Commutator: $[\hat{A},\hat{B}] = (\hat{A}\,\hat{B} - \hat{B}\,\hat{A})$

- When two operators act sequencially on a function $f(x)$ as

$$\hat{A}\hat{B}f(x) = \hat{A}\{\hat{B}f(x)\} = \hat{A}h(x) = g(x)$$

$$\hat{B}\hat{A}f(x) = \hat{B}\{\hat{A}f(x)\} = \hat{B}\tilde{h}(x) = \tilde{g}(x)$$

- If $g(x) = \tilde{g}(x)$, then

  $(\hat{A}\hat{B} - \hat{B}\hat{A})f(x) = 0$ or $[\hat{A},\hat{B}] = 0 \;\Rightarrow\;$ $\hat{A}$ and $\hat{B}$ are "commutative“

- If $g(x) \neq \tilde{g}(x)$, then

  $(\hat{A}\hat{B} - \hat{B}\hat{A})f(x) \neq 0$ or $[\hat{A},\hat{B}] \neq 0 \;\Rightarrow\;$ $\hat{A}$ and $\hat{B}$ are "noncommutative"

Many operators do not commute

Example: For $\hat{x} = x$ and $\hat{p}_x = -i\hbar\dfrac{d}{dx}$, $[\hat{x},\hat{p}_x] = ?$

For an arbitrary function $f(x)$

$$[\hat{x},\hat{p}_x]f(x) = \hat{x}\{\hat{p}_x f(x)\} - \hat{p}_x\{\hat{x}f(x)\}$$

$$= -xi\hbar\frac{df(x)}{dx} + i\hbar\frac{d}{dx}\{xf(x)\}$$

$$= -xi\hbar\frac{df(x)}{dx} + xi\hbar\frac{df(x)}{dx} + i\hbar f(x)$$

$\Rightarrow [\hat{x},\hat{p}_x] = i\hbar$

$\Rightarrow$ $\hat{x}$ and $\hat{p}_x$ do not commute

$\Rightarrow$ Position and linear momentum of a particle cannot be determined simultaneously with infinite precision

Many operators do not commute

Example: *For* $\hat{A} = \dfrac{d}{dx}$ and $\hat{B} = x^2$, *evaluate* $[\hat{A},\hat{B}]$

When evaluating commutator, it is essential to include an arbitrary function $f(x)$. Otherwise, you will find spurious result.

$$[\hat{A},\hat{B}]f(x) = \{2xf(x) + x^2\frac{df(x)}{dx}\} - \{x^2\frac{df(x)}{dx}\} = 2xf(x)$$

If we don't include $f(x)$, *then*

$$[\hat{A},\hat{B}] = \frac{d}{dx}x^2 - x^2\frac{d}{dx} \neq 2x - x^2\frac{d}{dx}$$

Which is erroneous.

The Heisenberg Uncertainty Principle (1927)

- Apart from the error involve because of quality of the measurement, classical mechanics does not have any limitations on the accuracy of the measurement of an observable.

- But, in quantum mechanics, there are inherent uncertainties in the simultaneous measurement of observables which are **complementary** (x *and* p_x or E and t).

- **Example:** In classical mechanics, x and p_x of a particle may be determined simultaneously with desired accuracy, but in quantum mechanics it's NOT possible!

- **There is a lower limit due to inherent uncertainty!** If Δx is the position uncertainty, and Δp_x is the momentum uncertainty, then inevitably,

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \quad [\hbar/2 = h/4\pi = 0.527\times10^{-34} \text{ J s} = = 0.527\times10^{-27} \text{ erg s}]$$

- Operators corresponding to complementary observables do not commute:

$$[\hat{x}, \hat{p}_x] = i\hbar \neq 0 \; i.e. \, \hat{x}\hat{p}_x f(x) \neq \hat{p}_x \hat{x}\, f(x)$$

Example: If uncertainty in the position of an electron is 100 pm, the minimum uncertainty in its momentum and its velocity will be 5.272×10^{-25} kg m s^{-1} and 5.79×10^{5} m s^{-1}, respectively.

i.e. $\Delta p_x \geq 5.272 \times 10^{-25}$ kg m s^{-1} and $\Delta v_x \geq 5.79 \times 10^{5}$ m s^{-1}.

The Heisenberg Uncertainty Principle (1927)

- The de Broglie wave for a particle is made up of a superposition of very large number of waves of the form

$$\psi(x,t) = ASin\ 2\pi\left(\frac{x}{\lambda} - \nu t\right) = ASin\ 2\pi(\kappa x - \nu t)$$

A is amplitude, κ is reciprocal wavelength.

- The waves which constitute the wave packet have different wavelengths

- It can be shown that

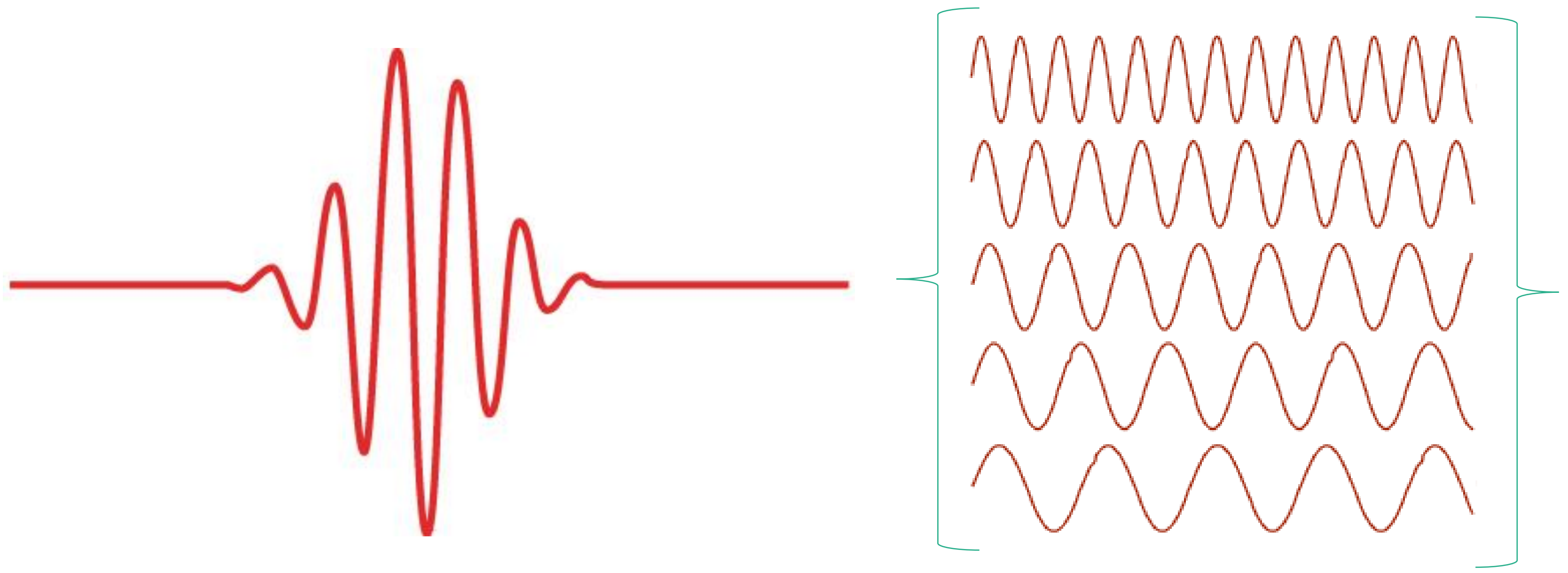
$$\Delta x \Delta \kappa = \Delta x \Delta \frac{1}{\lambda} \geq \frac{1}{4\pi} \Rightarrow \Delta x \Delta p_x \geq \frac{\hbar}{2}$$

$$p_x = \frac{h}{\lambda} \Rightarrow \frac{1}{\lambda} = \frac{p_x}{h}$$

Similarly, $\Delta y \Delta p_y \geq \frac{\hbar}{2}$ and

$$\Delta z \Delta p_z \geq \frac{\hbar}{2}$$

Physical Meaning: If we use a photon of shorter wavelength to determine the position of the electron more accurately, due to its strike with the electron, the disturbance in the momentum, is greater and therefore Δp_x is greater.



Wave packet: Superposition of waves (right) gives rise to formation of a wave packet.

- **It can also be shown that**

$$\Delta t \Delta \nu \geq \frac{1}{4\pi} \Rightarrow \Delta t \Delta \frac{E}{h} \geq \frac{1}{4\pi} \Rightarrow \Delta t \Delta E \geq \frac{\hbar}{2}$$

$$E = h\nu$$

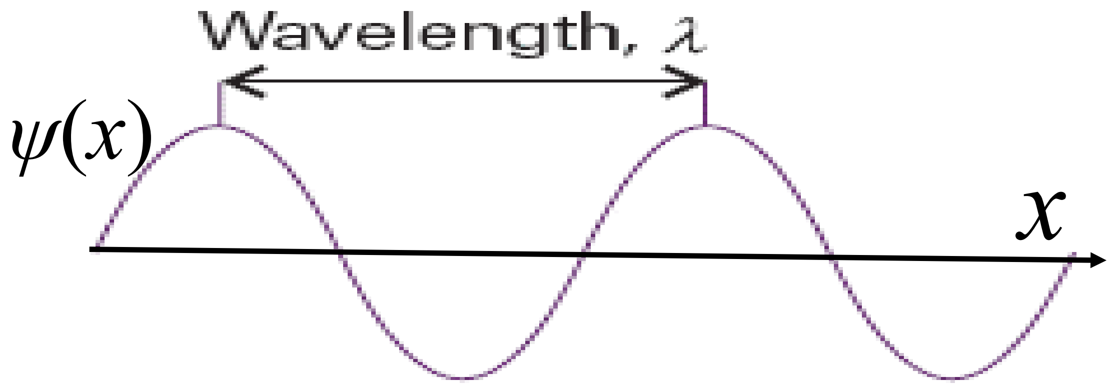
Physical Meaning:

- Excited atom with shorter life-time will emit wider range of frequencies (due to enhanced uncertainty in the energy level).
- If the excited atom live long life-time, the emitted radiation will be nearly monochromatic and spectral lines will be sharp.

The Schrödinger Equation (1926): Time-independent form

Classical case: Wave equation for harmonic motion of a one-dimensional string

$\psi(x)$: displacement of string at position x
λ: wavelength of the displacement



$$\frac{d^2\psi(x)}{dx^2} = -\left(\frac{2\pi}{\lambda}\right)^2 \psi(x) \Rightarrow -\left(\frac{\lambda^2}{4\pi^2}\right)\frac{d^2\psi(x)}{dx^2} = \psi(x)$$

$$E = \frac{1}{2}mv^2 + V = \frac{p^2}{2m} + V \Rightarrow p = \sqrt{2m(E-V)} \Rightarrow \lambda = \frac{h}{p} = \frac{h}{\sqrt{2m(E-V)}}$$

$$\Rightarrow -\left(\frac{h^2}{8\pi^2 m}\right)\frac{d^2\psi(x)}{dx^2} = (E-V)\psi(x)$$

$$\Downarrow$$

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

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

$$\hat{H}\psi = E\psi$$

Time-independent Schrödinger equation

The Schrödinger Equation (1926): Time-independent form

- For three-dimensional case

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z)+\hat{V}(x,y,z)\psi(x,y,z)=E\psi(x,y,z)$$

$$\nabla^2=\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$$

Time-independent Schrödinger equation

$$\hat{H}\psi_n=E_n\psi_n$$

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The Schrödinger Equation (1926): Time-dependent form

- The time dependence of wavefunctions is governed by the time-dependent Schrödinger equation

One-dimension

$$\hat{H}\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x,t)}{dx^2} + \hat{V}(x,t)\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}$$

Three-dimension

$$\hat{H}\psi(x,y,z,t) = i\hbar\frac{\partial\psi(x,y,z,t)}{\partial t}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z,t) + \hat{V}(x,y,z,t)\psi(x,y,z,t) = i\hbar\frac{\partial\psi(x,y,z,t)}{\partial t}$$

- For most cases $\hat{\mathrm{H}}$ does not depend on time explicitly and in these cases we can apply method of separation of variables

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x,t)}{dx^2} + \hat{V}(x)\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}$$

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

$$\hat{H}\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}$$

$$\hat{H}[\psi(x)f(t)] = i\hbar\frac{\partial[\psi(x)f(t)]}{\partial t}$$

$$\underbrace{\frac{1}{\psi(x)}\hat{H}\psi(x)}_{\text{Function of } x \text{ only}} = \underbrace{\frac{i\hbar}{f(t)}\frac{df(t)}{dt}}_{\text{Function of } t \text{ only}}$$

$\Rightarrow$ LHS = RHS = Constant

Using time independent Sch. Eq.

$$\frac{1}{\psi(x)}\overbrace{\hat{H}\psi(x)}^{E\psi(x)} = \frac{i\hbar}{f(t)}\frac{df(t)}{dt}$$

$$\Rightarrow \frac{df(t)}{dt} = \frac{1}{i\hbar}Ef(t) = -\frac{i}{\hbar}Ef(t)$$

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

Integrating both sides

$$\Rightarrow \ln f(t) = -\frac{i}{\hbar}Et + C$$

$\psi(x, t = 0) = \psi(x)$
$t = 0, f(t) = 1$

$$\Rightarrow f(t) = e^{-iEt/\hbar}$$

$$\Rightarrow \psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

If we use $E = h\nu = \hbar\omega$

$$\Rightarrow \psi(x,t) = \psi(x)e^{-i\omega t}$$

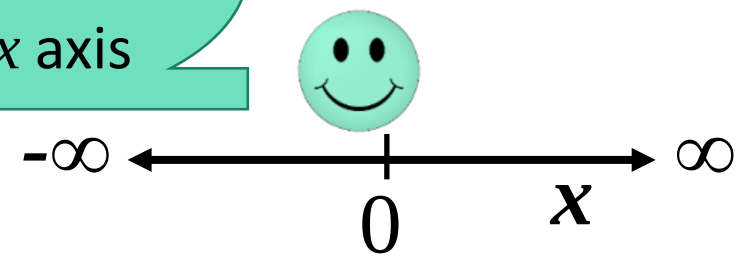
If we had used time-independent SE as

$$\hat{H}\psi_n = E_n\psi_n$$

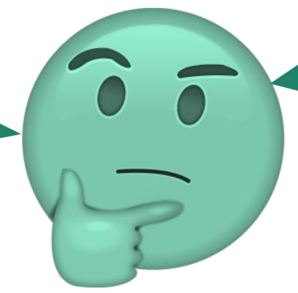
$$\Rightarrow \psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar}$$

Particle in Free Space

I am free to to move along x axis



Am I allowed to have any value of energy? How about my momentum?



Let's see what Schrödinger Equation is suggesting.

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

$$\hat{V}(x)=0,\ -\infty<x<\infty$$

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

$$\frac{d^2\psi(x)}{dx^2}=-\frac{2mE}{\hbar^2}\psi(x)=-k^2\psi(x)$$

where $k=\frac{\sqrt{2mE}}{\hbar}$

- **Second order differential equation, can be solved by inspection. We could chose sine, cosine or exponential functions for solution to this equations.**

$$\psi(x)=\mathrm{A}e^{+ikx}+\mathrm{B}e^{-ikx}$$ where A and B are constants.

- $\frac{d^2\psi(x)}{dx^2}=(ik)^2\mathrm{A}e^{+ikx}+(-ik)^2\mathrm{B}e^{-ikx}=(ik)^2\left[\mathrm{A}e^{+ikx}+\mathrm{B}e^{-ikx}\right]=-k^2\psi(x)$

(Passing the test that the function is indeed the solution of the Sch. Eq.)

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

- There is no quantization of energy
- The constant may take any value and thus any energy is allowed

$$\hat{p}_x\psi(x)=-i\hbar\frac{d\left(\mathrm{A}e^{+ikx}+\mathrm{B}e^{-ikx}\right)}{dx}=-i\hbar\left[ikAe^{+ikx}-ik\mathrm{B}e^{-ikx}\right]=\hbar kAe^{+ikx}+(-\hbar k)\mathrm{B}e^{-ikx}]$$

$$\psi(x)=\mathrm{A}e^{+ikx}+\mathrm{B}e^{-ikx}$$

$\psi=\psi_{\rightarrow}$ + $\psi_{\leftarrow}$

Particle with linear momentum $+k\hbar$ | Particle with linear momentum $-k\hbar$