Schrödinger Equation Review

- Dynamic equation that governs the evolution of the QM wave function Ψ

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

- SOV

$$\Psi(\vec{x},t)=\psi(\vec{x})\phi(t)\ \Rightarrow \frac{1}{\psi}\left[\frac{-\hbar^2}{2m}\nabla^2\psi+V\psi\right]=\frac{i\hbar}{\phi}\frac{d\phi}{dt}=const=E$$

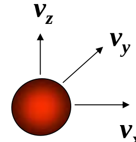
- **Time-dependent solution**

$$\boxed{\phi(t)=e^{-i\frac{E}{\hbar}t}}$$

- **Time independent Schrödinger equation**

$$\boxed{\nabla^2\psi+\frac{2m}{\hbar^2}(E-V)\psi=0}$$

Free Particle



- Begin by looking at simple moving particle moving through free space without any forces on it
  - no forces means V=0
  - Schrödinger eqn. becomes $\nabla^2\psi+\frac{2mE}{\hbar^2}\psi=0$
  - try SOV to get solution $\psi(x,y,z)=X(x)Y(y)Z(z)$

$$YZ\frac{d^2X}{dx^2}+XZ\frac{d^2Y}{dy^2}+XY\frac{d^2Z}{dz^2}=\frac{-2mE}{\hbar^2}XYZ$$

$$\frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}+\frac{1}{Z}\frac{d^2Z}{dz^2}=\frac{-2mE}{\hbar^2}$$

  - each term must be a constant, let $E=E_x+E_y+E_z$

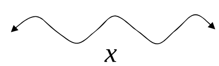
Free Particle (con't)

$$\frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}+\frac{1}{Z}\frac{d^2Z}{dz^2}=\frac{-2m}{\hbar^2}\left(E_x+E_y+E_z\right)$$

- Break into 3 indep. equations

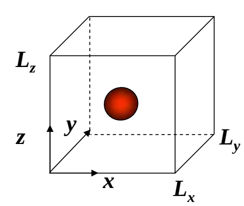
$$\frac{d^2X}{dx^2}+\frac{2mE_x}{\hbar^2}X=0;\quad \frac{d^2Y}{dy^2}+\frac{2mE_y}{\hbar^2}Y=0;\quad \frac{d^2Z}{dz^2}+\frac{2mE_z}{\hbar^2}Z=0$$

- Solutions $X \propto \cos\left[\left(\frac{2mE_x}{\hbar^2}\right)^{1/2}\left(x-x_0\right)\right];\quad etc.$
- For free particle, from classical mechanics $E_x = m\mathrm{v}_x^2/2$
  - DeBroglie wavelength $\lambda = h/p_x = h/m\mathrm{v}_x$
- So if we know v_x exactly $X \propto \cos\left[\frac{2\pi}{\lambda}\left(x-x_0\right)\right]$



  - extends to infinity
    ⇒ location of particle can't be localized (✓Heisenberg)

Particle in a Box



- Same equation (no potential)
  - no forces means V=0, so still have

$$\nabla^2\psi+\frac{2mE}{\hbar^2}\psi=0$$

  - so same gen'l. solution as free particle

$$\psi(x,y,z)=X(x)Y(y)Z(z)\qquad \frac{d^2X}{dx^2}+\frac{2mE_x}{\hbar^2}X=0,\ \text{etc.}$$
$$E=E_x+E_y+E_z$$

  - by requiring particle to be somewhat localized (in box) ψ must be zero outside box
    - B.C. $X(0)=X(L_x)=Y(0)=Y(L_y)=Z(0)=Z(L_z)=0$
  - this looks like the bounded string ($f''+K^2f=0$), but with $K_i^2=\frac{2mE_i}{\hbar^2}$

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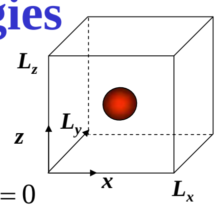
Particle in a Box: Energies



- Solution of ODE's

  $X = A_x \cos(K_x x) + B_x \sin(K_x x)$; etc.

- Apply B.C.

  $A_i = 0 \quad \sin(K_x L_x) = \sin(K_y L_y) = \sin(K_z L_z) = 0$

- Periodic B.C. thus gives eignevalues $\Rightarrow K_i L_i = n_i \pi$

  $n_i = 1, 2, 3, \ldots \qquad K_i^2 = \frac{2mE_i}{\hbar^2}$

  $$E_{i,n_i} = \frac{h^2}{8m}\frac{n_i^2}{L_i^2}$$

  large L means smaller spacing between energies

- Note

  $$E_{tot}(n_x, n_y, n_z) = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

  - if $L_x \neq L_y \neq L_z$ then each specific "state" (n_x,n_y,n_z) has different energy $\Rightarrow$ **nondegenerate states**
  - otherwise get states with same energies (**degenerate**)
    - e.g., $L_x = L_y \Rightarrow$ (4,2,n_z) has same E as (2,4,n_z)
  - number of states with same E is called g

    g*≡degeneracy of energy level *E

and $\int_{-\infty}^{\infty} |\psi|^2 = 1$

$\Rightarrow B_{i,n} = \square$

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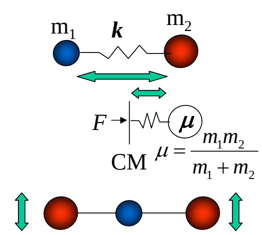
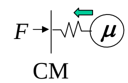
Harmonic Oscillator (1-D)



bending (e.g., elastic beam

- Vibration of particles fixed along a line (linear vibrator) with "spring" potential
  - best to describe motion with center-of-mass coordinates
- Schrödinger Eq. $\quad \nabla^2 \psi + \frac{2m}{\hbar^2}(E - V)\psi = 0$
- V=?
  - related to force, $\quad \frac{dV}{dx} = -F$
  - from classical mech. for spring with fixed spring constant $\quad F = -kx \quad \therefore V = \frac{1}{2}kx^2$
    - relate to frequency $\quad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \Rightarrow V = 2\pi^2 \mu \nu^2 x^2$

HO (1-D): Solutions



- Sch. Eqn. for HO

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}\left(E-2\pi^2 m\nu^2x^2\right)\psi=0$$

- B.C. and constraints

$$\psi\to 0 \text{ as } x\to\pm\infty \qquad \int_{-\infty}^{\infty}|\psi|^2=1$$

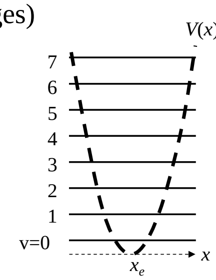
- Solution (from Hermite's ODE) $\frac{d^2\psi}{d\rho^2}+\left(\frac{2E}{h\nu}-\rho^2\right)\psi=0$
- Result
  - **eigenvalues** $\boxed{E_v=h\nu(v+1/2)}$ $\qquad \rho\equiv 2\pi x\sqrt{\frac{m\nu}{h}}$
  - **quantum numbers** $v=0,1,2,\ldots$
  - **eigenfunctions**

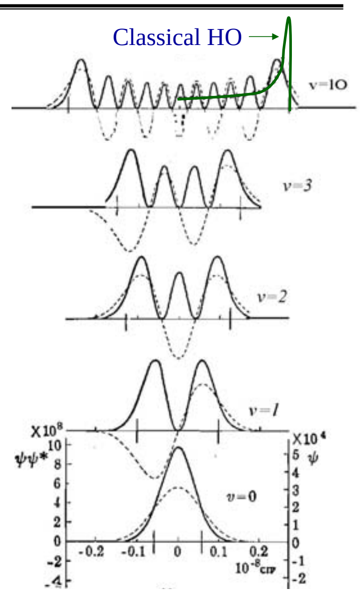
$$\psi_v=\left[\left(\frac{2m\nu}{h}\right)^{1/2}\frac{1}{2^v v!}\right]^{1/2}e^{-\rho^2/2}H_v(\rho)$$

Hermite Polynomial of order v $\quad H_v(\rho)=(-1)^v e^{\rho^2}\frac{d^v}{d\rho^v}\left(e^{-\rho^2}\right)$ $\quad H_0=1; H_1=2\rho; H_2=4\rho^2-2$; $H_3=8\rho^3-12\rho$

HO (1-D): Results

- $E_{min}\neq 0$ $(=1/2\, h\nu)$
- Equally spaced energy states/levels
- For lowest energy state (v=0) most probable to find mass (particle) at x=0
  - compare to classical result, particle always spends most of its "time" at turning points (edges)
- For high v, QM results do (on avg.) approach classical result





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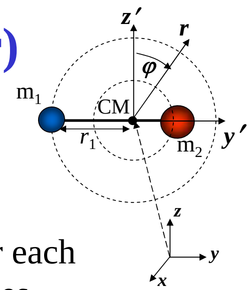
Rigid Rotor (Linear)



- Look at planar rotation of particles along line with rigid spacing
  - assume V=0 (KE only)
- Could write 2 Schrödinger eqs. (one for each particle) but better to use CM coordinates

$$\nabla^2\psi_{tot} + \frac{(m_1+m_2)}{\mu r^2}\frac{\partial^2\psi_{tot}}{\partial\varphi^2} + \frac{2(m_1+m_2)E_{tot}}{\hbar^2}\psi_{tot} = 0$$

- SOV

$$\psi_{tot} = F(x,y,z)\Phi(r,\varphi) \qquad E_{tot} = E_{tr,CM} + E_{rot}$$

- Get .

$$\nabla^2 F + \frac{2m_{tot}E_{tr}}{\hbar^2}F = 0$$ already solved = translational motion of "total" particle $$\nabla^2\psi_{tr} + \frac{2mE_{tr}}{\hbar^2}\psi_{tr} = 0$$

$$\frac{d^2\Phi}{r^2 d\varphi^2} + \frac{2\mu E_{rot}}{\hbar^2}\Phi = 0$$ looks like 1-D free particle with $m\rightarrow\mu$, $x\rightarrow r\varphi$ $$\frac{d^2X}{dx^2} + \frac{2mE_x}{\hbar^2}X = 0$$

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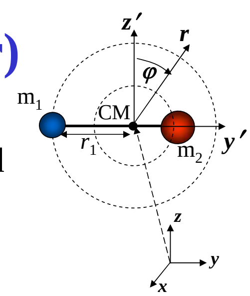
Rigid Rotor (Linear)



- So for this rigid rotor with rotation, we can divide motion into translational and rotational modes and $E_{tot}=E_{tr}+E_{rot}$
- E_{tr} and E_{rot}
  - from previous solutions $$E_{tr,n_i} = \frac{h^2}{8m}\frac{n_i^2}{L_i^2}$$

large *I* means smaller spacing between energy of each QM state

$$E_{rot,n_\varphi} = \frac{h^2}{2\mu}\frac{n_\varphi^2}{r^2} = \frac{h^2 n_\varphi^2}{2I}$$ ← moment inertia

$$n_\varphi = 0,1,2,3,...$$

- This solution was for rotor confined to fixed plane that is parallel to y-z plane

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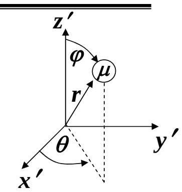
3-D Rigid Rotor



- For more general case, can write Schrödinger Eqn. with CM translation already removed already

$$\frac{1}{r^2}\frac{\partial.}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}+\frac{1}{r^2\sin\theta}\frac{\partial^2}{\partial\varphi^2}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{2\mu E_{rot}}{\hbar^2}\psi=0$$

0, rigid

- SOV (polar coord.) $\psi(\theta,\varphi)=\Phi(\varphi)\Theta(\theta)$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2IE_{rot}}{\hbar^2}\sin^2\theta=0$$

  – each term must be same, equal to a constant ($\equiv -m^2$)
- Solutions
  – Φ $\Phi_m(\varphi)=\frac{1}{\sqrt{2\pi}}e^{im\varphi}$ $m=0,\pm1,\pm2,\pm3,\ldots$ **to satisfy periodicity BC $\Phi(0)=\Phi(2\pi)$**

  for $\int_0^{2\pi}|\Phi|^2=1$

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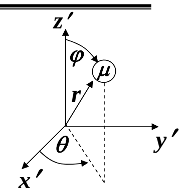
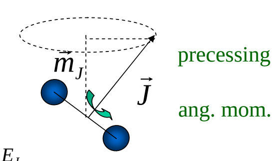
3-D Rigid Rotor

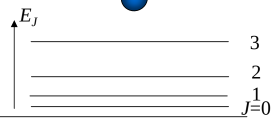


- Θ solution
  – Eigenfunctions $\Theta_{J,m}(\theta)=\left[\frac{2J+1}{2}\frac{(J-|m|)!}{(J+|m|)!}\right]^{1/2}P_J^{|m|}(\cos\theta)$ ← Associated Legendre Functions
  – Eigenvalues

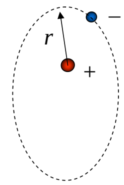
$$\boxed{E_J=J(J+1)\frac{\hbar}{2I}}\qquad J=0,1,2,\ldots\qquad |m|\le J\qquad m=0,\pm1,\pm2,\pm J$$

- So for 3-D rigid rotor
  – each energy level has discrete energy $E_J \propto J(J+1)/I$
    - J=rotational (ang. mom.) quantum #
    - for large J, $E_J \propto J^2$ like the planar rotor
  – there are $2J+1=g_J$ different states with same energy, $m=-J,-J+1,\ldots.J$
    - m=magnetic quantum #





Electronic Energy



- Recall H atom
  - looks like a rotor of 2 particles (nucleus and electron)
  - but not rigid (*r* can change)
  - and there is a (electrostatic) potential *V*(*r*) between particles ⇒ **electronic energy**
- QM analysis
  - separate KE from electronic energy
  - use SOV, work in polar coordinates

n=1,2,3…
l=n-1, n-2, …,0
m=-l,-l+1,...,l

m=0, ±1, ±2,…
l=|m|,|m|+1, …
n=l+1, l+2,…

$$\psi(r,\theta,\varphi)=R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\varphi)$$

PLUS need electron spin, m_s=±1/2

- 3 quantum numbers (n, l, m)

n: radial or principal
l: azimuthal or orbital ang. mom., like J
m: magnetic