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Chapter 3 : Equation of Schrödinger

The work plan

1) Wavefunction: Schrödinger's Equation

    1.1) Differential operators in quantum physics

    2.2) The time-independent Schrödinger equation

2) Basic Developments

    2.1)The Probability Interpretation of the Wavefunction

    2.2) Properties of the Schrödinger equation

    2.3) Solving of the Schrödinger Equation

        2.3.1) The Time-Independent Schrödinger Equation

        2.3.2) Normalizing the Wavefunction

1) Wavefunction: Schrödinger's Equation

Schrödinger's equation can be derived from the classical wave equation

$$\frac{\partial^2}{dr^2}\Psi\left(\vec{r},t\right)-\frac{1}{V^2}\frac{\partial^2}{dt^2}\Psi\left(\vec{r},t\right)=0$$

Where the solution of this equation is written

$$\psi\left(\vec{r},t\right)=A\exp i\left(\vec{k}.\vec{r}-wt\right) \quad \text{for} \quad \begin{cases} \vec{p}=\hbar.\vec{k} \\ E=\hbar w \end{cases}$$

$$\psi\left(\vec{r},t\right)=A\exp\frac{i}{\hbar}\left(\hbar\vec{k}.\vec{r}-\hbar wt\right)\Leftrightarrow\psi\left(\vec{r},t\right)=A\exp\frac{i}{\hbar}\left(\vec{p}.\vec{r}-Et\right)$$

Differentiating the wave with respect to time, it comes:

$$\frac{d}{dt}\psi\left(\vec{r},t\right)=-\frac{i}{\hbar}E.A\exp\frac{i}{\hbar}\left(\vec{p}.\vec{r}-Et\right)\Leftrightarrow\frac{d}{dt}\psi\left(\vec{r},t\right)=-\frac{i}{\hbar}E\psi\left(\vec{r},t\right)$$

$$i.\hbar\frac{d}{dt}\psi\left(\vec{r},t\right)=E\psi\left(\vec{r},t\right)\qquad\text{so}\quad\boxed{E\equiv i.\hbar\frac{d}{dt}}$$

Similarly, the gradient of this wave function gives:

$$\nabla\psi\left(\vec{r},\vec{t}\right)=\frac{i}{\hbar}\vec{p}.A\exp\frac{i}{\hbar}\left(\vec{p}.\vec{r}-Et\right)\Leftrightarrow\nabla\psi\left(\vec{r},\vec{t}\right)=\frac{i}{\hbar}\vec{p}\psi\left(\vec{r},\vec{t}\right)$$

$$-i\hbar\nabla\psi\left(\vec{r},\vec{t}\right)=\vec{p}\psi\left(\vec{r},\vec{t}\right)\qquad\text{so}\quad\boxed{\vec{p}\equiv-i\hbar\nabla}$$

According to classical physics, mechanical energy is given by:

$$E = E_c + E_p = \frac{p^2}{2m} + V(\vec{r})$$

Multiplying with the wave function

$$E\,\Psi(\vec{r},\vec{t}) = \frac{p^2}{2m}\Psi(\vec{r},\vec{t}) + V(\vec{r})\Psi(\vec{r},\vec{t})$$

and finally using the previous results, we have:

$$\left(i.\hbar\frac{d}{dt}\right)_E \Psi(\vec{r},\vec{t}) = \frac{\left(-i.\hbar\nabla\right)_P^2}{2m}\Psi(\vec{r},\vec{t}) + V(\vec{r})\Psi(\vec{r},\vec{t})$$

$$\frac{-\hbar^2}{2m}\Delta\Psi\left(\vec{r},t\right)+V\left(\vec{r}\right)\Psi\left(\vec{r},t\right)=i.\hbar\frac{d\Psi\left(\vec{r},t\right)}{dt}$$

$$\boxed{\left[\frac{-\hbar^2}{2m}\Delta+V\left(\vec{r}\right)\right]\Psi\left(\vec{r},t\right)=i.\hbar\frac{d}{dt}\Psi\left(\vec{r},t\right)}$$

finally:

$$\boxed{\mathrm{H}\Psi\left(\vec{r},t\right)=E\Psi\left(\vec{r},t\right)}$$

1.1) Differential operators in quantum physics

To each physical quantity of classical mechanics, make correspond a differential operator

	Energy	**Cartesian components of $\overrightarrow{P}$**		
Physical quantities	E	P_x	P_y	P_z
Differential operators	$i\hbar\frac{\partial}{\partial t}$	$-i\hbar\frac{\partial}{\partial x}$	$-i\hbar\frac{\partial}{\partial y}$	$-i\hbar\frac{\partial}{\partial z}$

2.2) The time-independent Schrödinger equation

$$\Psi(\vec{r},t)=\Phi(\vec{r})\,f(t)$$

by replacing in the Schrödinger equation and by dividing the two members by $\Phi(\vec{r})$

we then obtain:

$$\frac{-\hbar^2}{2m}f(t)\Delta\Phi(\vec{r})+V(\vec{r})\,f(t)\Phi(\vec{r})=i.\hbar\frac{d}{dt}f(t)\Phi(\vec{r})$$

$$\frac{-\hbar^2}{2m}f(t)\Delta\Phi(\vec{r})+V(\vec{r})\,f(t)\Phi(\vec{r})=i.\hbar\Phi(\vec{r})\frac{df(t)}{dt}$$

$$\boxed{i.\hbar\frac{1}{f(t)}\frac{df(t)}{dt}=\frac{-\hbar^2}{2m}\frac{1}{\Phi(\vec{r})}\Delta\Phi(\vec{r})+V(\vec{r})}$$

The left member depends only on time, the right member only on coordinates:

equality is only possible if the two members are equal to a constant ***C***.

$$\begin{cases} \dfrac{-\hbar^2}{2m}\dfrac{1}{\Phi(\vec{r})}\Delta\Phi(\vec{r})+V(\vec{r})=C \\ i.\hbar\dfrac{1}{f(t)}\dfrac{df(t)}{dt}=C \end{cases} \Leftrightarrow \begin{cases} \dfrac{-\hbar^2}{2m}\Delta\Phi(\vec{r})+V(\vec{r})\Phi(\vec{r})=C\Phi(\vec{r}) \Rightarrow \boxed{C=E} \\ i.\hbar\dfrac{1}{f(t)}\dfrac{df(t)}{dt}=C \end{cases}$$

$$i.\hbar\frac{1}{f(t)}\frac{df(t)}{dt}=E \Leftrightarrow \frac{df(t)}{f(t)}=-\frac{i}{\hbar}Edt$$

By integrating each member, we obtain:

$$\ln f(t)=-\frac{i}{\hbar}Et \Leftrightarrow f(t)=e^{-i\left(\frac{E}{\hbar}\right)t}$$

And so the total wave function is:

$$\Psi(\vec{r},t)=\Phi(\vec{r})e^{-i\left(\frac{E}{\hbar}\right)t}$$

where $\Phi(\vec{r})$ is the solution of the equation:

$$\mathrm{H}\Phi(\vec{r}) = E\Phi(\vec{r})$$

which is called the *time-independent Schrödinger equation* or the eigenvalue equation of $\boldsymbol{H}$.

2) Basic Developments

The behavior of a particle of mass *m* subject to a potential *V (x)* is described by the following partial differential equation:

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

where *ψ(x, t)* is called the *wavefunction*.

- The wavefunction contains information about where the particle is located,
- Its square being a probability density.
- A wavefunction must be "well behaved," in other words it should be defined and continuous everywhere.
- In addition it must be square-integrable, meaning: $\int_{-\infty}^{+\infty}|\psi(x,t)|^2\,dr<\infty$

Activity 01

Let two functions Ψ and Φ be defined for $0 \leq x < \infty$. Explain why $\Psi(x) = x$ cannot be a wavefunction but $\Phi(x) = e^{-x^2}$ could be a valid wavefunction.

2.1)The Probability Interpretation of the Wavefunction

At time *t*, the probability of finding the particle within the interval *x* and *x* + *dx* is given by the *square* of the wavefunction. Calling this probability $dP(x,t)$, we write:

$$dP(x,t) = |\Psi(x,t)|^2\, dx$$

The square is given by $|\Psi(x,t)|^2$ as opposed to $\Psi(x,t)$ because in general, the wavefunction can be complex.

The probability *P* that a particle is located within $a \leq x \leq b$ is:

$$P = \int_a^b |\Psi(x,t)|^2\, dx$$

It is common to denote a probability density $|\Psi(x,t)|^2$ as $\rho(x,t)$.

The total probability for any distribution must sum to unity. If the probability distribution is discrete with *n* individual probabilities p_i, this means that:

$$\sum_i p_i = 1$$

For a continuous probability distribution *ρ(x)*, the fact that probabilities must sum to unity means that:

$$\int_{-\infty}^{+\infty} \rho(x)dx = 1$$

In quantum mechanics, this condition means that the particle is located somewhere in space with certainty

$$\int_{-\infty}^{+\infty} |\Psi(x,t)|^2\, dx = 1$$

Activity 02

Suppose that a certain probability distribution is given by $P(x) = \frac{9}{4}\frac{1}{x^3}$ for

$1 \leq x \leq 3$. Find the probability that $\frac{5}{2} \leq x \leq 3$.

Activity 03

Consider a particle traped in a well with potential given by:

$$V = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & otherwise \end{cases}$$

Show that $\psi = A\sin(kx)exp^{\frac{-iEt}{\hbar}}$ solves the Schrödinger equation provided

That

$$E = \frac{\hbar^2 k^2}{2m}$$

2.2) Properties of the Schrödinger equation

The Schrödinger equation has two important properties. These are:

1. The equation is linear and homogeneous
2. The equation is first order with respect to time—meaning that the state of a system at some initial time to determines its behavior for all future times.

An important consequence of the first property is that the superposition principle holds. This means that if $\psi_1(x,t), \psi_2(x,t), \ldots, \psi_n(x,t)$ are solutions of the Schrödinger equation, then the linear combination of these functions:

$$\Psi = C_1\psi_1(x,t) + C_2\psi_2(x,t) + \cdots C_n\psi_n(x,t) = \sum_{i=1}^{n} C_i\psi_i(x,t)$$

is also a solution.

2.3) Solving of the Schrödinger Equation

We have seen that when the potential is time-independent and the solution to the Schrödinger equation is given by:

$$\Psi(x,t) = \Phi(x) e^{-i\left(\frac{E}{\hbar}\right)t}$$

The spatial part of the wavefunction, $\Phi(x)$, satisfies the time-independent Schrödinger equation.

2.3.1) The Time-Independent Schrödinger Equation

Let $\Psi(x,t) = \Phi(x)exp\left(\frac{-iEt}{\hbar}\right)$ be a solution to the Schrödinger equation with time-independent potential $V = V(x)$. The spatial part of the wavefunction $\Phi(x)$ satisfies:

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Phi}{\partial x^2} + V(x)\Phi(x) = E\,\Phi(x)$$

where E is the energy of the particle. This equation is known as the time independent Schrödinger equation.

Solutions that can be written as $\Psi(x,t) = \Phi(x)exp\left(\frac{-iEt}{\hbar}\right)$ are called stationary.

A solution $\Psi(x,t) = \Phi(x)exp\left(\frac{-iEt}{\hbar}\right)$ to the Schrödinger equation is called stationary because the probability density does not depend on time:

$$|\Psi(x,t)|^2 = \Psi^*(x,t)\,\Psi(x,t)$$

$$|\Psi(x,t)|^2 = \left[\Phi(x)exp\left(\frac{-iEt}{\hbar}\right)\right]^* \Phi(x)exp\left(\frac{-iEt}{\hbar}\right)$$

$$|\Psi(x,t)|^2 = \Phi(x)^* exp\left(\frac{iEt}{\hbar}\right)\Phi(x)exp\left(\frac{-iEt}{\hbar}\right)$$

$$|\Psi(x,t)|^2 = \Phi(x)^*\Phi(x)$$

Activity 04

Suppose $\Psi(x,t) = A(x - x^3)exp\left(\frac{-iEt}{\hbar}\right)$. Find $V(x)$ such that the Schrödinger equation is satisfied.

2.3.2) Normalizing the Wavefunction

When a wavefunction that solves the Schrödinger equation is multiplied by an undetermined constant A, we normalize the wavefunction by solving:

$$\frac{1}{A} = \int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \, dx$$

The normalized wavefunction is then $A\,\Psi(x,t)$.

Activity 05

The wave function for a particle confined to $0 \leq x \leq a$ in the ground state was found to be:

$$\Psi(x) = A \sin\left(\frac{\pi x}{a}\right)$$

where A is the normalization constant. Find A and determine the probability that the particle is found in the interval $\frac{a}{2} \leq x \leq \frac{3a}{4}$.

Activity 06

A particle of mass *m* is trapped in a one dimensional box with a potential described by:

$$V = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & otherwise \end{cases}$$

Solve the Schrödinger equation for this potential.

Activity 07

$$\Psi(x) = Ae^{-\lambda(x-x_0)^2}$$

Find A such that $\Psi(x)$ is normalized. The constants λ and x_0 are real.

Knowing that:

$$\int_{-\infty}^{\infty} e^{-z^2}\,dz = \sqrt{\pi}$$

Activity 08

Let $\Psi(x) = Ae^{\left(\frac{-|x|}{2a}\right)}e^{i(x-x_0)}$.

Find the constant A by normalizing the wavefunction.

2.3.2) Expansion of the Wavefunction and Finding Coefficients

Earlier we noted that the superposition principle holds

$$\psi_n(x,t) = \Phi_n(x)\exp(-iE_nt/\hbar)$$

At time $t = 0$, any wavefunction Ψ can be written as a linear combination of these states:

$$\psi(x,0) = \sum C_n\Phi(x)$$

If we set $E = \hbar\omega$, the time evolution of this state is then:

$$\psi(x,t) = \sum C_n\Phi_n(x)e^{-iw_nt}$$

Since any function Ψ can be expanded in terms of the Φ_n, we say that the Φ_n are a set of basis functions.

2.3.2.1) Find the constants C_n in the expansion of

To find the constants C_n in the expansion of Ψ , we use the inner product.

The inner product of two wave functions $\Psi(x)$ and $\Phi(x)$ is defined by:

$$(\Phi, \psi) = \int \Phi^*(x)\psi(x)dx$$

The square of (Φ, Ψ) tells us is the probability that a measurement will find the system in state $\Phi(x)$, given that it is originally in the state $\Psi(x)$.

Basis states are orthogonal. That is:

$$\int \Phi_m^*(x)\Phi_n(x)dx = \delta_{mn} \qquad \delta_{mn} = \begin{cases} 0 & \text{if } m \neq n \\ 1 & \text{if } m = n \end{cases}$$

If a state $\Psi(x,0)$is written as a summation of basis functions $\Phi_n(x)$, we find the n th coefficient of the expansion $\boldsymbol{C_n}$ by computing the inner product of $\Phi_n(x)$ with $\Psi(x,0)$. That is:

$$C_n = (\Phi_n(x), \psi(x,0)) = \int \Phi_n^*(x)\psi(x,0)dx$$

Notice that:

$$\int \Phi_n^*(x)\psi(x,0)dx = \int \Phi_n^*(x)\sum c_m\Phi_m(x)dx$$

$$= \sum c_m \int \Phi_n^*(x)\Phi_m(x)dx = \sum c_m\delta_{mn} = c_n$$

2.3.2.2) The Meaning of the Expansion Coefficient

If a state is written as $\Psi(x,t) = \sum C_n \Phi_n(x) e^{-i\omega_n t}$, the modulus squared of the expansion coefficient C_n is the probability of finding the system in state $\Phi_n(x)$, i.e.: Probability system is in state $\Phi_n(x) = |C_n|^2$

Another way to put this is, if a state $\Psi(x,t) = \sum C_n \Phi_n(x) e^{-i\omega_n t}$ and we measure the energy, what is the probability we find $E_n = \hbar\,\omega_n$? The answer is $|C_n|^2$. Since the coefficients C_n define probabilities, it must be true that:

$$\sum |C_n|^2 = 1$$

Activity 09

A particle of mass *m* is trapped in a one-dimensional box of width *a*. The wavefunction is known to be:

$$\psi(x) = \frac{i}{2}\sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right) + \sqrt{\frac{1}{a}}\sin\left(\frac{3\pi x}{a}\right) - \frac{1}{2}\sqrt{\frac{2}{a}}\sin\left(\frac{4\pi x}{a}\right)$$

If the energy is measured, what are the possible results and what is the probability of obtaining each result? What is the most probable energy for this state?