

Summary: rules of the Quantum game (POSTULATES)

1) At a fixed time t_0 , the state of a physical system is completely defined by its wave-function $\psi(x, t_0)$ (i.e. from $\psi(x, t_0)$ you can derive any accessible property of the system under study).

→ 3) Every measurable physical quantity A is represented by an operator A acting on $\psi(x, t_0)$

Example: the position $x \rightarrow x \cdot \psi(x, t_0)$

the momentum $p \rightarrow -i\hbar \frac{\partial}{\partial x} \psi(x, t)$

4) The process of the measurement:

4a) If we repeat many times the measurements of A on various identical systems described by the wavefunction $\psi(x, t_0)$ we need NOT get always the same result. The average of the results we

get is $\langle A \rangle = \int \psi^*(x, t_0) A \psi(x, t_0)$ ^{constant}

4b) We get always the same result iff $A \psi(x, t_0) = (a) \psi(x, t_0)$

4c) Collapse of the wave-function: if the result of a measurement of A is the value v , then during the measurement the wavefunction suddenly changes from $\psi(x, t_0) \xrightarrow{t_0} \psi_v(x, t_0)$ where this new form satisfies

$$A \psi_v(x, t_0) = v \psi_v(x, t_0)$$

2) Linearity: if $\psi_1(x, t_0)$ is an acceptable physical state and $\psi_2(x, t_0)$ is another acceptable physical state for the same system, then also $\psi_1(x, t_0) + \psi_2(x, t_0)$ is acceptable (acceptable = it can occur in nature)

Schrodinger Equation

So far we focused only on "kinematics", that is on how it is possible to extract physical information from the wavefunction which we supposed to be given in a certain form.

Now I want to address dynamical questions, that is explain how the wave-function changes in time, depending on the physical situation. To keep things simple we keep living in

our 1-dimensional world where there exists only one particle (!). The simplest possible situation is that no force acts on this particle - what would be the equation governing the time evolution

of ψ ? To derive it we take the following simple recipe:

1) Write down the energy this particle would have in classical mechanics. Two choices

Fully relativistic expression

$$E^2 = p^2 c^2 + m^2 c^4$$

Non-relativistic approximation

$$\frac{p^2}{2m} = KE$$

2) Promote the classical quantities p, E etc. to the corresponding operation on the wavefunction

$$- \hbar^2 \frac{\partial^2}{\partial x^2} \psi = - \hbar^2 c^2 \frac{\partial^2}{\partial x^2} \psi + m^2 c^4 \psi$$

$$- \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi = i \hbar \frac{\partial}{\partial t} \psi$$

Neglect the rest mass!
see later

KLEIN-GORDON

SCHRÖDINGER

In this course (and probably in the rest of your undergraduate studies!) you will study just the non-relativistic Schrodinger equation - why! The reason is hidden in Einstein relation $E = mc^2$ which tells us that mass and energy are the same thing. In a relativistic theory the number of particles is NOT conserved and a very energetic particle can use part of its energy to create another particle - So the framework of quantum mechanics is not sufficient and you'll need something known as Quantum Field Theory - So I will not give you a law describing processes where the number of particles changes - For those cases you have only one piece of information: the conservation laws (energy / momentum) - so let us focus on a non-relativistic particle (like an electron with energy of few eV) - The equation describing the time evolution of ψ is

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi = i\hbar \frac{\partial}{\partial t} \psi$$

By applying the same recipe we can easily generalize the above equation to cases where the electron is subject to some external force F that can be derived from a potential $U(x)$ $F = -\frac{dU}{dx}$ - In fact in this case the classical energy is $K.E + U(x)$

So the Schrödinger equation reads

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

Any solution to this equation represents a physically possible time evolution of a wave function. If we fix the wave function at a certain time to $\psi(x, t_0)$ then the form of ψ at later times is completely determined by the Schrödinger equation

(so the probabilistic nature of Quantum mechanics is hidden in the interpretation of ψ , not in the Schrödinger equation) —

In this course we will be interested only in a very particular kind of solutions known as "Stationary States". These are

wave function of the form

$$\psi_E(x, t) = \psi_E(x) e^{-\frac{i}{\hbar} E t}$$

This is just a constant

These states are called stationary because the probability of finding

the particle in a certain place does not change in time

$$P(x) = \psi_E^*(x, t) \psi_E(x, t) = \left[\psi_E^*(x) e^{\frac{i}{\hbar} E t} \right] \left[e^{-\frac{i}{\hbar} E t} \psi_E(x) \right] = |\psi_E(x)|^2$$

Another key-feature of these stationary wavefun. is that they describe

the particle in a state of definite energy E . In fact

by using $\psi_E(x, t)$ in the general 1-D Schrödinger equation

I get the following result (known as time independent Schrödinger equation):

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi_E(x)}{dx^2} e^{-\frac{i}{\hbar} Et} + U(x) \psi_E(x) e^{-\frac{i}{\hbar} Et} = E \psi_E(x) e^{-\frac{i}{\hbar} Et}$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_E(x)}{\partial x^2} + U(x) \psi_E(x) = E \psi_E(x)$$

The operator $\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right]$ acting on the wave function is usually called Hamiltonian H and represent the total energy (kinetic + potential) of the particle. Now we can appreciate why we could neglect the rest-mass energy.

→ Input: the most general acceptable wave-function can be written as linear combination of stationary states (states with definite energy or Eigenstates of H).

most generic

$$\psi = \sum_k \psi_{E_k}(x) e^{-\frac{i}{\hbar} E_k t} \quad k=1, \dots$$

Now if instead of $E = KE + U$ we write also the contribution of the rest mass energy we would get a different $\hat{\psi}$

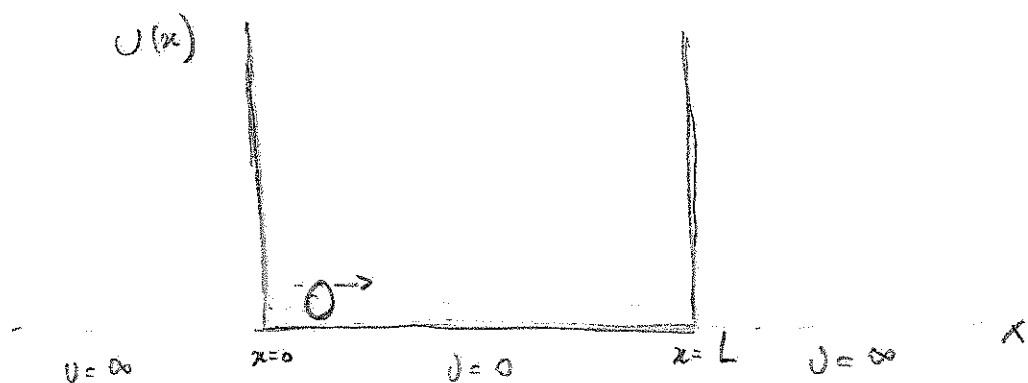
$$\hat{\psi} = \sum_k \psi_{E_k} e^{-\frac{i}{\hbar} (E_k + mc^2) t} = e^{-\frac{i}{\hbar} mc^2 t} \psi$$

So $\hat{\psi}$ is just the old ψ multiplied by an overall phase that does not have any physical consequences (for instance

$$P(x) = \psi^* \psi = \hat{\psi}^* \hat{\psi}, \text{ etc.})$$

Let me now study some quantum mechanical system by using the Schrödinger equation

PARTICLE IN A BOX



$$-\frac{\hbar^2}{2m} \frac{d^2 \psi_E}{dx^2} = E \psi \quad 0 \leq x \leq L$$

$$\psi(x) = 0 \quad \text{when} \quad x \leq 0 \quad \text{or} \quad x \geq L$$

This is a second order differential equation (actually a rather simple one) and so the most general solution depends on 2 arbitrary constants

$$\psi_E(x) = A_1 e^{ikx} + A_2 e^{-ikx} \quad \text{is a solution if}$$

$$\frac{\hbar^2 k^2}{2m} = E \quad \rightsquigarrow \quad \text{which fixes } k \text{ in function of } E$$

What about A_1 and A_2 ? These are fixed by the boundary conditions ($\psi(x=0) = \psi(x=L) = 0$) and by the

$$\text{normalization condition} \quad \int \psi_E^*(x) \psi_E(x) = 1$$

Let me consider the first boundary condition

First boundary condition

$$0 = \psi_E(0) = A_1 + A_2 \Rightarrow -A_2 = A_1 \quad \text{with } \kappa = \frac{\sqrt{2mE}}{\hbar}$$
$$\Rightarrow \psi_E(x) = A_1 [e^{i\kappa x} - e^{-i\kappa x}] = 2iA_1 \sin \kappa x$$

Second boundary condition

$$0 = \psi_E(L) = 2iA_1 \sin \kappa L \Rightarrow \kappa L = \pi n \quad n = 1, 2, \dots \text{ (Plots)}$$

$\Rightarrow \kappa = \frac{\pi n}{L}$... which means that energy is quantized!

$$E = \frac{\hbar^2 \kappa^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2L^2 m} = \frac{h^2 n^2}{8mL^2}$$

- Each stationary state describe a different energy level! As n becomes bigger the energy increases (\Rightarrow describes a particle that bounces forth and back faster).
- The stationary levels $\psi_E(x)$ are exactly equal to the de Broglie standing waves you have seen in the exercises of week 5. (In fact the values of E for each level is exactly the one we got with de Broglie's rules of standing waves!)

Normalization condition: $P(x) = \psi_E^*(x) \psi_E(x) = 4|A_1|^2 \sin^2 \frac{\pi n}{L} x$

$$1 = \int_{-\infty}^{+\infty} \psi_E^*(x) \psi_E(x) dx = \int_0^L P(x) dx = 4|A_1|^2 \int_0^L \sin^2 \frac{\pi n}{L} x dx = 4|A_1|^2 \frac{L}{2}$$

$\psi_E(x)$ and $P(x)$ are zero outside the interval $0 \leq x \leq L$

$$|A_1| = \frac{1}{\sqrt{2L}}$$

so the normalized (stationary) wave functions are

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi n}{L} x} \quad n=1, 2, 3, \dots$$

I now use the label n (instead of E) to indicate the energy level ($E_n = \frac{h^2 n^2}{8mL^2}$). I also chose the phase of A_1 to simplify

the form of ψ_n (by eliminating the factor of i) -

Let us see some physical properties of these solutions

- Let us compute the average position of the particle when it is in the state $\psi_n(x)$

$$\begin{aligned} \langle x \rangle_{\text{state } n} &= \int_0^L \psi_n^*(x) x \psi_n(x) dx = \frac{2}{L} \int_0^L x \sin^2 \frac{\pi n}{L} x dx = \\ &= \frac{2}{L} \int_0^L x \frac{1 - \cos \frac{2\pi n}{L} x}{2} dx = \frac{1}{L} \left[\int_0^L x dx - \int_0^L x \cos \frac{2\pi n}{L} x dx \right] \\ &= \frac{1}{L} \left[\frac{L^2}{2} - \left(x \frac{L}{2\pi n} \sin \frac{2\pi n x}{L} \Big|_0^L - \int_0^L \frac{L}{2\pi n} \sin \frac{2\pi n x}{L} dx \right) \right] = \frac{L}{2} \end{aligned}$$

This is zero

This is what we expected also in the classical theory if we interpret the probability average as time average (not by chance!)

what about $\langle p \rangle_{\text{state } n}$

$$\langle p \rangle_{\text{state } n} = \frac{2}{L} \int_0^L \sin \frac{\pi n x}{L} \frac{\pi n}{L} \cos \frac{\pi n x}{L} dx = 0$$

again

Let me now compute the deviation $\Delta x^2 = (x - \langle x \rangle)^2$

$$\langle \Delta x^2 \rangle = \frac{2}{L} \int_0^L \sin^2\left(\frac{\pi n}{L} x\right) \left(x - \frac{L}{2}\right)^2 dx \quad y = x - \frac{L}{2}$$

$$= \frac{2}{L} \int_{-L/2}^{L/2} \sin^2\left(\frac{\pi n}{L} y + \frac{\pi n}{2}\right) y^2 dy$$

\swarrow n even \searrow n odd

$$= \frac{2}{L} \int_{-L/2}^{L/2} \sin^2\left(\frac{\pi n}{L} y\right) y^2 dy$$

$$= \frac{2}{L} \int_{-L/2}^{L/2} \left(\cos^2 \frac{\pi n y}{L}\right) y^2 dy$$

$$= \frac{1}{L} \int_{-L/2}^{L/2} \left(y^2 - y^2 \cos \frac{2\pi n y}{L}\right) dy$$

similar

$$= \frac{1}{L} \left[\frac{L^3}{12} - \left(y^2 \sin \frac{2\pi n y}{L} \Big|_{-L/2}^{L/2} - 2 \int_{-L/2}^{L/2} y \sin \frac{2\pi n y}{L} dy \right) \frac{L}{2\pi n} \right]$$

$$= \frac{L^2}{12} + \frac{1}{\pi n} \int_{-L/2}^{L/2} y \sin \frac{2\pi n y}{L} dy$$

$$= \frac{L^2}{12} - \frac{L}{2\pi^2 n^2} y \cos \frac{2\pi n y}{L} \Big|_{-L/2}^{L/2} + \frac{L}{2\pi^2 n^2} \int_{-L/2}^{L/2} \cos \frac{2\pi n y}{L} dy = \frac{L^2}{12} - \frac{L^2}{2\pi^2 n^2}$$

$$\langle \Delta p^2 \rangle = \frac{2}{L} \int_0^L \sin \frac{\pi n x}{L} \left(-i\hbar \frac{\partial}{\partial x}\right) \left(-i\hbar \frac{\partial}{\partial x}\right) \sin \frac{\pi n x}{L}$$

$$= \frac{\hbar^2 \pi^2 n^2}{L^2} = \frac{\hbar^2 n^2}{4L^2} \quad \leftarrow \text{This is also related to } E$$

$$\Delta x^2 \Delta p^2 = \hbar^2 \left(\frac{\pi^2 n^2}{12} - \frac{1}{2} \right) \xrightarrow{\text{for } n=1} \hbar^2 \left(\frac{\pi^2}{12} - \frac{1}{2} \right) > \hbar^2 \left(\frac{9}{12} - \frac{1}{2} \right) = \frac{\hbar^2}{4}$$

Notice a strange (but expected) features of Quantum mechanics

- The particle can never be at rest (Heisenberg uncertainty principle)

An estimate of Δp is given by the relation $\Delta x \Delta p \geq \frac{\hbar}{2}$

So the lowest possible Δp is $\geq \frac{\hbar}{2L/2}$ where I used $\Delta x \sim \frac{L}{2}$

$$\Rightarrow \frac{\Delta p^2}{2m} = E \sim \frac{\hbar^2}{2mL^2}$$

- The particle energies are quantized (only the value

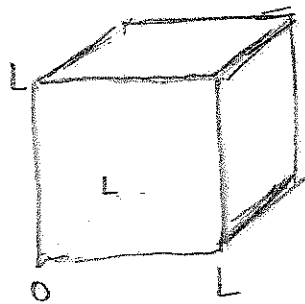
$$\frac{\hbar^2 \pi^2 n^2}{2mL^2} \text{ are possible})$$

\Rightarrow Now let me consider (for a change!) a three-dimensional system:

a cubic box

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} \psi(x,y,z) + \frac{\partial^2}{\partial y^2} \psi(x,y,z) + \frac{\partial^2}{\partial z^2} \psi(x,y,z) \right) = E \psi(x,y,z)$$

where ψ is zero outside the box



The system is quite simple because in this case the total wave functions is just the product of three 1D wave functions

$$\psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{\pi n_1}{L} x\right) \sin\left(\frac{\pi n_2}{L} y\right) \sin\left(\frac{\pi n_3}{L} z\right)$$

or in general

$$= \frac{2^{3/2}}{\sqrt{L_1 L_2 L_3}} \sin\left(\frac{\pi n_1}{L_1} x\right) \sin\left(\frac{\pi n_2}{L_2} y\right) \sin\left(\frac{\pi n_3}{L_3} z\right)$$

Now each stationary state is determined by a triplet of integer numbers $\{n_1, n_2, n_3\}$ and has energy $E = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2)$.

Of course the state of minimal energy is $n_1=1, n_2=1$ and $n_3=1$ and it is unique $E_1 = \frac{3\hbar^2 \pi^2}{2mL^2}$. The next level of energies is $E_2 = \frac{6\hbar^2 \pi^2}{2mL^2}$ and can be obtained in 3 different ways

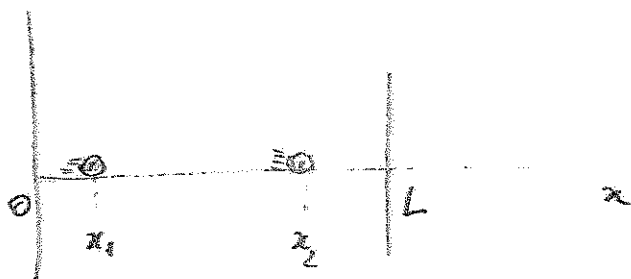
$n_1=1$	$n_1=1$	$n_2=2$	Higher energetic states can be degenerate in energy (and in order to distinguish among them I need to measure another quantity)
$n_2=1$	$n_2=2$	$n_2=1$	
$n_3=2$	$n_3=1$	$n_3=1$	

This phenomenon is called degeneracy (i.e. when two states with different quantum numbers have the same energy). Notice that this can happen only if the three lengths of the box (width, height, depth) have special values (for instance if they are equal as in the example discussed here).

⇒ Now let me consider another "complication": we want to describe a system with more than one particle. The simplest thing would be to study 2 particles in a (1-dimensional) box. How can I describe this situation? The most natural thing is to introduce a function $\psi_1(x_1)$ describing the 1st particle, a function $\psi_2(x_2)$ describing the second particle and then define the global wave-function (describing the whole system) to be

Just the products of ψ_1 and ψ_2

$$\psi(x_1, x_2) = \psi_1(x_1) \psi(x_2)$$



Notice that this is a 1D system: both x_1 and x_2 are on the same axis, but x_1 describes the position of the 1st particle and x_2 the position of the second one

The (time independent) Schrödinger equation for $\psi(x_1, x_2)$ is

$$\left\{ \begin{aligned} -\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2} \psi(x_1, x_2) - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial x_2^2} \psi(x_1, x_2) &= E \psi(x_1, x_2) \end{aligned} \right.$$

$$\left\{ \begin{aligned} \psi(x_1, x_2) &= 0 \quad \text{if } x_1 \text{ or } x_2 \geq L, \quad x_1 \text{ or } x_2 \leq 0 \end{aligned} \right.$$

kinetic energy of the 1st particle

kinetic energy of the second particle

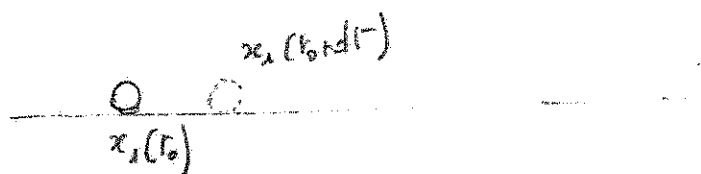
The state of lowest energy is

$$\psi(x_1, x_2) = \frac{2}{L} \sin \frac{\pi x_1}{L} \sin \frac{\pi x_2}{L}$$

Everything looks nice and simple... but something strange happens if the two particles I put in the box are identical (like two electrons). In this case how can

I distinguish between the particles?

In classical physics I could distinguish the two "identical" particles by their position-trajectory: if I label the position of the 1st particle at the time t_0 with $x_1(t_0)$ then at a slightly later time $t_0 + \delta t$ the same particle will be close to $x_1(t_0)$



Now we know that in quantum mechanics the wave function does not usually describe a particle with a definite position. So we can not use this to distinguish the two identical particles... whatever you try you will discover that there is no way to distinguish the two particles in Q.M.!! What's the consequence of this on the form of the wave function $\psi(x_1, x_2)$? Since there is no difference between particle "1" and "2" then the most natural requirement is that $\psi(x_1, x_2)$ should be symmetric in the exchange of $x_1 \leftrightarrow x_2$.

$$\psi(x_1, x_2) = \psi(x_2, x_1) \quad (\text{bosons})$$

However this is not what always happens. For certain kinds of particles the global wave function has to be odd in the exchange $x_1 \leftrightarrow x_2$

$$\psi(x_1, x_2) = -\psi(x_2, x_1) \quad (\text{fermions})$$

Examples: the electron is a fermion, while the photon is a boson (even if it can not be described by a Schrödinger equation since the non-relativistic approximation does not apply).

This has a very important consequence: two fermions (as for instance two electrons) can not stay simultaneously in the same wave-function. If the "first" electron is described by

$\sqrt{\frac{2}{L}} \sin \frac{\pi x_1}{L}$ the "second" one can not be described by the same wave-function because we would get a symmetric global wave-function

$\psi(x_1, x_2) = \frac{2}{L} \sin \frac{\pi x_1}{L} \sin \frac{\pi x_2}{L}$ ($\psi(x_1, x_2) = \psi(x_2, x_1)$) instead of an anti-symmetric one. The "second" electron need to have a different

wavefunction, for instance $\sqrt{\frac{2}{L}} \sin \frac{2\pi x_2}{L}$. So we have

$$\psi(x_1, x_2) = \frac{1}{L} \left(\sin \frac{\pi x_1}{L} \sin \frac{2\pi x_2}{L} - \sin \frac{\pi x_2}{L} \sin \frac{2\pi x_1}{L} \right)$$

which indeed satisfies $\psi(x_1, x_2) = -\psi(x_2, x_1)$. This ψ

describes one electron in the state of minimal energy ($n=1$)

and the other in the first excited state ($n=2$). Then we have

Pauli exclusion principle: two electrons (fermions) can not have

the same quantum numbers (the same wavefunction).

→ This is crucial in the explanation of atomic/molecular properties