy function of the Force

1. left hand side (LHS) of SE is first evaluated for ? (x,0), i.e. t = 0, as it is not dependent on time, i.e. we make partial derivations and add the influence of the potential energy function on ? (x,0)

LHS of SE equals right hand side (RHS) of SE result must be equal to $\frac{\partial \Psi}{\partial t}$ at t = 0, i.e. initial rate of change of wave function

2. from $\frac{\partial \Psi}{\partial t}$ at t = 0, RHS of SE, we compute ? (x,dt), the wave function at an infitesimal small time interval (dt) later by superposition

? (x,dt) = ? (x,0) + $[\frac{\partial \Psi}{\partial t}]_0$ dt

3. that results gets plucked in at LHS of SE again, but now we evaluate ? (x,dt), i.e. this time make the partial derivations for ? (x,dt) add the influence of the potential energy function on ? (x,dt) (just like we did for t = 0, first step), result is again equal to RHS of SE

4. from $\frac{\partial \Psi}{\partial t}$ at t = dt, RHS of SE, we compute ? (x,dt_2), the wave function at an infitesimal small time interval (dt_2) later by superposition

? (x,dt_2) = ? (x, dt) + $[\frac{\partial \Psi}{\partial t}]_{dt}$ dt_2

……

each such repetition advances ? (x,dt_{n-1}) one step in time dt_n forward

until we have the time $(t > 0)$ we want to investigate our particle again – it can all be done by computer quickly and numerically

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“Somebody could still asks: How does it work? What mechanism is represented by the wave function? Nobody has ever found a mechanism behind the wave function. Nobody can explain more that we have just discussed. Nobody will give you an explanation about what is going on at a deeper level. As a matter of fact, we do not have an inkling about a basic mechanism from which the wave function could be derived.” *R. P. Feynman, 1971*

numerical solutions of Schrödinger equations are fine but how may one obtain a mathematical expression for **? (x,t)**

mathematical procedure called separation of variables,

? (x,t) = $y\ (x)f(t) = y\ (x)e^{-iwt}$

if U(x) potential energy is function of x only (not of t) !!!

$$i\hbar \frac{df(t)}{dt} = Ef(t)$$

$$-\frac{\hbar^2}{2m}\frac{d^2y\ (x)}{dx^2} + U(x)y\ (x) = Ey\ (x)$$

with E = h f = 2p $\hbar$ **f = ?** $\hbar$ **so ? =** $\frac{E}{\hbar}$

we can look at the e$^{-i?\,t}$ factor above which describes the time dependency if the potential energy does not depend on time – so that time dependency factor is

$$e^{-\frac{iE}{\hbar}t}$$

in equations above, E is the total energy, which we can normalize to be the kinetic energy plus the potential energy, (if we set rest energy $E_0 = 0$, as a reference form which energy is counted - which we can do arbitrarily)

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

rearranged for further use and called, time independent, steady-state, or stationary Schrödinger equation in one dimensions

if we have an arbitrary potential energy function U(x) there are no explicit analytical solutions to this equation

y **must be "well behaved" just as ? has to** in order to give sensible results for probabilities, i.e. finite everywhere including +- ∞ , single valued for any x, continuous,

and "smooth" – which is $\frac{dy}{dx}$ must also be continuous and single valued (the Serway book says here: wherever U(x) has a finite value, other books say all the time)

– all of them are mathematical conditions, so called boundary conditions

<u>if we can separate the variables,</u>

we also get ? (x,t)^2 = y^2, meaning all probabilities we calculate from **? (x,t) will not depend on time, are static or stationary**

expansion to three dimensions straightforward

$$\frac{\partial^2 y\,(x,y,z)}{dx^2}+$$

$$\frac{\partial^2 y\,(x,y,z)}{dy^2}+$$

$$\frac{\partial^2 y\,(x,y,z)}{dz^2}+$$

$$\frac{2m}{\hbar^2}\{E-U(x,y,z)\}y\,(x,y,z)=0$$

consequence at least 3 quantum numbers, taking account of the spin of the electron it will be 4 for electrons confined to be in an atom

let’s look at a free particle in the plane wave approximation, also called a harmonic wave

free non-relativistic particle means no force on it F = 0 = $-\frac{dU}{dt}$,
no force means no potential energy U(x), and no dependence of the potential energy on t, as particle is free, all energy is kinetic
E = ½m v^2
one dimensional time independent SE simplifies to

$$\frac{d^2y\,(x)}{dx^2}+[\frac{2m}{\hbar^2}\{\frac{mv^2}{2}\}]y\,(x)=0$$

½m v^2 can be rewritten as $\frac{p^2}{2m}$, multiplying within the straight bracket yields [$(\frac{p}{\hbar})^2$]

p = $^{h}/_{?}$ and $\hbar=\frac{h}{2p}$ so $(\frac{p}{\hbar})^2$ = $(^{2p}/_{?})^2$ = k^2 per definition of wave number

$$\frac{d^2y\,(x)}{dx^2}+k^2y\,(x)=0\_\_\,for\_a\_free\_particle$$

$y\,(x)=e^{ikx}$

$y\,(x)=Ae^{ikx}$

$y\,(x)=e^{-ikx}$

$y\,(x)=Be^{-ikx}$

$y\,(x)=Ae^{ikx}+Be^{-ikx}$ most general

are all solution of one dimensional time independent Schrödinger equation, where A and B are arbitrary constants (such constants appear generally in solutions to the SE and we will define then in the normalization process)

we had

? (x,t) = $y\ (x)f(t) = y\ (x)e^{-iwt}$

so in order to get most general solution of time dependent SE

? (x,t) we multiply most general time independent solution $y\ (x)$ **with time dependence** e^{-iwt}

? (x,t) = $(Ae^{ikx} + Be^{-ikx})e^{-iwt} = Ae^{ikx-iwt} + Be^{-ikx-iwt} =$
$Ae^{i(kx-wt)} + Be^{-i(kx-wt)}$

where is that free particle? answer: calculate **? (x,t)**^{2}

remember any function (be it exponential or sinusoidal) of from (kx ± ? t) represents a traveling wave

for (kx - ? t) wave is traveling to the right

for (kx +? t) wave is traveling to the left,

lets decide our particle should travel to the right, we can do that by setting B = 0 in the most general solution
so **? (x,t)**^{2}**= ? * ? =**

$$Ae^{-i(kx-wt)} \cdot Ae^{i(kx-wt)} = A^2 \cdot e^0 = A^2 \cdot 1$$

so the probability is a constant A^2 = **? $_0$(x,t)**^{2} at all places and times we may have as well calculated $y(x)^2$ to find the probability of finding the particle for any x we want

$$y(x)^2 = y(x)^* \, y(x) \;=$$

$$Ae^{-ikx} \cdot Ae^{i(kx)} = A^2 \cdot e^0 = A^2 \cdot 1$$

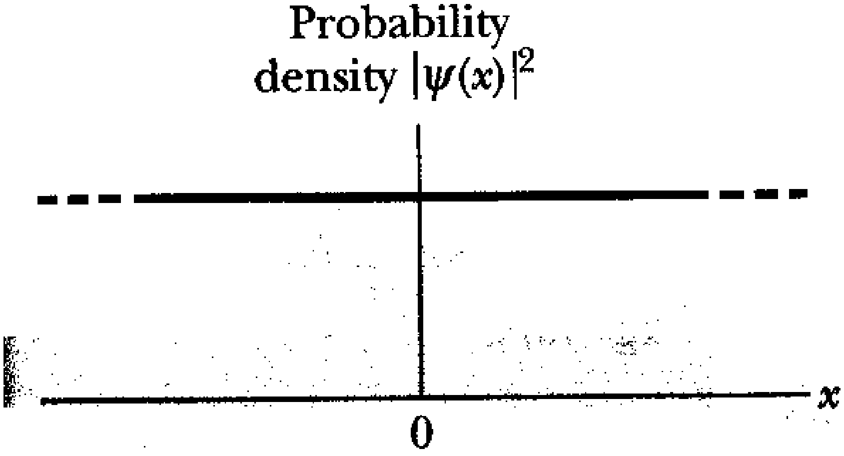


Fig. 39-11 A plot of the probability density $|\psi|^2$ for a free particle moving in the positive x direction. Since $|\psi|^2$ has the same constant value for all values of x, the particle has the same probability of detection at all points along its path.

analyzing the graph we see that the probability of finding the particle in any one segment of equal length ? x or dx is absolutely the same as it is a constant, so the particle has equal probabilities to be at any place, there is no most likely place so let’s assume we have a **free particle moving to the right,** expressed by wave function, see what happens if we put it into Schrödinger equation

? (x,t) = $Ae^{i(kx-wt)} = A[\cos kx - wt) + i\sin(kx - wt)]$

where A is a constant, let’s differentiate partially for x and t and put our derivates into the time dependent (one dimensional) Schrödinger equation

$$\frac{\partial\Psi}{\partial t} = -iwAe^{i(kx-wt)} = -iw\Psi$$

$$\frac{\partial\Psi^2}{\partial x^2} = (ik)^2 Ae^{i(kx-wt)} = -k^2\Psi$$

as it is a free particle, it is not under the influence of a force, so it has constant (time and position independent) net potential energy U(x) = U_0, which may be zero or any other value (remember potential energy levels can be set arbitrarily)

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

plugging our derivates in

$$-\frac{\hbar^2}{2m}(-k^2)\Psi + U_0\Psi = i\hbar(-iw)\Psi$$

which we can divide by ? !!!

and we get

$$\frac{\hbar^2 k^2}{2m} + U_0 = \hbar w$$

as we know $\hbar w = E_{total} = KE + PE$

so what is $\frac{\hbar^2 k^2}{2m}$ with $k^2 = (^{2p} / _{?})^2$ and $p^2 = (^{h} / _{?})^2 = m^2 v^2$

$\frac{\hbar^2 k^2}{2m}$ = ½ m v^2 is kinetic energy of the free particle moving

to the right ***QED, formalism makes sense***

as long as there is no net force, a particle does not change momentum, and moves in a straight line at constant speed, uniform linear motion – just the same for macroscopic particles is stated in Newton's first law,

Newton's first law is contained in, i.e. it is actually a solution of Newton's second law, just as harmonic (plane) wave is a solution of, i.e. is (contained in), Schrödinger's law
free particle solution can also be written as

? (x,t) = $Ae^{i(kx-wt)} = A[\cos kx - wt) + i\sin(kx - wt)]$

with E = h f = 2p $\hbar$ **f and ? =** $^{\mathbf{h}}/_{\mathbf{p}}$ **=** $\frac{2p\hbar}{p}$

? (x,t) =

$$Ae^{i(2p\frac{x}{l}-2p\cdot ft)} = Ae^{-i2p(ft-\frac{x}{l})} = Ae^{-i2p(\frac{E}{2p\hbar}t-\frac{p}{2p\hbar}x)} = Ae^{-\frac{i}{\hbar}(Et-px)}$$

where E = $\frac{p^2}{2m}+U(x,t)$ = KE + PE

Let's look again at probability density, normalization and boundary conditions

normalization:

P(x) dx = ? (x,t)^2 dx

is probability that particle will be found in infinitesimal interval dx about the point x,

P(x) is called probability density (here in m^{-1}also m^{-2} or m^{-3}

as probability has to be a single value at every (x) point we care to look at to make sense, ? (x,t) and ? (x,t)^2 have to be single valued and continuous functions (of x and t) to make sense, in addition, they have to be smooth

general solutions to the Schrödinger equation contain arbitrary constants which we can arbitrarily assign values to, so a good idea is to use these constants for normalization procedures

If we know the particle must be somewhere (within some length, or area, or volume for which we have precise values, e.g. x_1 and x_2 ($x_1 < x_2$) or even infinite values +-∞ we specify the arbitrary constant so that

$\int_{x_1}^{x_2} \Psi(x,t)^2 \, dx = 1 = 100\%$ meaning the particle does exist between x_1 and x_2 with 100 % certainty at all times

any wave function which satisfied this conditions is said to be normalized ? (x,t)

if we have such a normalized ? (x,t), we can calculate the probability of the particles existence between a and b, where a = x_1 and b = x_2 in % by

$P = \int_a^b \Psi(x,t)^2 \, dx$ so if we forget to normalize we have just P ~ probability of finding the particle there and then, with normalization this becomes a measure in %

in all cases P is just the area under a curve

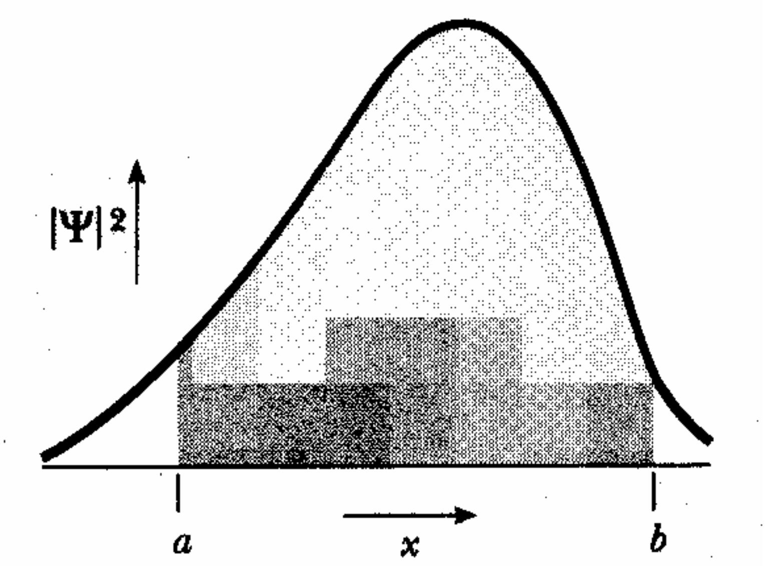


Figure 5.1 The probability for a particle to be in the interval $a \leqslant x \leqslant b$ is the area under the curve from a to b of the probability density function $|\Psi(x, t)|^2$.

this sets a strict condition to ? if it is not only to be a function that happens to solve the Schrödinger equation, but also to represent the pilot/guiding/matter wave of a real particle

the **area under the curve has to be finite** so that it can normalized to be 1 or 100 %, so ? (x,t) has to go to zero for x_1 and x_2 otherwise ? $(x,t)^2$ would not go to zero and the area under the curve would not be finite

example: Bohr radius in hydrogen atom

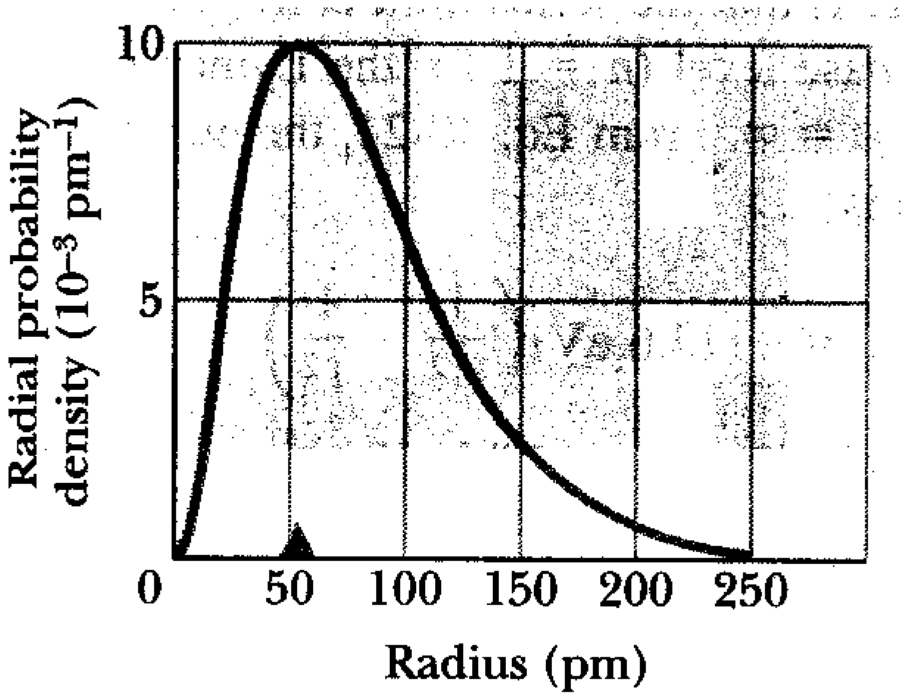


Fig. 40-18 A plot of the radial probability density $P(r)$ for the ground state of the hydrogen atom. The triangular marker is located at one Bohr radius from the origin, and the origin represents the center of the atom.

boundary conditions **<u>must be fulfilled for ? (x,t) to represent a real particle</u>**

well behaved functions

? and y must be “well behaved” in order to give sensible results for probabilities,

i.e. finite everywhere,

single valued for any x (and t),

continuous, i.e. having x (and t) values everywhere (unless V(x) is infinite)

and “smooth” – which is $\frac{dy}{dx}$ must also be continuous wherever U(x) has a finite value

in addition to being a solution of the Schrödinger equation

so ***boundary conditions and requirements of normalization*** will make it possible for us to decide **which solution of Schrödinger equation represent real particles** and which are a purely mathematical construct

example free "particle"

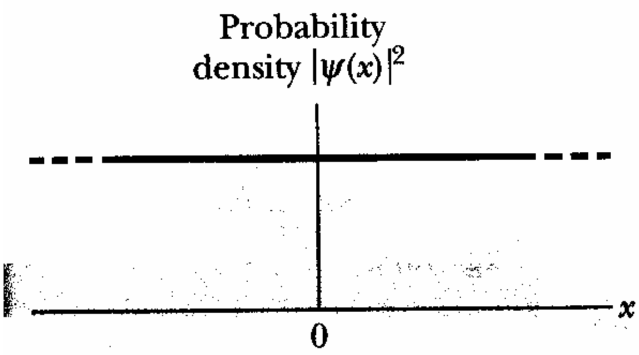


Fig. 39-11 A plot of the probability density $|\psi|^2$ for a free particle moving in the positive x direction. Since $|\psi|^2$ has the same constant value for all values of x, the particle has the same probability of detection at all points along its path.

note that the solution of the Schrödinger equation that describes this particle can not be (easily) normalized, as the area under the parallel line reaching from – to + infinity is infinite!!!, ***that, however, was implied by the definition above***

so this wave function does not describe a "real physical" particle, it is however a very useful starting model for a real particle as we can construct form such waves by means of superposition an acceptable model for a real particle, just as we did for electromagnetic waves in chapter 4

that real particle will then have a wave function that can be normalized and the plot of it probability density function will show a pulse with has finite values at some region Δx, peaking somewhere, and going to zero everywhere else, especially when x approaches +- infinity

let's look at the uncertainty principle again,

$$\Delta x \cdot \Delta p_x \approx \hbar \geq {}^{\hbar}\!/_{2}$$

and apply it to the free particle in the graph above

if the particle is free, no net force acts on it, Newton's 1st law states, if there is no net force acting, there is no change in momentum, so

$\Delta p_x = 0$ which amounts to a violation of the uncertainty principle, a model can violate the principle, but not a real particle, so the free particle described by one plane wave function (rather that a sum of many plane wave functions) is not a real particle

having a free particle described by a pulse will again mean we have mathematical uncertainties

? x ? k ˜ 1

? ? ? t ˜ 1

in the model that translate to real physical uncertainties when we make a physical interpretation of the model by replacing ? k with $\frac{2p}{\Delta l} = \frac{2p\Delta p}{h}$ (after de Broglie) and multiplying both sides with $\hbar = \frac{h}{2p}$

(analogously: applying the definition of ? = 2p f and E = h f (Plank-Einstein equation) gives physical meaning to ? ? ? t ˜ 1) so we don't violate with the mathematical model for the pulse/wave bundle/wave packet Heisenberg's uncertainty principle and this describes a real particle,

in addition, the area under a pulse will of course be finite, so we can normalize our wave function

Expectation values and Operators

the solutions to the Schrödinger equation contain everything that can be known (i.e. which the uncertainty principle allows us to know) about the movement of an entity that is a wave-particle with mass

so lets extract the (arithmetic) mean position – which is also called the expectation value, (your book states here incorrectly the average position, an average does not refer to a distribution/population but the arithmetic mean does),

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} f_i x_i$$

where f is the dimensionless frequency of occurrence of one particular value of x
(forget about p 215 lower half and p 216 top paragraph, I am pretty sure that is incorrect as I did not find a similar Modern Physics treatment in Beiser and Tipler

short maths into

if the “sample of x values” is large the mean of these values may be taken as an estimate of the distribution/population mean

the sum of all discrepancies form the mean is zero

$$\sum_{i=1}^{n}(x_i - \overline{x}) = 0$$

the variance of the mean

$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n} f_i(x_i - \overline{x})^2$$

for large ***n*,** one can approximate ***n*** with ***n-1*** and use the variance of the population

$\mathrm{var}(x) = \frac{1}{n}\sum_{i=1}^{n} f_i(x_i - m)^2 \approx \frac{1}{n-1}\sum_{i=1}^{n} f_i(x_i - m)^2$ as a measure of variance of the sample

standard deviation (s) is the square root of the variance and another measure of the amount of scatter in the data

if s = 0 then var(x) = 0, there is no spread in the data and the distribution is called sharp the uncertainly principle now tells us that particle positions (x) can only been know with probabilities, i.e. its distribution is never sharp and always fuzzy

back to the expectation value, <x>

$$< x >= \int_{-\infty}^{\infty} x\Psi(x,t)^*\Psi(x,t)dx$$

where ? (x,t) has to be

normalized

definition

the arithmetic mean of x that would be expected from measurements of the positions of a large number of particles with the same wave function!

don’t confuse with probability of finding a particle in an infinitesimal interval around x – it’s completely different things, so P = 0 may be compatible with a finite expectation value <x>

e.g. for an infinite square well and even quantum number wave functions: P($^L/_2$) = 0, but <x> = $^L/_2$ because ? ^{2} and also y ^{2} are symmetric about that point

to calculate we have the definition of the expectation value <x>

$$< x >= \int_{-\infty}^{\infty} xy(x)^*y(x)dx$$

we need normalized wave functions, and they are

$$y_n = \sqrt{\frac{2}{L}} \sin \frac{npx}{L}, \underline{\hspace{3cm}} n = 1,2,3,\ldots$$

as there is no *i*(s) $\sqrt{-1}$, the conjugate complex function has the same form and the y^2 are simply

$$y_n^2 = \frac{2}{L} \sin^2 \frac{npx}{L}, \underline{\hspace{3cm}} n = 1,2,3,\ldots$$

so the integral becomes

$$< x >= \int_{-\infty}^{\infty} x y\,(x)^* y\,(x) dx = \frac{2}{L} \int_0^L x(\sin \frac{npx}{L})(\sin \frac{npx}{L}) dx$$

$$< x >= \frac{2}{L} \int_0^L x \cdot \sin^2 \frac{npx}{L} dx = \frac{2}{L} [\frac{x^2}{4} - \frac{x \sin(\frac{2npx}{L})}{\frac{4np}{L}} - \frac{\cos(\frac{2npx}{L})}{8(\frac{np}{L})^2}]_0^L$$

since sin (np) = 0, cos (2np) = 1 and cos 0 = 1, for all values of n the expectation value of x is

$$< x >= \frac{2}{L} (\frac{L^2}{4}) = \frac{L}{2}$$

in all quantum states, the arithmetic mean position of the particle is in the middle of the box

for n = 2,4,6 the “average” position is also $^{L}/_{2}$ and this has nothing to do with $y^{2} = 0$ the probability density of finding the particle there

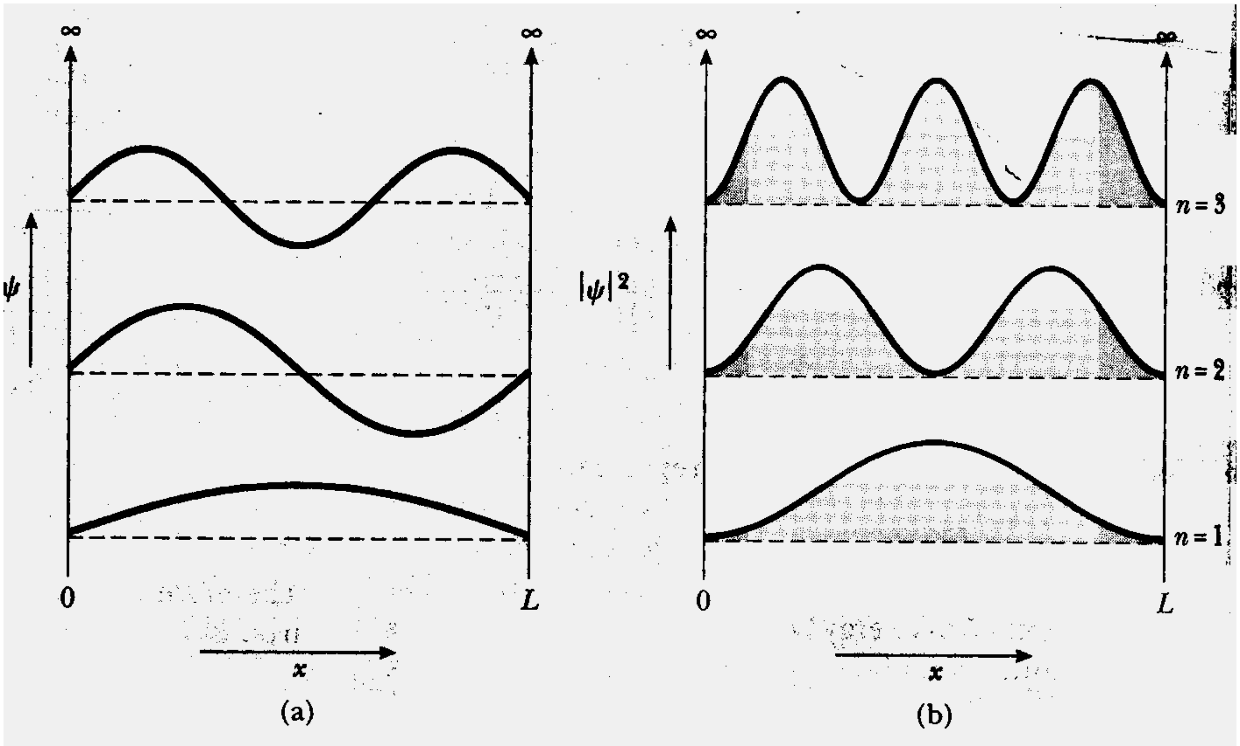


Figure 5.11 The first three allowed stationary states for a particle confined to a one-dimensional box. (a) The wavefunctions for $n = 1, 2,$ and 3. (b) The probability distributions for $n = 1, 2,$ and 3.

now the expectation value of any function of x can be calculated the same way

$$< f(x) >= \int_{-\infty}^{\infty} f(x)\Psi(x,t)^{*}\Psi(x,t)dx$$

so f(x) can be potential energy U(x) for example

however no function p = p(x) exist by virtue of the uncertainty principle, ? p_x ? x $=\frac{\hbar}{2}$ if both of these entities vary in a fuzzy way there simply can't be a relation between the two of them (there is simply no classical path in quantum mechanics)

p = mv but p ? p(x) in quantum mechanics

there is the same problem with expectation value of E, a there is an uncertainty principle as well ? E ? t $=\frac{\hbar}{2}$ only if we are considering a stationary state, i.e. when there is no time dependency and no ? t, no such uncertainty, we will have sharp values for energy

so what we need here are operators

operator is a mathematical concept telling us what to do with the operand that follows it

e.g. $(\frac{\hbar}{i}\frac{\partial}{\partial x})$ $(x^2 t)$ means that one has to take the partial x derivate of the function $(x^2 t)$ and multiply it with $\frac{\hbar}{i}$

so $(\frac{\hbar}{i}\frac{\partial}{\partial x})$ $(x^2 t) = \frac{\hbar}{i}\cdot 2xt$

what is $(\frac{\hbar}{i}\frac{\partial}{\partial x})$ $(\cos x) = -(\frac{\hbar}{i})\ \sin x$

entities for which we have operators are called observables as they have physical meaning and can be observed (although subject to the uncertainty principle)

now $(\frac{\hbar}{i}\frac{\partial}{\partial x})$ **is actually the momentum operator [p] that gives us the expectation value of the momentum <p>**

$$< p >= \int_{-\infty}^{\infty} \Psi(x,t)^* \frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(x,t)dx$$ note that the order of factors is important, there is only one way of doing it correctly

similarly

$$< p^2 >= \int_{-\infty}^{\infty} \Psi(x,t)^* \frac{\hbar}{i}\frac{\partial}{\partial x}\{\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(x,t)\}dx$$

first one operator is applied to its operand yielding the operand for the second operator (which will again stand to the right of the operator)

for example: calculate the expectation value <p> for the ground state wave function in the infinite square well, we know it is a stationary state (standing wave) so it is time independent, we know the particle is trapped in the well, so it is never outside, so we can restrict the integral to the well

the (normalized and time independent) wave function for that state is $y = \sqrt{\frac{2}{L}}\sin\frac{px}{L}$ as there are no i(s) in it the conjugate complex of that functions $y*$ is also $\sqrt{\frac{2}{L}}\sin\frac{px}{L}$

so $$< p >= \int_0^L \sqrt{\frac{2}{L}}\sin(\frac{px}{L})(\frac{\hbar}{i}\frac{\partial}{\partial x})\sqrt{\frac{2}{L}}\sin(\frac{px}{L})dx$$

simplifies to $$< p >= \frac{\hbar}{i}\frac{2}{L}\frac{p}{L}\int_0^L \sin(\frac{px}{L})\cos(\frac{px}{L})dx = 0$$

this is of course because sin x = 0 at the nodes!!

so the expectation value <p> is zero, what does it mean, simply the particle is just as likely moving to the right as it is moving to the left, the arithmetic mean must, thus, give zero

generally operators are written in sharp straight brackets, i.e. [p] or with a “caret”, i.e. $\hat{p}$

as there are many more observables, entities with physical meaning that are allowed to be known by the uncertainty principle, there are many more operators that give us expectation values of these observables total energy operator [E] = $i\hbar\frac{\partial}{\partial t}$

kinetic energy operator non relativistic

[KE] = $\frac{<p>^2}{2m} = \frac{1}{2m}(\frac{\hbar}{i}\frac{\partial}{\partial x})^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

Potential energy operator [(PE)] = [U] = U(x)

now let’s see if everything is consistent with the Schrödinger equation

E = KE + U so we must also have [E] = [KE] +[U]

that is equivalent to $i\hbar\frac{\partial}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x} + U$

now we multiply both sides with Ψ (it has to come from the left as these “guys” are operators)

and get $i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + U(x)\Psi$

so postulating both

[E] = $i\hbar \frac{\partial}{\partial t}$

[p]= $\frac{\hbar}{i} \frac{\partial}{\partial x}$

is equivalent to postulating the Schrödinger equation !!!

now notice the operators of kinetic and potential energy are only involving spatial coordinate x, we can define a combined operator for the total energy that also involves only the spatial coordinate x, this is call the Hamiltonian operator [H]

[H] = $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U$

sum of kinetic and potential energy operator must also be total energy operator that involves only time coordinate (t)

E = $i\hbar \frac{\partial}{\partial t}$

so we have actually two total energy operators and if they operate on the same wave function, the must yield the same observable expectation value !! again multiplying with Ψ yields

$$[H]\Psi = [E]\Psi$$

the “pretty compact” version of the Schrödinger equation

Eigenvalues and Eigenfunctions

for simplicity we deal here only with time independent wave functions, if something is in a steady state the uncertainty principle ? E ? t = $\frac{\hbar}{2}$ does not apply, there is all the time in the world, so the energy has settled into a stationary state an exact value, it is only when it jumps between stationary states that there is a ? t again, and with it an uncertainty of energy that shows up in a widths of a spectral line

“eigen” is German and means self, so what is meant here is combinations of real numbers (values) and functions that are equivalent to the action of an operator on these functions.

(if you know about systems of linear equations and matrix representation, you have the very same things, combinations of vectors with values that are “self” solutions to the problem, was invented in Göttingen by Jordan and Hilbert, who told Born und Heisenberg about it, …)

mathematical definition $[G]?_n = g_n ?_n$ where
e.g. operator $\frac{d^2}{dx^2}$ has eigen function $y = e^{2x}$
what is the eigenvalue to this functions and operator

$$\frac{d^2}{dx^2} e^{2x} = \frac{d}{dx}\left(\frac{d}{dx} e^{2x}\right) = \frac{d}{dx} 2e^{2x} = 4e^{2x}$$

as the eigen function was just e^{2x} the (generally real) number 4 is for that function exactly equivalent to the operator $\frac{d^2}{dx^2}$

back to physics

eigenfuctions are here again solutions to the Schrödinger equation, we deal only with time independent form if we are looking at stationary states such as in the case of a particle in a box we get sharp values for certain operators such as the total energy operator, so there is no expectation value for energy as there is no arithmetic mean of measurements on many identical particles, if we are dealing with an eigenvalue/eigenvector problem the eigenvalue is just one value, e.g. a definitive energy for every eigenfunction, , eigenfunction and eigenvectors are refereeing to a set of quantum numbers that are integers

*from particle in an infinite square well, you know****, energy comes only in discrete values,*** $E_{n,}$ ***these are the eigenvalues to the eigenfunctions*** y_n

so time independent Schrödinger equation can be written most compactly

$$[H]y_n = E_n y_n$$

for correct description of atoms we will have a second set of eigenvalues and eigenfuctions, because angular momentum is in nature also quantized not only energy, so there will be another quantum number *actually there will be two more sets of eigenfunctions and eigenvalues as a state of an electron in an atom is described by 4 quantum numbers*

Model: Particle in a box with infinitely large potential barriers, infinite square well

infinite barriers, the particle is always confined, never outside

exercise: deriving form of the wave function under the boundary conditions

it’s a stationary state, so we use time independent Schrödinger equation

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

so $y\,(x) = 0$ outside the box

inside box U(x) = 0

$$\frac{d^2 y\,(x)}{dx^2} + \frac{2mEy\,(x)}{\hbar^2} = 0 = \frac{d^2 y\,(x)}{dx^2} + k^2 y\,(x)$$

solutions of this ordinary partial equation are sin kx and cos kx so most general solution is

$y\,(x) = A\sin kx + B\cos kx$ inside the box 0 < x <L

how about x = 0 = L?

well interior wave must match exterior wave to be continuous everywhere, but the slope $\frac{dy}{dx}$ is not continuous, so it is not a real physical situation, just a model that may approximate a real physical situation pretty well

so interior wave must vanish at x and L

we can obtain this by setting

$y\,(0) = B = 0\_\_\_\; for\_x = 0$ so the cosine herm is gone

$y\,(L) = A\sin kL = 0\_\_\_\; for\_x = L$ this requires kL=np where n is 1,2,3, …

because k = $^{2p}/_{?}$ this is equivalent to fitting an integer number of half-wave length into the box

using k = $^{np}/_{L}$

and remembering that

$$\frac{d^2y\,(x)}{dx^2} + \frac{2mEy\,(x)}{\hbar^2} = 0 = \frac{d^2y\,(x)}{dx^2} + k^2y\,(x)$$

was our starting point

we find that the particles energy is quantized

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2 h^2}{8mL^2}$$

just the same result as we obtained in Chapter 4 from nodes of standing wave conditions

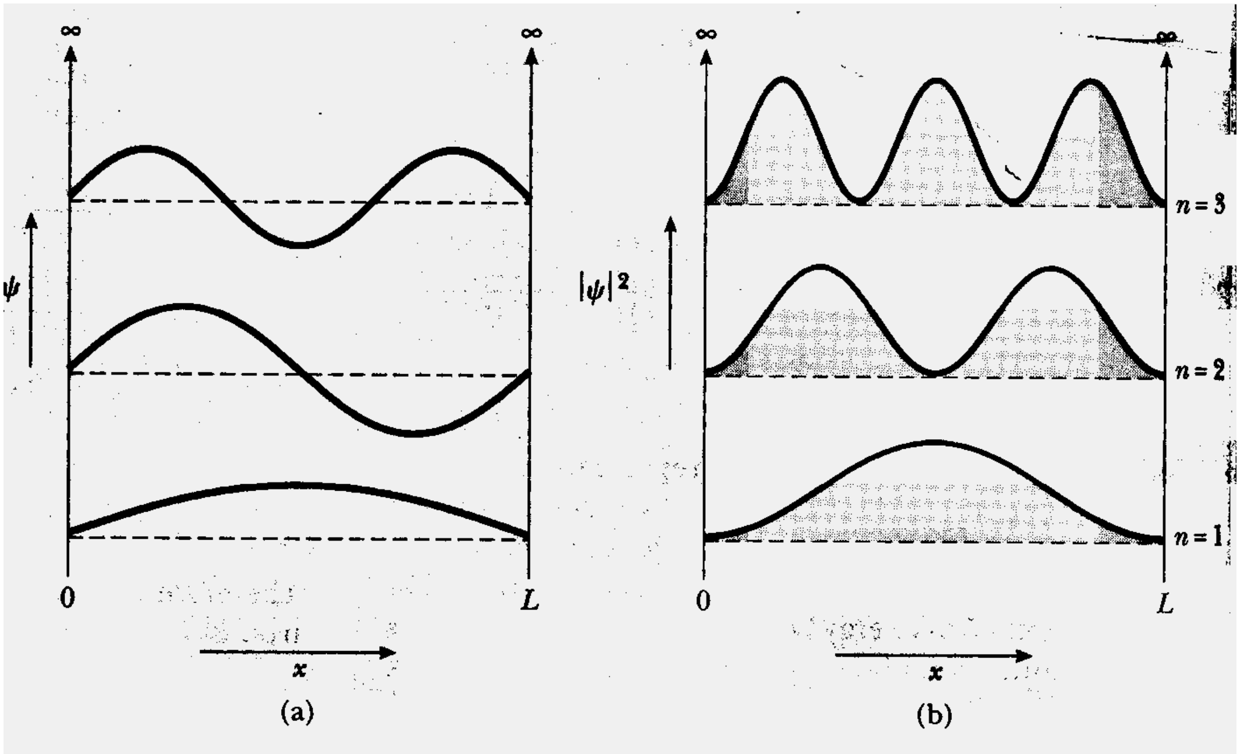


Figure 5.11 The first three allowed stationary states for a particle confined to a one-dimensional box. (a) The wavefunctions for $n = 1, 2,$ and 3. (b) The probability distributions for $n = 1, 2,$ and 3.

looking at $y_{n>1}(x)^2$ there are places besides the walls (x and L) where the particle can never be found!!!

for $y_2(x)^2$ the particle is never at $^1/_2$ L for $y_3(x)^2$ the particle is never at $^1/_3$ and $^2/_3$ L

how does the particle get over these points ??? well it’s particle-wave duality not just a particle of which we have an intuitive idea how it is supposed to move – something we can’t grasp with or brain having evolved over time looking only at classical phenomena – and of course, there is no path the wave-particle could follow

so far we only looked at $y_n(x)^2$ to make calculations of actual probabilities, we need to normalize the wave functions

$$P = \int_0^L y\,(x)^2\,dx = 1 = A^2 \int_0^L \sin^2\left(\frac{npx}{L}\right)dx$$

there is a trigonometric identity: 2 $\sin^2$ T = 1 – cos2T so we get

$$1 = A^2 \int_0^L \sin^2\left(\frac{npx}{L}\right)dx = A^2\,\frac{1}{2}\int_0^L 1 - \cos\left(\frac{2npx}{L}\right)dx$$

now cos $\frac{2px}{L}$ integrates to sin $\frac{2px}{L}$ which is zero at x = 0 and x = L

$\int_0^L 1 \cdot dx$ is just L – 0 = L

so 1 = $\frac{A^2 L}{2}$ from which we get the normalization factor

A = $\sqrt{\frac{2}{L}}$

our wave functions ready to be evaluated for probability densities in % are, thus,

$$y_n(x) = \sqrt{\frac{2}{L}} \sin(\frac{npx}{L})$$ with n = 1, 2, 3, …

one more thing on the infinite square well

the lowest energy state is given by n = 1

what would happen is n = 0 ?

$$\frac{d^2 y(x)}{dx^2} = 0$$ **is to be solved !**

solution is wave function

$$y\,(inside\_box) = Ax + B$$

this wave function has to be zero at x and L, this requires both A and B to be zero

$$y\,(inside\_box) = Ax + B = 0\_everywhere!!!$$

is we look at the probability of finding this particle

$$\int_0^L \Psi(x,t)^2\,dx = 0 = 0\% = there\_is\_no\_such\_particle$$

so n = 0 and E = 0 are not possible !!!

returning to wave function for particle in infinitely deep box / infinite square well

$$y_{\,n}(x) = A\sin\frac{npx}{L}$$

for each of the quantum numbers, 1, 2, 3, … there is a specific wave function describing everything that is permitted to be known by the uncertainty principle

one last thing on the infinite square well

with assuming impenetrable walls of infinite height, we actually violated one of the boundary conditions for physical meaningful wave functions:

derivates of wave function with respect to space coordinates (x,y,z), i.e. $\frac{\partial \Psi(x,t)}{\partial x}$ or $\frac{\partial y\,(x)}{\partial x} = \frac{dy}{dx}$ must be continuous, this means slopes must be continuous

in the infinite square well model, the wave functions just “kind of stopped” at the walls, analogous to a classical wave on a string of a guitar, that would stop and get reflected back making up the standing wave – making music ...

but the real world is different on a quantum level, if it is to be a real particle that is represented by a solution to the Schrödinger equation, the slope has to be continuous, so a real particle-wave does not stop at any barrier, it always “leaks” into the barrier, and if the barrier is not infinitely thick (which it never really is in the real world either) the particle has a probability to be found outside the well, when it has “tunneled” through the barrier (as it didn’t have enough energy to go over the top of the wall)

so let’s sum up:

in nature, there are no infinite potentials **energy walls**, so we should consider an alternative model**,**

finite square well, particle in a box with finite wall heights

(of either <u>infinite thickness </u>or finite thickness, again there are no walls of infinite thickness, but we modify our model one thing at a time)

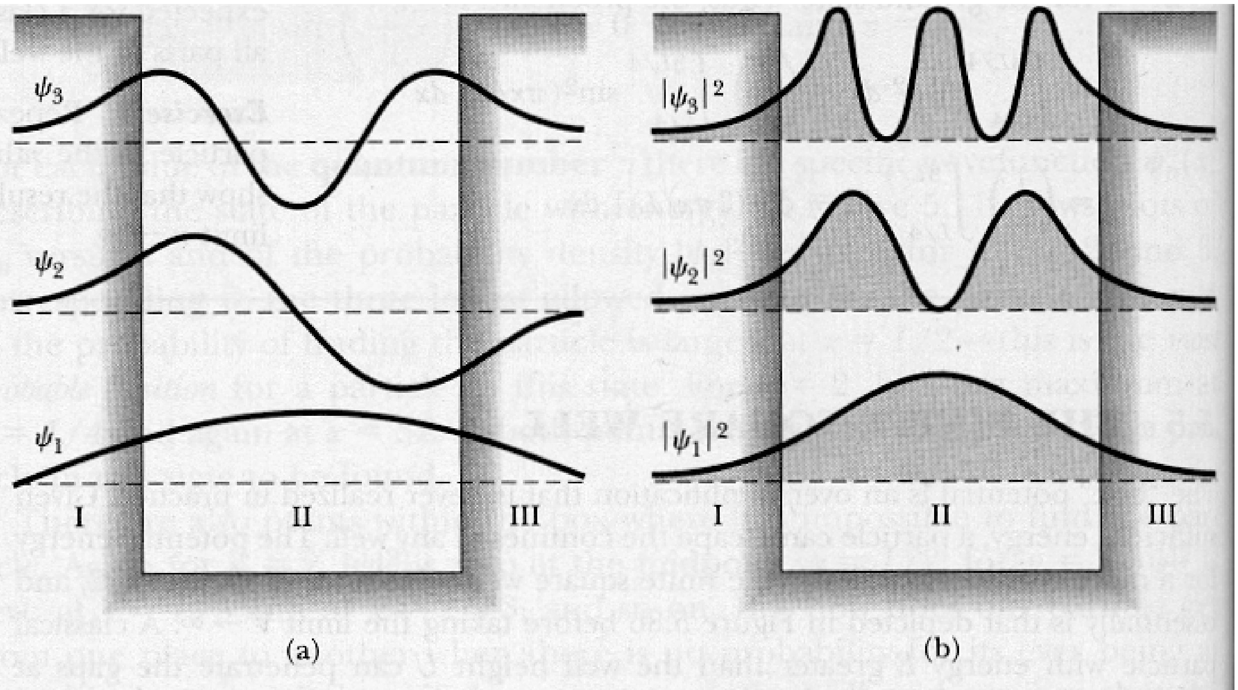


Figure 5.13 (a) Wavefunctions for the lowest three energy states for a particle in a potential well of finite height. (b) Probability densities for the lowest three energy states for a particle in a potential well of finite height.

if it has sufficient kinetic energy, classical particle can go over the top of a finite wall and move freely outside, but with reduced speed corresponding to the diminished total energy kinetic energy KE = E-PE= E-U > 0

but if total E is smaller than the height of the potential energy walls of the well, i.e. E-PE = E-U < 0, there is no kinetic energy left to roam freely, so classical particle can't be outside the wall and moving, it is trapped forever in 0 < x < L

In quantum mechanics, because of the condition

$\frac{\partial \Psi(x,t)}{\partial x}$ **or** $\frac{\partial y\,(x)}{\partial x}=\frac{dy}{dx}$ **must be continuous, i.e. slopes must be continuous,**

a particle leaks out into the potential walls !!!

This is because ? is never zero outside the well, so the probability of finding the particle there ? ^{2} is not zero either, so the particle is actually there !!!

so lets look at the parts of the wave function that penetrated into potential walls

solutions to the (time independent) Schrödinger equation

$y_I(x)=Ce^{ax}$ for x < 0, section I, where C is a constant we can use for fit to the second segment

$y_{III}(x) = De^{-ax}$ for x > L, section III, where D is a constant we can use for fit to the second segment

and $a = \sqrt{\frac{2m(U-E)}{\hbar^2}}$ is a positive constant, as U is taken to be zero in the well and some positive value outside the well

so we have an exponential decay, *that's pretty fast,* from of the constant a, we can see that the heavier the particle is and/or the larger the difference U – E, (i.e. the larger – KE of the bound state) the faster $y\,(x)$ decays in the walls, if the walls are infinitely wide, the wave function decays to zero

general solution for region II is

$$y_{II}(x) = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x$$

as U(x) = 0 in the well

and k = $\frac{\sqrt{2mE}}{\hbar}$ as usual

but as sin (0) = 0 we have to set A = 0 and can only use the second part with “cos” functions

that “cos” function’ has to match with the functions for section I and III at x = 0 and L and its first derivate with respect to x has to match as well (smoothness condition of wave functions that describes real particles) for x = 0 and L this can only be achieved for certain energy levels E_n which are all smaller that their counterparts from the infinite square well of the same widths

$$E_n^{\inf inite\_square\_well} = \frac{\hbar^2 k^2}{2m} = \frac{n^2 h^2}{8mL^2}$$

example say we have n = 1 and $y_{II}(L) = \frac{1}{2} y_{II}^{\max}$, i.e. y_{II} at the wall is only half the maximal value of this function at the center

so we can say cos kL = $^1/_2$

kL = 60° = $^p/_3$

k = $^p/_{3L}$ k = $\frac{\sqrt{2mE_1}}{\hbar}$ from above, resolved for E_1

$$E_1^{finite\_square\_well} = \frac{p^2 \hbar^2}{18mL^2} = \frac{1^2 h^2}{18mL^2}$$

<u>for that particular scenario</u> exactly 2.25 times smaller due to the particular height and widths of the square potential well, i.e. U and L, that results in the value of the wave function at L just being half the maximum value (which we have in the center of the well)

on can also see form the graph that the wavelength that fit into a finite square well (with leakage into the barriers) are somewhat larger than those wavelength that would fit into an infinite square well of the same widths, larger wavelength correspond after de Broglie (? = $^{h} / _{p}$) to smaller momenta (p), and momenta are liked to kinetic energy by KE = $\frac{p^2}{2m}$

the similarity between finite and infinite square well is also expressed in the concept of a penetration depth d

per definition $d = \frac{1}{a} = \frac{\hbar}{\sqrt{2m(U-E)}}$

at a distance d beyond each of the well edges the amplitude of the wave function has fallen to $^{1}/_{e}$ of its value at the edges, and approached zero exponentially, i.e. very very fast beyond d

with that we can make an approximation

$$E_n^{finite\_square\_well} = \frac{n^2 p^2 \hbar^2}{2m(L+2d)^2}$$

(which shall be sufficiently accurate if d << L)

which effectively says that the widths of the well is “extended” by ± d, i.e. a total of 2 d, and we have the same relation to calculate the energy levels as we had before for the infinite square well

now d is dependent on E, see relation above, so solving for $E_n^{finite\_square\_well}$ by this approximation will be an iterative process

semiconductor quantum dots- at last the real thing

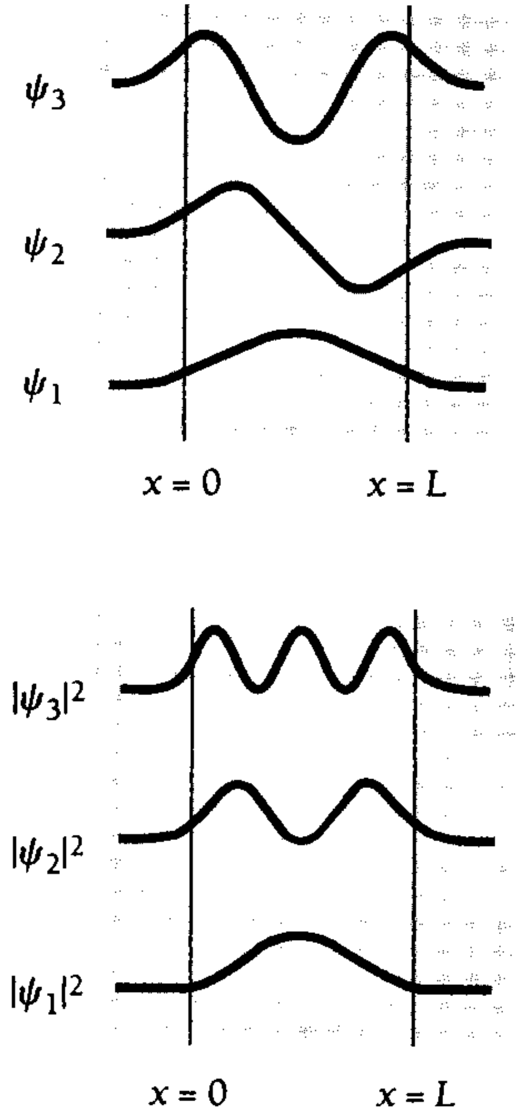


Figure 5.8 Wave functions and probability densities of a particle in a finite potential well. The particle has a certain probability of being found outside the wall.

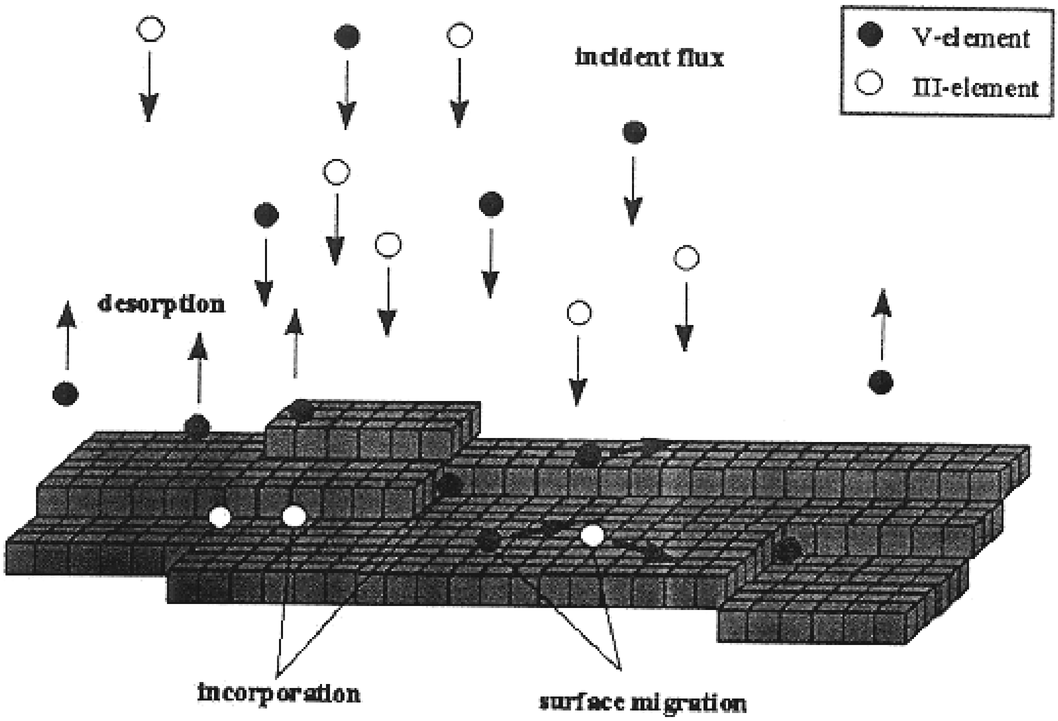
trap for an electron and a hole in a semiconductor is realized by embedding a semiconductor entity of the order of magnitude 10 nm diameter and with a smaller band gap into a semiconductor matrix with a larger band gap

particle in these “wells” is bound state of an electron and a hole, if free it’s called an exciton, if it is trapped it’s called an excitonic polaron

usual quantum mechanical treatment with Schrödinger equation, … applies, as a very crude approximation it is a three-dimensional square box with finite (height and thickness) potential energy walls, the matter wave leaks into the barrier and to some extend tunnels through it, otherwise a device could not work

it’s also called a pseudo-atom as there are discrete energy level, so there is the analogue of spectral lines

quantum dots such as this may be used in future for new computer architectures such as quantum cellular automata



deposition, surface diffusion, interdiffusion are random events, smaller band gap semiconductor (alloy) usually larger lattice constant, *(one way of self-assembly, resulting in "cake with raisins")*

epitaxially grown quantum dots compressively strained and possess random distribution of atoms ?
ordinarily strained QDs

over time, atomic ordering as observed by transmission electron microscopy

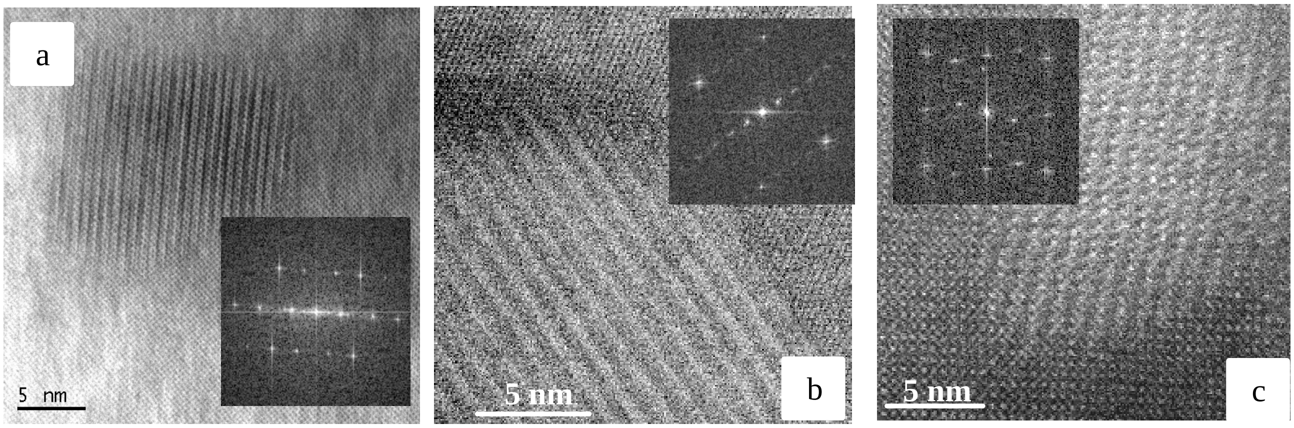


Figure 1: (In,Ga)Sb agglomerates in GaSb matrix; **(a)** [001] plan-view HRTEM image which was recorded at 500 ºC and after a thermal treatment in the electron microscope at temperatures of the order of magnitude of the growth temperature for several hours, ref. 14, suggesting that the transformed structure of this QD rather than its original sphalerite prototype structure is thermodynamically stable; **(b)** <110> cross section Z-contrast STEM image, showing a QD with atomic ordering in every forth ± (002) plane; power spectra as inserts; **c)** [001] atomic resolution Z-contrast STEM images of structurally transformed In(As,Sb) QDs in InAs matrix.

(from one of my papers, see web pages, if interested)

PSU’s new more than $ 1,000,000 microscope, would itself not be possible without modern physics and Schrödinger’s equation, because design of electromagnetic lenses is quite involved, ray optics does not do the job, it’s too crude an approximation

Quantum states of Harmonic Oscillator, a very useful approximation

say a particle is in potential well subject to a linear restoring force $\vec{F} = K \cdot \vec{x}$ with force constant K

corresponding potential energy is $U(x) = ½ K x^2$ we had something like it as a mass on a spring, a very long pendulum with a small elongation, …. anything that is limited to small excursions (x) around a stable equilibrium position

near the stable equilibrium position, say x = a, the potential energy can be approximated by a parabola:

$U(x) = U(a) + ½K(x-a)^2$

under the condition that the curvature of that parable must match

that of U(x) at the point x = a, this condition is fulfilled if

$K = \frac{d^2U}{dx^2}\Big|_a$

and U(a) is potential energy in equilibrium position a, which we can of course define as the zero level from which all potential energies are measured,
analogously we can use coordinate shift and define a = 0 on the x axis

with these two conventions we have

$U(x) = U(a) + ½K(x-a)^2 = 0 + ½K(x-0)^2 = ½K x^2$

in other words, a particle that is limited to small enough excursions about a stable equilibrium position approximately behaves as if it were attached to a string with a force constant prescribed by the curvature of the true potential at equilibrium

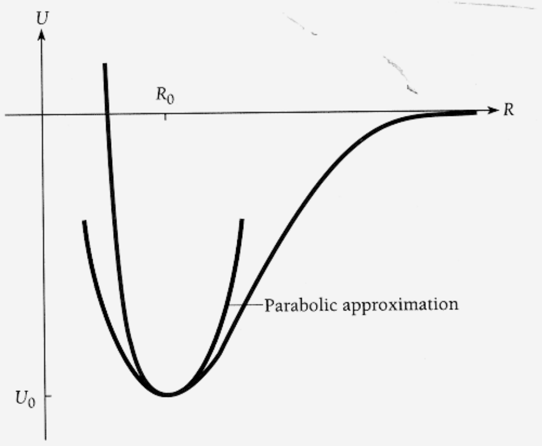


Figure 8.18 The potential energy of a diatomic molecule as a function of internuclear distance.

now if the oscillation is simple harmonic (as in classical physics), with angular frequency $w = \sqrt{\frac{K}{m}}$ (don't confuse K - the force constant with k the wave number) and we can write for the potential energy

$$U(x) = \frac{1}{2}K x^2 = \frac{1}{2} m ?^2 x^2$$

and put this potential energy function into the time independent Schrödinger equation

$$\frac{d^2 y(x)}{dx^2} = \frac{2m}{\hbar^2}\left(\frac{1}{2}mw^2x^2 - E\right)y(x)$$

as we are interested in the stationary states of the system

the kind of wave functions we had so far in this chapter are all for constant potential energy function, either zero or some finite value for all x, here the potential energy is a function of x^2

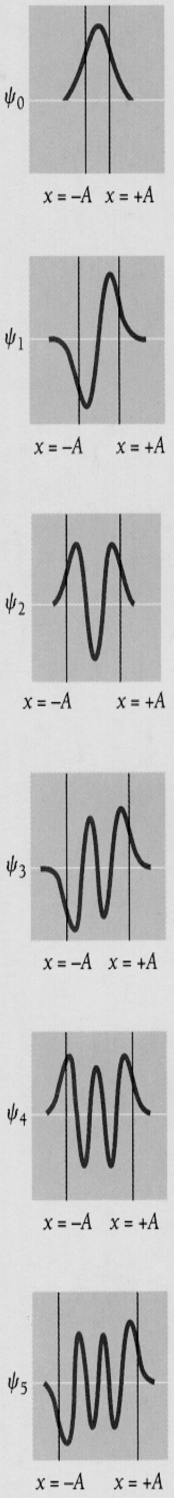


Figure 5.12 The first six harmonic-oscillator wave functions. The vertical lines show the limits $-A$ and $+A$ between which a classical oscillator with the same energy would vibrate.

ground state, n = 0, note is a mathematical consequence

$$y_0 = \left(\frac{mw}{p\hbar}\right)^{1/4} e^{-mwx^2/2\hbar}$$

and E_0 = ½ $\hbar w$ = ½ h f (also called zero point energy, as it is for n = 0 lowest quantum number

$E_1 = {}^3/_2$ h f, $E_2 = {}^5/_2$ h f ,
$E_n = (n + {}^1/_2)$ h f, n = 0, 1, 2, 3

so ? E = hf or some multiple of hf, Planck was right in his 1901 paper !!!

-A = x = A are the limits a classical oscillator would have,
in a sense these limits are barriers of the potential well, and there is a "lot of leakage" into these barriers, so in a classical picture the string would get overstretch so severely that it may not spring back

note that even a classical oscillator does have a zero point energy = ½ h f ***because things never stand still in nature***

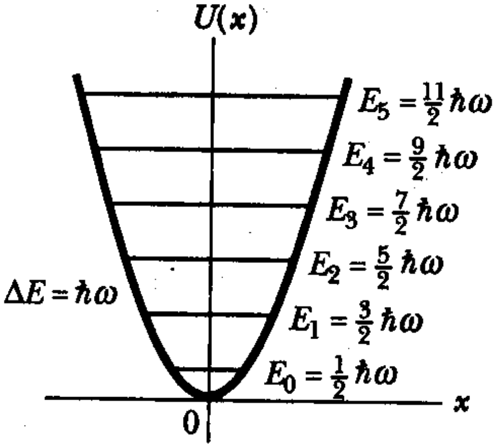


Figure 5.18 Energy level diagram for the quantum oscillator. Note that the levels are equally spaced, with a separation equal to $\hbar\omega$. The ground state energy is E_0.

that leakage into the barriers is shown below as well for y_n^2 so the particle is actually at these positions with certain probabilities

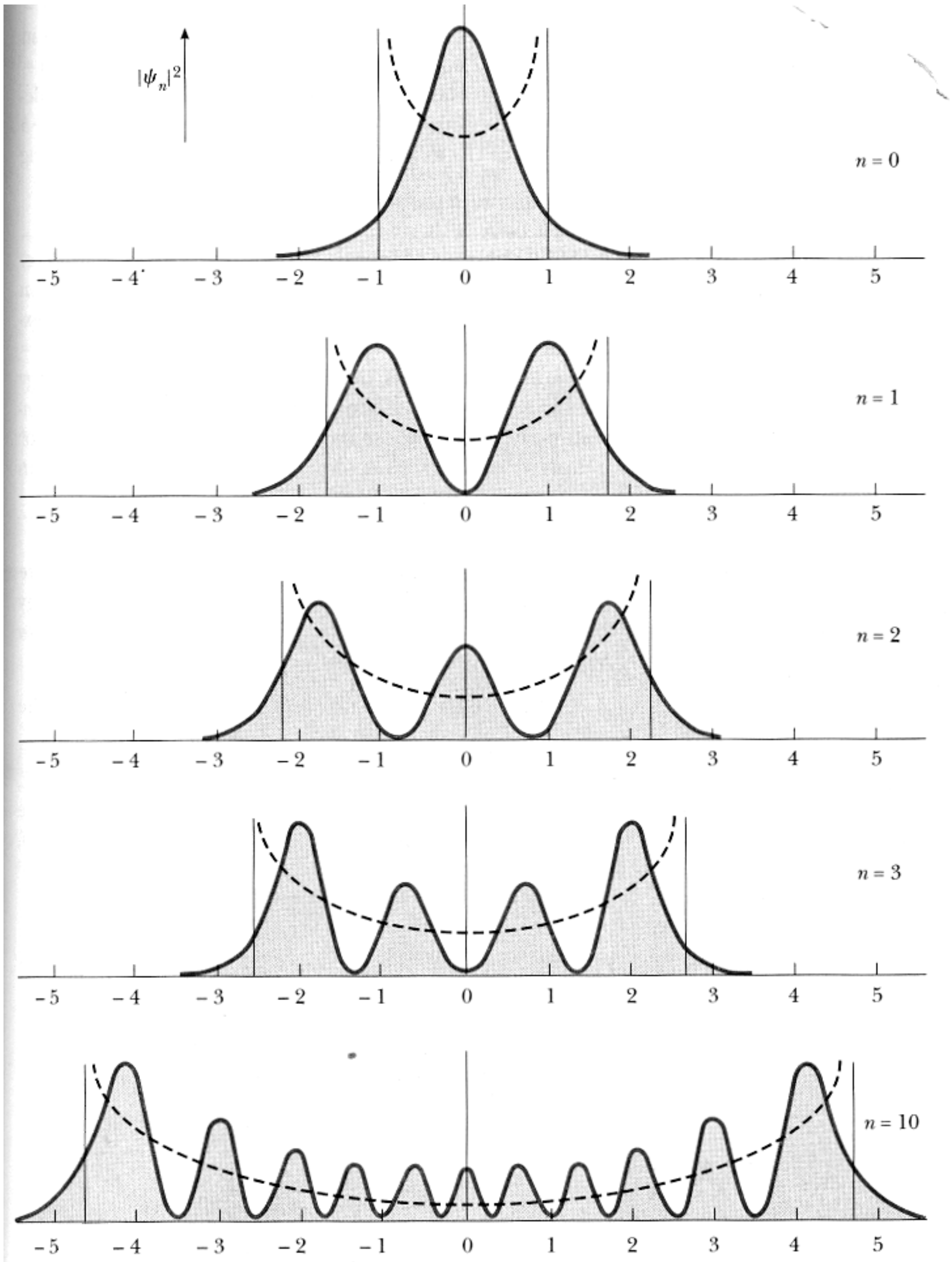


Figure 5.19 Probability densities for a few states of the quantum oscillator. The dashed curves represent the classical probabilities corresponding to the same energies.

for large quantum numbers classical physics (dashed lines) and quantum physics (curves) give corresponding probabilities of finding the particle

Transitions between states and selection rules

energy levels revealed when system makes transitions,

either to a higher energy state as a result of excitation (absorption of energy)

or to a lower energy state as a result of relaxation (de-excitation, emission of energy , if it is an electron this is usually electromagnetic radiation)

form classical physics: if a charge q is accelerated, it radiated electromagnetic radiation, remember that’s how X-rays are produced, if a charge oscillates, the radiation is of the same frequency as the oscillation

if we have charged particle (charge q), we define charge density

$r_n = qy_n{}^*y_n$ this quantity is time independent, stationary state, i.e. does not radiate, quantum mechanical explanation of Bohr’s postulate, let’s say n is the ground state

with this wave function y_n goes a certain (eigen-value) energy E_n, as long as the charged particle is in this energy state it does not radiate, it does neither lose nor gain energy say it gained just the right amount of energy to go to an excited state, this means eigen-value (energy) and wave function eigen-function change

let’s now consider how the particle returns to the ground state

only if a transition form one wave function (m) to another wave function (n) is made, the energy changes ? E = E_m –E_n from one definitive value (excited stationary state, e.g. m) to the other definitive value (relaxed stationary state, e.g. n), $E_m > E_n$

as wave function for a particle that can make a transition, we need time dependent wave function ? (x,t), as it is two different states m and n, we have a superposition

? $_{m,n}$(x,t) = a ? $_m$(x,t) + b ? $_n$(x,t)

initially say a = 1, b = 0, electron in excited state, m

while in transition a < 1, b <1, electron is oscillating between states

finally a = 0, b = 1, electron in relaxed state, n

we can calculate frequency of this oscillation

expectation value that a particle can be in a transition is

$$< x >= \int_{-\infty}^{\infty} x\Psi_m(x,t)^* \Psi_n(x,t)dx$$

if this expectation value = 0 because the integral is zero, there is no transition possible

multiplied with the charge q, we have a dipole moment

$$q < x >= q \int_{-\infty}^{\infty} x \Psi_m (x,t) * \Psi_n (x,t) dx$$ that radiates

$q<x> \; = (2 \, q \, a \, b \cos (?_{mn} \, t) \int_{-\infty}^{\infty} x y_n {}^* y_m dx) + \text{constant}$

which we can interpret as the expectation value is oscillating due to cos function, the frequency of this oscillation

is the difference of the eigenvalues of the functions divided by h-bar

$?_{mn} = \dfrac{E_m - E_n}{\hbar} = 2p \, f$ in other words, **?E = h f**

absence of a transition because the integral is zero is usually described as a selection rule

for harmonic oscillator: ? n = ± 1, so there is no transition between n = 4 and n = 2, **it is always one hf that is emitted or absorbed,** just as Plank had to assume in order to make his radiation formula fit the experimental data

for infinite square well ? n = 1, 3, 5 but not 2, 4 ,6

since, e.g. $\int_0^L \sin(\frac{2px}{L}) dx \sin(\frac{px}{L}) dx = 0$