- **Atomic Structure: Schrödinger equation, the hydrogen atom;**

- **The chemical bond: simplest molecules H_2^+ and H_2;**

- **Vibration of diatomics: harmonic oscillator and Morse potential**

Reference Text Books:

- Peter Atkins and Julio De Paula, Elements of Physical Chemistry, 7th/8th/10th editions

- Robert J. Silbey, Robert A Alberty and Moungi G Bawendi, Physical Chemistry, 7th edition

- Ira N Levine, Physical Chemistry, 6th edition

- Nivaldo J. Tro, Chemistry, A Molecular Approach, 4th edition

de Broglie Wavelength

- **Albert Einstein for photon (1905):** $E = mc^2 = h\nu = \frac{hc}{\lambda}$ $\Rightarrow$ $mc = \frac{h}{\lambda}$ Planck's constant, h=6.6 × 10^{-34} m^2 kg /s

- **Louis de Broglie analogy for particles (1924):** $mv = p = \frac{h}{\lambda}$ $\Rightarrow$ $\lambda = \frac{h}{mv} = \frac{h}{p}$

de Broglie wavelength

- **Total energy of the particle:** $E = K + V = \frac{p^2}{2m} + V = \frac{(h/\lambda)^2}{2m} + V$ $\Rightarrow$ $2m(E - V) = (h/\lambda)^2$ $\Rightarrow$ $\lambda = \frac{h}{\sqrt{2m(E-V)}}$

(i) de Broglie wavelength of an electron $(m_e$=9.1 $\times 10^{-31}$kg, v $= 5.9 \times 10^6\, m/s$): $\lambda = 1.23 \times 10^{-10}\, m$

$\Rightarrow$ Comparable to atomic size or a chemical bond

(ii) de Broglie wavelength of a bullet $(m = 0.5\,$g, v $= 400\, m/s)$: $\lambda = 3.3 \times 10^{-33}\, m$

$\Rightarrow$ Negligibly small as compare to the bullet size

(iii) de Broglie wavelength of a cricket ball $(m = 200\,$g, v $= 160\, km/hr)$: $\lambda = 7.425 \times 10^{-35}\, m$

$\Rightarrow$ Negligibly small as compare to the ball size

(iv) de Broglie wavelength of a person $(m = 70\,$kg, v $= 5\, km/hr)$: $\lambda = 6.79 \times 10^{-36}\, m$

$\Rightarrow$ Negligibly small as compare to the size of the person

Postulates of Quantum Mechanics

- **Postulate One:** The state of a system is completely described by a wavefunction $\psi(\mathbf{r},t)$. If the wavefunction is not explicit function of time t, then the state is completely described by time-independent wavefunction $\psi(\mathbf{r})$.

- **Postulate Two:** For every observable in classical mechanics, there is corresponding linear Hermitian operator in quantum mechanics.

- **Postulate Three:** The possible measured values of the physical observable O for a system in state ψ_n are the eigenvalues a_n which satisfy an eigenfunction-eigenvalue relationship: $\hat{O}\psi_n = a_n\psi_n$, where $\hat{O}$ is the operator corresponding to the observable O.

- **Postulate Four:** For a general state described by the wavefunction ψ, the average or expectation value for a series of measurements corresponding to the operator $\hat{O}$ is given by

$$\langle a \rangle = \frac{\int_{volume} \psi^*(\boldsymbol{r})\,\widehat{O}_{\,observable}\,\psi(\boldsymbol{r})d\boldsymbol{r}}{\int_{volume} \psi^*(\boldsymbol{r})\psi(\boldsymbol{r})d\boldsymbol{r}} = \int_{volume} \psi^*_{norm}(\boldsymbol{r})\hat{O}_{observable}\,\psi_{norm}(\boldsymbol{r})d\boldsymbol{r}$$

- **Postulate Five:** The wavefunction of a system changes with time according to the time-dependent Schrödinger equation $\hat{H}\psi(\mathbf{r},t) = i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t}$ where $\hat{H}$ is the Hamiltonian operator for the system.

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Properties of a well-behaved wavefunction

- ψ may be a complex function and therefore may involve $i = \sqrt{-1}$

Required Property	Why?
- ψ must be finite and single valued at any point	- To guarantee that there is only a single value for the probability at any point
- ψ must also be square-integrable	- Should be able to use $\psi^*\psi = \|\psi\|^2$ as a probability density, since any probability density must integrate over all space to give a total value of 1, which is clearly not possible if the integral of $\|\psi\|^2$ is infinite. - One consequence of this proposal is that $\|\psi\|^2$ must tend to 0 for infinite distances
- ψ must be a smooth continuous function of its coordinates,	A rapid (discontinuous) change would mean that the derivative of ψ was very large. Since the momentum of the system is found using the <u>momentum operator</u>, which is a first order derivative of ψ, this would imply an infinite momentum, which is not possible in a physically realistic system.
- First derivatives of ψ w.r.t. the coordinates must be continuous.	A discontinuous first derivative would imply an infinite second derivative, and since the <u>energy</u> of the system is found using the second derivative of ψ, a discontinuous first derivative would imply an infinite energy, which again is not physically realistic.

- $\psi(\mathbf{r},t)$ **may be a real or a complex function**

  →Complex number contain both real and imaginary part, $\psi = a + ib;$ a, b are real constant

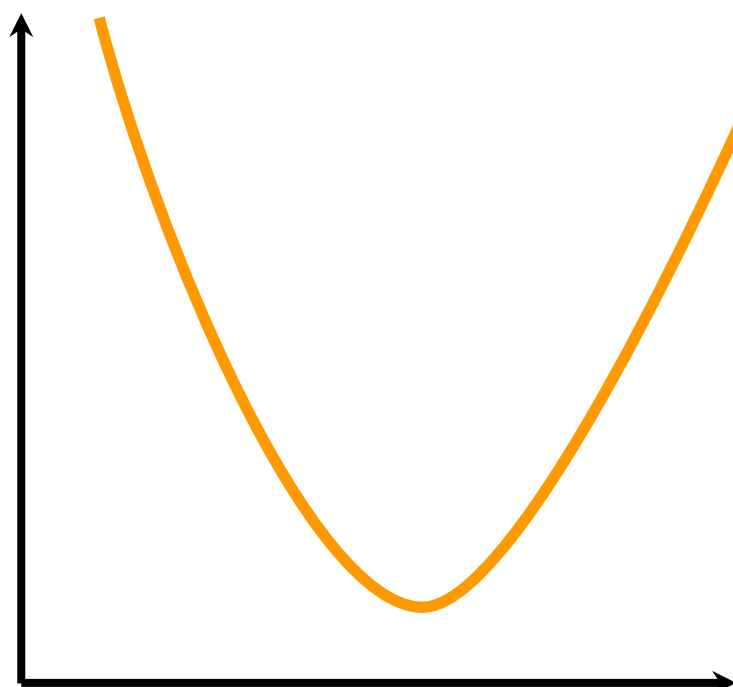 →Complex conjugate of ψ is then $\psi^* = a - ib$

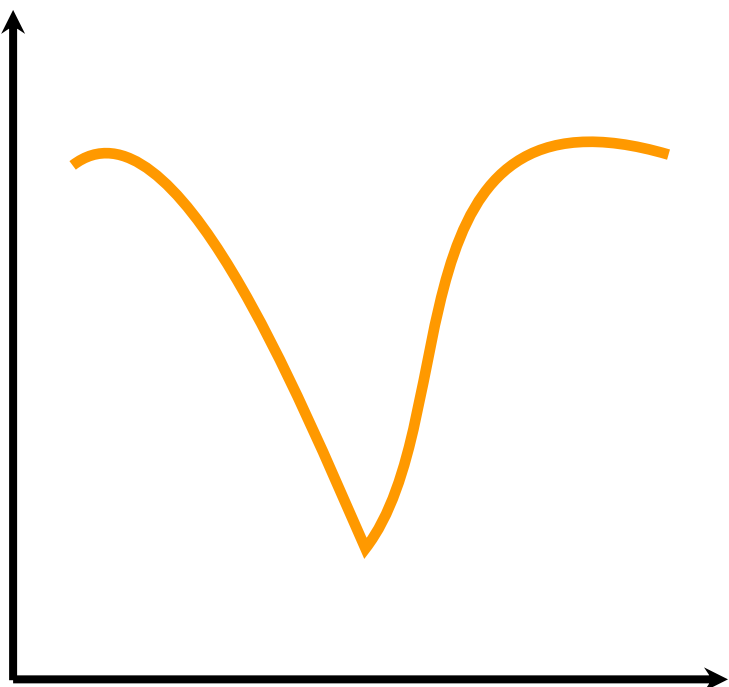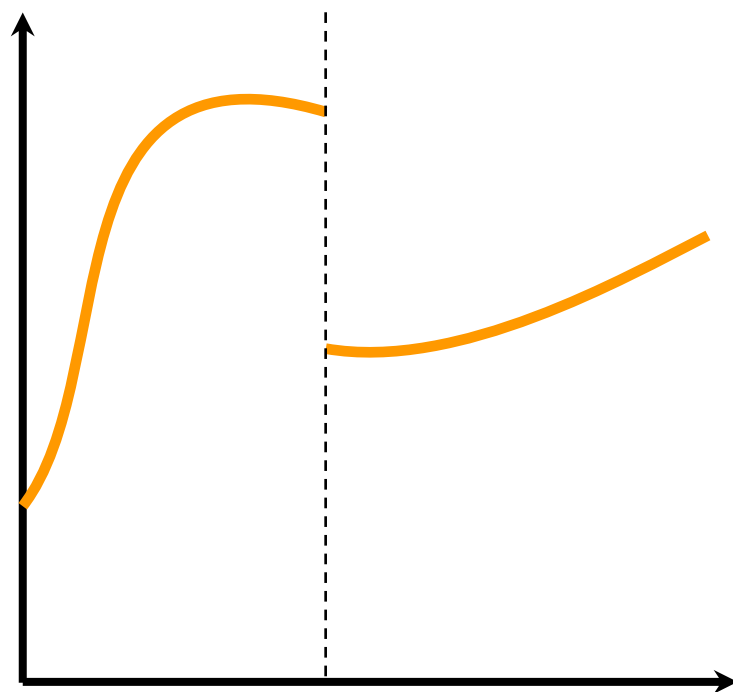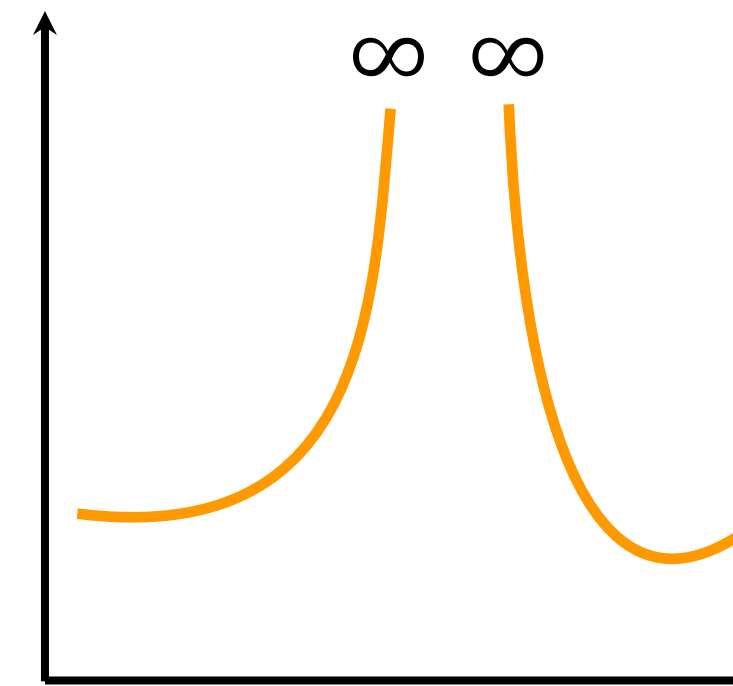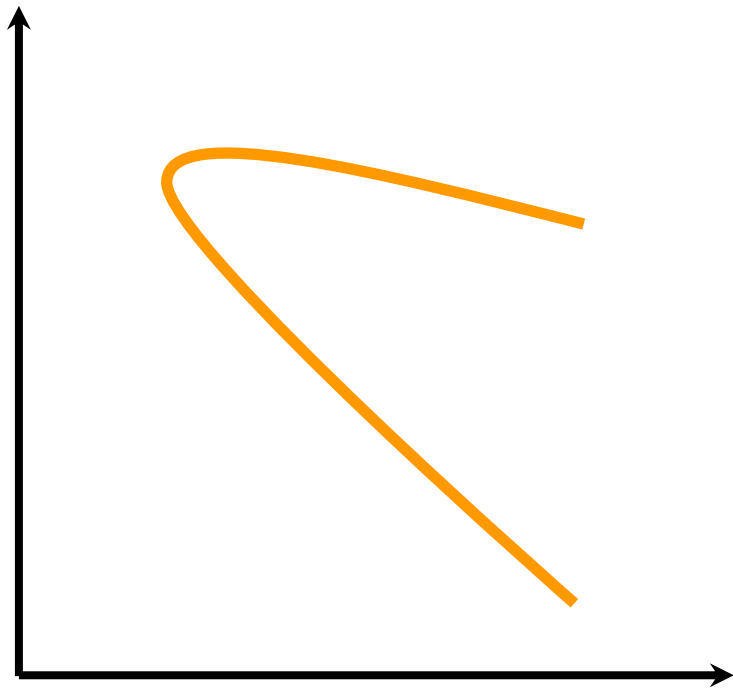 → $\psi^*\psi = (a + ib)(a - ib) = a^2 + b^2$

  → $\psi^*\psi = |\psi|^2$ is squared magnitude of ψ

  → $\psi^*\psi = \psi^2$ if $\psi^* = \psi$ in cases where ψ is real

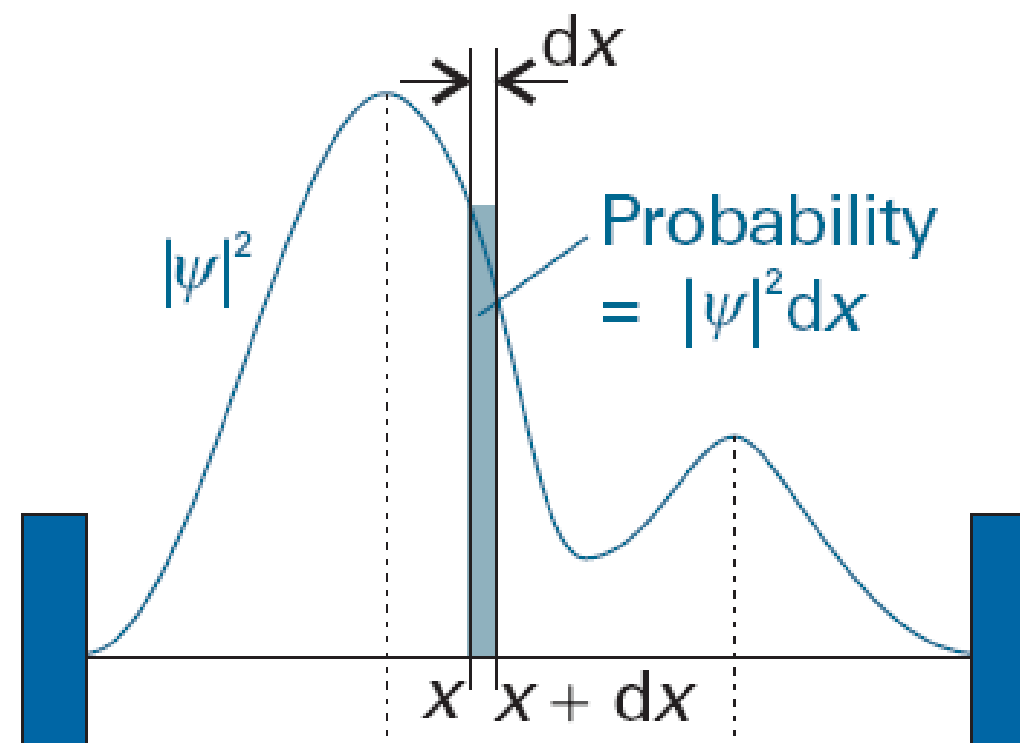- **Must be single valued at any point,** ψ **and** $d\psi/dr$ **are continuous.**

Un-acceptable Wavefunctions

Physical Significance of $\psi^*\psi$ or $|\psi|^2$ [Max Born, 1926]

- Physically, $\psi^*\psi = |\psi|^2$ can be interpreted as a **probability distribution or probability density** for the system.

- For a particle moving in one-dimension, $|\psi(x)|^2\, dx$ is probability of finding the particle between x and $x + dx$.

- **Probability (P) of finding the particle between x_1 and x_2 is given by**

$$P(x_1 \leq x \leq x_2) = \int_{x_1}^{x_2} \psi^*\psi\, dx$$

For a particle moving in three-dimension, $|\psi(x,y,z)|^2\, dxdydz$ is probability of finding the particle in a region centered at (x, y, z) and with volume $dxdydz$.

- **Because the particle must lie somewhere within the region of interest, the probability of finding the particle over the entire region must be equal to 1.**

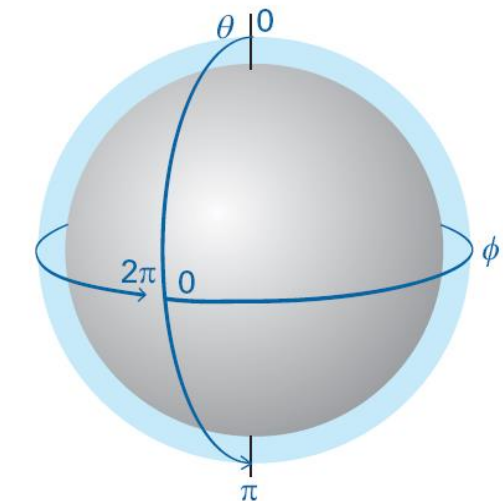**Normalization Condition:** $$\int_{All\ space} \psi^*\psi\, d\tau = 1$$

In cartesian coordinates

For three-dimensional system, the wavefunction is normalized if,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^*(x,y,z)\, \psi(x,y,z)\, dxdydz = 1$$
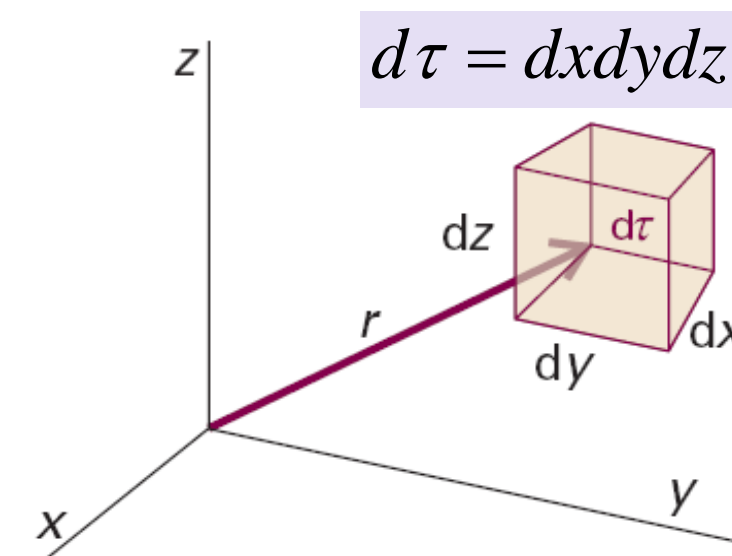
In spherical polar coordinates

$$\int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} \psi^*(r,\theta,\phi)\, \psi(r,\theta,\phi)\, r^2 dr\, \sin\theta\, d\theta d\phi = 1$$
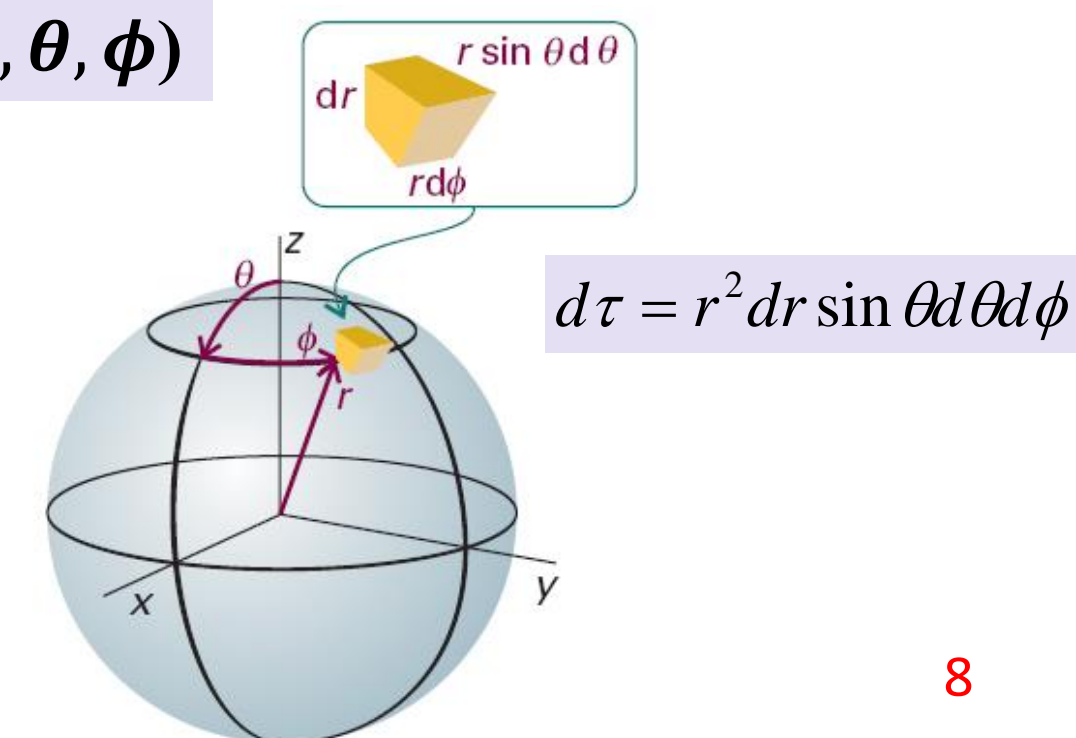
Cartesian versus Spherical Polar Coordinate System

$\psi(x, y, z)$

$\psi(r, \theta, \phi)$

$d\tau = dxdydz$

$d\tau = r^2 dr \sin\theta\, d\theta d\phi$

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Normalization of the wavefunction

What if ψ is not normalized?

$$\psi \rightarrow N\psi \quad \Rightarrow \quad N^2 \int_{All\ space} \psi^*\psi d\tau = 1 \quad \Rightarrow \quad N = \frac{1}{\left(\int_{All\ space} \psi^*\psi d\tau\right)^{1/2}}$$

For one-dimensional wavefunction

$$N^2 \int_{-\infty}^{\infty} \psi^*\psi dx = 1 \quad \Rightarrow \quad N = \frac{1}{\left(\int_{-\infty}^{\infty} \psi^*\psi dx\right)^{1/2}}$$

Example: Normalizing unnormalized wavefunction $\psi = e^{-r/a_0}$ for hydrogen atom

$$\psi \rightarrow \psi = Ne^{-r/a_0} \qquad N \text{ is normalization constant}$$

$$\underbrace{\int_{allspace} \psi^*\psi\ d\tau}_{1} = N^2 \overbrace{\int_0^{\infty} r^2 e^{-2r/a_0} dr}^{\frac{1}{4}a_0^3} \overbrace{\int_0^{\pi} \sin\theta d\theta}^{2} \overbrace{\int_0^{2\pi} d\phi}^{2\pi} = \pi a_0^3 N^2 \qquad \int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$\Rightarrow N = \left(\frac{1}{\pi a_0^3}\right)^{1/2}$$

Normalized wavefunction: $\psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$