Quantum Physics PY1T20/PYU11P20

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Quantum Physics Lecture 9: Schrodinger's Equation

Quantum Mechanics - *formalism*

- General properties of waves
- Expectation values
- Free particle wavefunction
- 1-D Schrodinger Equation
- 1-D "steady state" or "time-independent" Schrodinger Equation

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General properties of waves

Recall 1-D wave: $y = A\cos(\omega t - kx)$

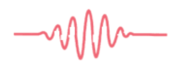
This is just one <u>possible</u> solution of the 1-D wave equation:

$$\frac{\delta^2 y}{\delta x^2} = \frac{1}{v^2}\frac{\delta^2 y}{\delta t^2}$$

In general $y = A\exp\left[-i(\omega t - kx)\right]$ where $i = \sqrt{-1}$

$= A\left[\cos(\omega t - kx) - i\sin(\omega t - kx)\right]$ *- the general (complex) solution.*

For 'waves' (of existence) in QM use wavefunction ψ



Recall UP and probability:

$|y|^2$ is a measure of probability of finding a particle at location x

In QM, ψ is in general complex, and <u>not</u> a "measureable" parameter *(such a momentum etc.)*

However, $|\psi|^2$ is! So must retain full complex solution, not just real part.

General properties of waves *cont.*

Three <u>other</u> required properties of wavefunction ψ

(1) single-valued and continuous

(2) derivative ($d\psi/dx$) single-valued and continuous

(3) normalisable: $\int |\psi|^2 dx = 1$

- i.e. integrated probability density <u>over all space</u> is unity

i.e. for 1-D case require $\int_{-\infty}^{+\infty} |\psi|^2 \, dx = 1$

If ψ is complex, what about $|\psi|^2$?

$|\psi|^2 = \psi^* \psi$ where ψ^* is complex conjugate of ψ

$\psi = A + iB$ and $\psi^* = A - iB$

$\psi^* \psi = (A - iB)(A + iB) = A^2 - (iB)^2 = A^2 + B^2$ *(i.e. real)*

Expectation values

Expectation value: “the mean value you would get if you measured a variable many times (in the same wavefunction each time)”

Multiply variable by probability density ($|\psi|^2$) and integrate.

eg. expectation value of 1-D position: $$\langle x \rangle = \frac{\int_{-\infty}^{+\infty} x|\psi|^2 \, dx}{\int_{-\infty}^{+\infty} |\psi|^2 \, dx}$$

If ψ is normalised then denominator = 1, in which case

$$\langle x \rangle = \int_{-\infty}^{+\infty} x|\psi|^2 \, dx$$

and for a general variable $G(x)$ the expectation value is

$$\langle G(x) \rangle = \int_{-\infty}^{+\infty} G(x)|\psi|^2 \, dx$$

Significance of expectation values

‘Expectation values’ are statistical measures of the outcome of a measurement, specifically the mean outcome over many (independent) measurements.

They are not always the most probable values.

Q. Sketch 3 wavefunctions in 1D such that :

1. The expectation value of position is the most probable value
2. The expectation value of position is not the most probable value
3. The particle will never be found near the expectation value of position.

Note: ‘uncertainties’ are statistical measures of the spread of outcomes of a measurement, specifically the standard deviation over many measurements.

Free particle wavefunction

….think simple wave, rather than wavegroup……

$$\psi = A \exp\left[-i(\omega t - kx)\right]$$

$$\omega = E/\hbar$$

$$k = 2\pi/\lambda = 2\pi\, p/h = p/\hbar$$

$$\boxed{\psi = A \exp\left[-i\left(E/\hbar\, t - p/\hbar\, x\right)\right]}$$

Replacing "wave-notation" (ω, k) with "particle notation" (E, p)

What is the "equation of motion", just as in Newton's Laws,
but for quantum particle……?

Schrodinger's equation

What is the "equation of motion", just as in Newton's Laws,
but for quantum particle……?

Some kind of differential equation like the wave equation $\left(\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2}\right)$.

Need superposition so every term must involve ψ once, e.g. $\frac{\partial \psi}{\partial x}, x^2\psi$ OK but e.g. ψ^2 not allowed.

Should have the solution $\psi = A \exp\left(-\frac{iEt}{\hbar} + \frac{ipx}{\hbar}\right) = Ae^{-iEt/\hbar}e^{ipx/\hbar}$

for a free particle, where $E = \frac{mv^2}{2} = \frac{p^2}{2m}$ (for non-relativistic particle of mass m).

Note: this last condition means it cannot be the wave equation because we need $\Rightarrow E = \hbar\omega = \frac{\hbar^2 k^2}{2m}$ (going back to 'wave notation'), but for the wave equation $\hbar\omega = \hbar v k$ -: the wave equation gives the wrong dispersion relation.

Schrodinger's equation

$$\psi = A\exp\left(-\frac{iEt}{\hbar} + \frac{ipx}{\hbar}\right) = Ae^{-iEt/\hbar}e^{ipx/\hbar} \qquad E = \frac{p^2}{2m}$$

Now consider partial differential with *x*

$$\frac{\partial\psi}{\partial x} = Ae^{-iEt/\hbar} \cdot \frac{ip}{\hbar} \cdot e^{ipx/\hbar} = \frac{ip}{\hbar}\psi$$

Re-arranged: $\frac{\hbar}{i}\frac{\partial}{\partial x}\psi = p\psi$ or: $-i\hbar\frac{\partial}{\partial x}\psi = p\psi$

Defines : momentum operator $\hat{p} = -i\hbar\frac{\partial}{\partial x}$ which 'acts' on this wavefunction to give (value of momentum) x wavefunction :

$$\hat{p}\psi = -i\hbar\frac{\partial\psi}{\partial x} = p\psi$$

$\Longrightarrow$

We can construct an operator which does the same thing but brings down a factor of the kinetic energy:

$$\frac{1}{2m}\hat{p}\hat{p}\psi = \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi$$
$$= \frac{p^2}{2m}\psi$$

Defines: kinetic energy operator $\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

Schrodinger's equation

$$\psi = A\exp\left(-\frac{iEt}{\hbar} + \frac{ipx}{\hbar}\right) = Ae^{-iEt/\hbar}e^{ipx/\hbar} \qquad E = \frac{p^2}{2m}$$

Now consider partial differential with *t*

$$\frac{\partial\psi}{\partial t} = \left(\frac{-iE}{\hbar}\right)\psi$$

So the operator $i\hbar\frac{\partial}{\partial t}$ [acting on this wavefunction] 'brings down a factor of E'.

So an equation satisfying our requirements is :

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

or :

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

Schrodinger Equation developed

The wave equation $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = i\hbar\frac{\partial\psi}{\partial t}$ has the correct solution for a free-particle (no potential).

Recognise the left-hand side as the kinetic energy operator acting on the wavefunction.

Generalise to the case of a particle in a potential, so that classically $E = \mathrm{KE} + \mathrm{PE} = \frac{p^2}{2m} + U(x,t)$

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

1D Schrodinger equation

Generalise to 3D: $\psi \to \psi(x,y,z,t)$ and

$$\boxed{\frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\psi + U\psi = i\hbar\frac{\partial\psi}{\partial t}}$$

3D Schrodinger equation

Steady State Schrodinger Equation

When U is <u>not</u> a function of t, get considerable simplification.

- The time-independent, or steady-state Schrodinger Equation.

Recall free particle wavefunction:

$$\begin{aligned}\psi &= A\exp\left[-i\left(\frac{E}{\hbar}t - \frac{p}{\hbar}x\right)\right] \\ &= A\exp\left[-i\frac{E}{\hbar}t\right]\exp\left[i\frac{p}{\hbar}x\right] \\ &= \psi'\exp\left[-i\frac{E}{\hbar}t\right] \qquad \text{where} \qquad \psi' = \psi'(x)\exp\left(i\frac{p}{\hbar}x\right)\end{aligned}$$

-- i.e. we have a solution which factors into (exp. function of time) and (function of position).

- Important fact: if U is independent of t, we can always find solutions of that form, just with a different position-dependence (i.e. different ψ', same exponential in time).
- To see this, substitute this form of ψ into 1D Schrodinger Equation….

Steady State Schroedinger Equation

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

$$LHS = i\hbar \frac{\partial}{\partial t}\left(\psi' \exp\left(-i \frac{E}{\hbar} t\right)\right) = E \psi' \exp\left(-i \frac{E}{\hbar} t\right)$$

$$RHS = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\left(\psi' \exp\left(-i \frac{E}{\hbar} t\right)\right) + U\left(\psi' \exp\left(-i \frac{E}{\hbar} t\right)\right)$$

$$= -\frac{\hbar^2}{2m} \exp\left(-i \frac{E}{\hbar} t\right) \frac{\partial^2 \psi'}{\partial x^2} + U \psi' \exp\left(-i \frac{E}{\hbar} t\right)$$

$$\Rightarrow E \psi' = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi'}{\partial x^2} + U \psi'$$

"drop the dash & re-write as":

$$\boxed{\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\mathrm{h}^2}(E - U)\psi = 0}$$