

Schroedinger's Equation

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Recapitulation of Wave Packets and Uncertainty Relations

- Classical view is that massive objects should be described by particle viewpoint and radiation should be described by wave viewpoint.
- Dynamical equation for particles is the Newton's second law (a second order differential equation in time, with spatial coordinates as dependent variables). Dynamical equation for waves is the wave equation (a second order differential equation in both time and in spatial coordinates with the oscillating *disturbance* as the dependent variable).
- In the Newtonian viewpoint, a particle has a well defined position and a well defined momentum. If we know the forces acting on the particle, we can find the position and the momentum exactly.
- A wave is typically assumed to have an infinite extent. It is characterized by its frequency and its wavelength or equivalently its wave number k and angular frequency ω .

Recapitulation of Wave Packets and Uncertainty Relations

- There are many **wave phenomena** involving massive objects.
 - vibrations of a stretched string or of deformed elastic surface
 - waves in fluids such as water waves

In the case of these phenomena, one of the spatial coordinates is becomes the oscillating variable and Newton's second law **transforms** into a wave equation, as it happens for a stretched string.

- To describe such phenomena, various mathematical techniques, including the concept of wave packet, were developed.
- A wave packet is a superposition of a number of waves with different values of k and ω . It is characterized by its average position x and the spread in position Δx and by its average wave number k and the spread in wave number Δk .
- Mathematically, it can be shown that, for **any wave packet** $\Delta x \Delta k \sim 1$. For Gaussian wave packets, this product takes the minimum value $1/2$.
- So far, everything is described by classical ideas and there is nothing quantum about it.

Recapitulation of Wave Packets and Uncertainty Relations

- Blackbody radiation and photoelectric effect required that radiation should be **quantized**, i.e. it should have particle like properties.
- Electron diffraction required that massive objects should have wave like properties.
- Simple solution is to try to describe both of them by wave packets. They have **reasonably well-defined** position. And through de Broglie hypothesis (which can be written as $p = \hbar k$), they have **reasonably well-defined** momentum. And they are made up of waves!
- So we require that both massive objects and radiation should be described wave packets. When the quantum hypothesis is applied to such wave packets, we get the Heisenberg uncertainty principle $\Delta x \Delta p_x \geq \hbar/2$.
- But, there is still something missing.

What is the dynamical equation which guides quantum evolution?

Non-commuting Observables

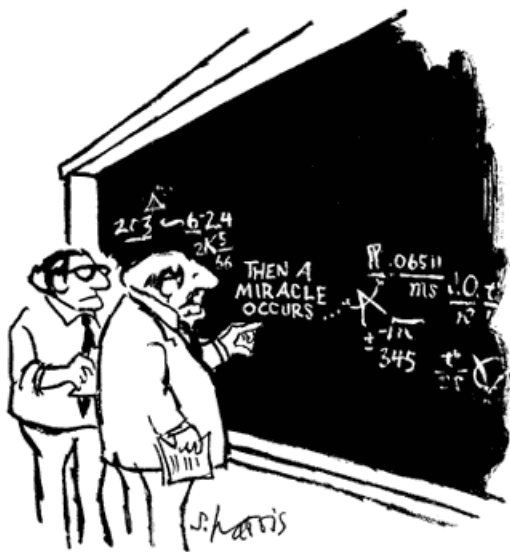
- Heisenberg is the first person to construct a valid quantum dynamical equation. He did it using non-commuting variables.
- It is our experience that product of two real numbers is independent of the order of multiplication. When we multiply 2 with 3 or 3 with 2, the answer is the same.
- In algebraic notation, we say, if p and q are two real variables then $pq - qp = 0$. Equivalently, we say, p and q **commute**.
- You can imagine two other variables m and n , for which $mn - nm \neq 0$. The algebra of such variables is called **non-commutative** algebra.
- Special case: If $mn + nm = 0$, then such variables are called **Grassmann** variables.
- Heisenberg realized that $\Delta x \Delta p_x \geq \hbar/2$, implies that the two variables x and p_x **do not commute**. They must obey the relation $xp_x - p_x x = i\hbar$.

Development of Quantum Mechanics

- Heisenberg developed a quantum dynamical equation with x and p_x as non-commuting variables. With his equation, he solved the problem of dynamics of an electron bound to a proton and obtained the Rydberg formula.
- Reaction of the physics community: Total disbelief!
- For two arbitrary matrices M and N , it is well known that $MN - NM$ in general is not zero. So, Max Born proposed that x and p_x should be treated as matrices. Thus, the first accepted formulation of Quantum Mechanics, is called **Matrix Mechanics**.
- Since Newton's time, physicists are used to thinking of dynamics in terms of differential equations. So they longed to have a differential equation for quantum mechanics also.
- Based on Hamilton-Jacobi theory of Classical Mechanics, Schroedinger **GUESSED** at a form of differential equation, which can describe the quantum dynamics of a wave packet.

Schroedinger Equation

- In this formulation, Schroedinger introduced a factor of i , in front of the time derivative appearing in Hamilton-Jacobi theory and obtained a differential equation.
- He applied this differential equation to an electron bound to a proton but moving with relativistic speeds (did it in 1920, five years before Heisenberg).
- Unfortunately, his answer did not match the experiment. The mismatch arose due to some very technical and subtle points involving the boundary conditions to be imposed on the differential equation.
- After Heisenberg's solution to hydrogen problem using matrix mechanics, Schroedinger took a second look at his solution. This time he considered the non-relativistic limit and found that he also could get Rydberg formula.
- When Schroedinger published his results, physicists (except Heisenberg) immediately accepted his formulation and used it to solve a variety of problems.



"I think you should be more explicit here in step two."

"Derivation" of Schroedinger Equation

- Let us consider a free particle, for which we have the relation $E = p^2/2m$. We want to describe it by a wave packet.
- Let us use the quantum conditions of Planck and de Broglie and write $E = \hbar\omega$ and $p = \hbar k$. Substituting it in the energy-momentum relation, we obtain

$$E = \frac{\hbar^2 k^2}{2m} \text{ and } \omega = \frac{\hbar k^2}{2m}.$$

- The simplest wave is described by $\psi(x, t) = e^{i(kx - \omega t)}$. We assume k to take both positive and negative values so that both right and left moving waves can be described.
- For such a wave,

$$\frac{\partial \psi}{\partial t} = -i\omega\psi(x, t) \text{ and } \frac{\partial \psi}{\partial x} = ik\psi(x, t).$$

- Consider the differential equation

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

"Derivation" of Schroedinger Equation

- If we substitute $\psi(x, t) = Ae^{i(kx - \omega(k)t)}$ (A a constant) in the differential equation, we get $\hbar\omega = \hbar^2 k^2 / 2m$, which is the energy momentum relation for a free particle of mass m .
- But the above $\psi(x, t)$ is wave of infinite extent. So, let us define a wave packet

$$\psi(x, t) = \int A(k) e^{i(kx - \omega(k)t)} dk.$$

On substitution in the above differential equation, once again we get $\hbar\omega = \hbar^2 k^2 / 2m$, the free particle energy-momentum relation.

- This gives us the hint that we should treat the energy and momentum as **differential operators**

$$E = i\hbar \frac{\partial}{\partial t} \text{ and } p_x = -i\hbar \frac{\partial}{\partial x}.$$

We do this to describe the dynamics of not only free particles but any other particles also.

Free particle Description by Schroedinger Equation

- Let us look at a few details of the description of movement of free particles by Schroedinger's equation. Let us assume that the amplitudes $A(k)$ are described a Gaussian function.

$$A(k) = \frac{C\alpha}{\sqrt{\pi}} \exp(-\alpha^2 k^2/2),$$

where C and α are constants.

- We construct the wave packet at $t = 0$ by

$$\psi(x, 0) = \int_{-\infty}^{+\infty} A(k) e^{ikx} dk = \frac{C\alpha}{\sqrt{\pi}} \int_{-\infty}^{+\infty} e^{(ikx - \alpha^2 k^2/2)} dk.$$

- To do the integral, we first complete the square in the exponent. This makes the exponent to be of standard Gaussian form. Then we look up in the table of integrals, the value for the integral of Gaussian from $-\infty$ to $+\infty$. This gives us the answer $\psi(x, 0) = Ce^{-(x^2/2\alpha^2)}$.
- The standard deviation for the above function is α , which is Δx . The standard deviation for $A(k)$ is $1/\alpha$, which is Δk .

Dispersion of a Free Particle Wave Packet

- If α is small, then the above wave packet describes a particle well localized at x . Then it has a broad distribution in k and hence in p_x , satisfying $\Delta x \Delta p_x \geq \hbar/2$.
- Construct $\psi(x, t)$ by putting the time dependence $e^{-i\omega(k)t}$, where $\omega(k) = \hbar k^2/2m$, in the integrand of the expression for $\psi(x, 0)$.
- Substitute this in the Schrodinger's equation and solve it to obtain the function $\psi(x, t)$. This will also be a Gaussian wave packet, but with width

$$\Delta x(t) = \sqrt{\alpha^2 + \left(\frac{\hbar t}{2m\alpha}\right)^2}.$$

The width of the wave packet increases with time.

- We say that the wave packet is dispersed if $\Delta x(t) > 10\Delta x(0)$.
- For an electron, localized to 10^{-10} m (atom size), $t = 10^{-15}$ s. For a one gram marble, localized to 10^{-4} m, $t = 10^{24}$ s, about a million times the age of the universe.

Time Independent Schroedinger's Equation

- In atomic physics, we are interested in finding the stable orbits or **stationary states** of an atom. How does the wave function ψ look for those states.
- In looking for solutions of such problems, we are not particularly interested in the time dependence of the solution. We know that the energy E for such stationary states is a constant.
- A fundamental theorem of differential equations is: Given a differential equation and associated boundary conditions, there is a unique solution.
- If we find a function, by guessing or some other means, which satisfies the differential equation and the boundary conditions, then **it is the solution**.
- We use a standard technique of partial differential equations. It is called **Separation of Variables**. We assume the x dependence and t dependence can be separated.

$$\psi(x, t) = \psi(x)\phi(t)$$

Time Independent Schroedinger's Equation

- Substituting this separated form in the Schroedinger's equation leads to

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

- Assuming $\psi(x, t) \neq 0$, we divide both sides by $\psi(x)\phi(t)$. We obtain

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

- The left hand side purely a function of t and the right hand side is purely a function of x . The equality is possible, only if both are equal to a constant. In this case the constant is the energy E .
- Solution to $i\hbar d\phi/dt = E\phi$ is given by

$$\phi(t) = \exp \left[-i \frac{Et}{\hbar} \right].$$

Time Independent Schroedinger's Equation

- The differential equation in x is

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

- This is called **Time Independent** Schroedinger's equation. Solutions of this equation are the stationary states with energy E .
- The above equation is valid for only free particles, for whom the energy is only the kinetic energy. The second derivative $-(\hbar^2/2m)d^2\psi/dx^2$ represents this kinetic energy.
- If a particle is subject to a potential $V(x)$ also, then the total energy $E = K.E. + P.E.$, leading to the final form of the time independent Schroedinger's equation

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

- In three dimensions, it is

$$-\frac{\hbar^2}{2m} \nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}).$$

Heisenberg vs Schoredinger

- It was mentioned earlier that Heisenberg, with the help of Born, developed matrix mechanics. He derived the uncertainty relations and also solved the Hydrogen atom problem by getting the Rydberg formula.
- Schroedinger also solved hydrogen atom problem and got the Rydberg formula by making very different assumptions.
- Who is right?
- Both are right! Schroedinger showed that the two formalisms, matrix mechanics and wave mechanics, are equivalent. So we now talk of only quantum mechanics.
- We mostly use Schroedinger formalism. But, in cases where it is advantageous, we use Heisenberg formalism.