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

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

- **Time-dependent solution**

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

- **Time-independent Schrödinger equation**

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

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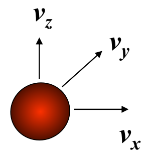
Free Particle

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



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

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

  - each term must be a constant, let $\varepsilon=\varepsilon_x+\varepsilon_y+\varepsilon_z$

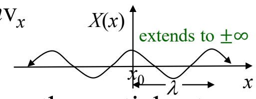
Free Particle (con't)

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

- Break into 3 independent equations (wave eqn in each coord.)

$$\frac{d^2X}{dx^2}+\frac{2m\varepsilon_x}{\hbar^2}X=0;\quad \frac{d^2Y}{dy^2}+\frac{2m\varepsilon_y}{\hbar^2}Y=0;\quad \frac{d^2Z}{dz^2}+\frac{2m\varepsilon_z}{\hbar^2}Z=0$$

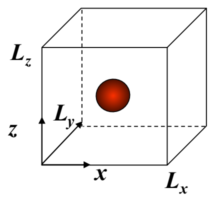
- Solutions $\quad X\propto\cos\left[\left(\frac{2m\varepsilon_x}{\hbar^2}\right)^{1/2}\left(x-x_0\right)\right];\quad etc.$
- Classical mechanics for free particle gives $\varepsilon_x=m\mathrm{v}_x^2/2$
  - and de Broglie wavelength $\lambda=h/p_x=h/m\mathrm{v}_x$
- Combining $\quad X\propto\cos\left[\frac{2\pi}{\lambda}\left(x-x_0\right)\right]$



- Since $|X(x)|^2$ represents probability of finding the particle at x, the position of our particle can't be localized

  but according to Heisenberg, we could know its velocity very accurately

Particle in a Box



- To localize the particle, let's confine it to a small bit of space, a "box"
- Same Schrödinger eqn (no potential)
  - so still have $\nabla^2\psi+\frac{2m\varepsilon}{\hbar^2}\psi=0$
  - so also same general solution as free particle

$$\psi(x,y,z)=X(x)Y(y)Z(z)\qquad \frac{d^2X}{dx^2}+\frac{2m\varepsilon_x}{\hbar^2}X=0,\ \text{etc.}$$

$$\varepsilon=\varepsilon_x+\varepsilon_y+\varepsilon_z$$

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

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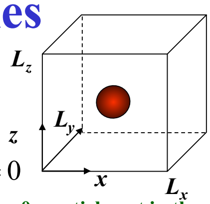
Particle in a Box: Energies



- Solution of ODE's

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

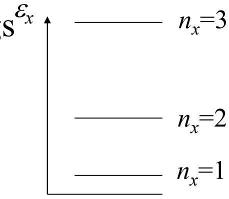
  $A_i = 0 \quad \sin(K_x L_x) = \sin(K_y L_y) = \sin(K_z L_z) = 0$
- Periodic B.C. thus give eigenvalues

  $\Rightarrow K_i L_i = n_i \pi \quad n_i = 1,2,3,\ldots$

  for n_i=0, particle not in the box (ψ=0 everywhere)

  energies of states (and velocities) now quantized!!

  $$K_i^2 = \frac{2m\varepsilon_i}{\hbar^2} \Rightarrow \boxed{\varepsilon_{i,n_i} = \frac{h^2}{8m}\frac{n_i^2}{L_i^2}} \quad \text{and } \varepsilon_{tot}(n_x,n_y,n_z) = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right)$$
- State energies and spacings
  - $\varepsilon_{x,1} = 1\ (h^2/8mL_x^2)$
  - $\varepsilon_{x,2} = 2^2\ (h^2/8mL_x^2) = 4\varepsilon_{x,1}$
  - $\varepsilon_{x,3} = 3^2\ (h^2/8mL_x^2) = 9\varepsilon_{x,1}$



energy spacing between states increases with n_i

larger L_i means smaller energy spacing between states

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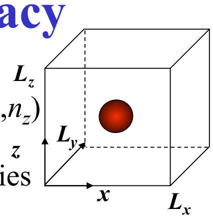
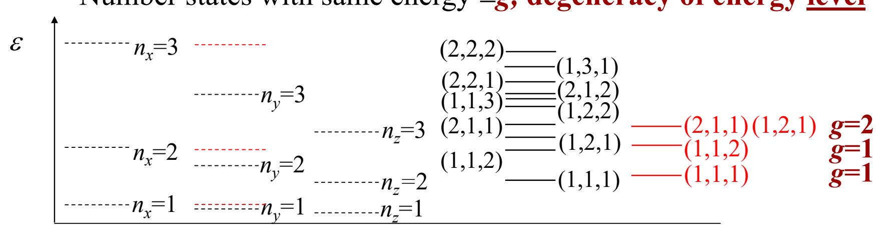
Particle in a Box: Degeneracy

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

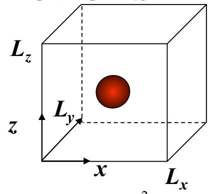


- If $L_x \neq L_y \neq L_z$, each specific quantum state (n_x,n_y,n_z) has different energy $\Rightarrow$ **nondegenerate states**
- Otherwise get multiple states with same energies $\Rightarrow$ **degenerate states**
  - e.g., $L_x = L_y \Rightarrow (2,1,n_z)$ has same ε as $(1,2,n_z)$
  - can also happen if L_i/L_j = integer
- Number states with same energy $\equiv$***g*, degeneracy of energy level**



Particle in a Box: Wave Functions

- Time-independent solution
  $\psi(x,y,z) = X(x)Y(y)Z(z)$
- So time-averaged probability of finding particle at $(x,y,z) \to (x+dx,y+dy,z+dz)$

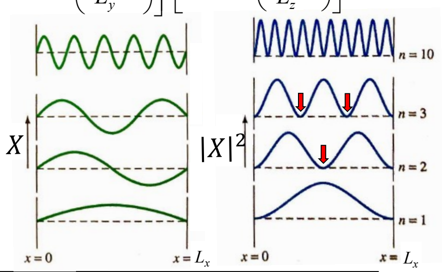


$$= \psi\psi^* dxdydz = \left[B_{x,n_x} \sin\left(\frac{n_x \pi}{L_x} x\right)\right]^2 \left[B_{y,n_y} \sin\left(\frac{n_y \pi}{L_y} y\right)\right]^2 \left[B_{z,n_z} \sin\left(\frac{n_z \pi}{L_z} z\right)\right]^2 dxdydz$$

$$\int_{-\infty}^{\infty} \psi\psi^* dxdydz = 1$$

$$\Rightarrow B_{i,n_i} = \sqrt{2/L_i}$$

- For given energy (or velocity)
  - particle can't exist at certain locations

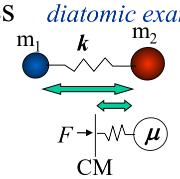


D. Giancoli, *Physics for scientists and engineers with modern physics*. 4th ed. (2008)

Molecular Vibrations

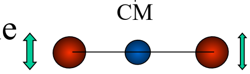
- In addition to translation, multi-atom molecules can also exhibit relative motions of their nuclei about the molecule's center-of-mass
- One such motion: vibrations
- Linear vibrator with "spring"-like potential
- Bending of linear molecule
- Nonlinear molec. vibrations

diatomic example

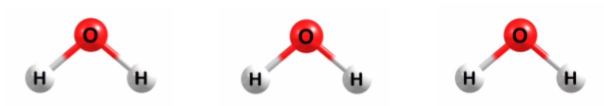


reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$



bending (e.g., elastic beam)



Bending Symmetric stretch Asymmetric stretch

https://dornshuld.chemistry.msstate.edu/books/icc/intro.html

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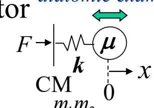
Harmonic Oscillator (1-D)

- Simplest vibration model is 1-D harmonic oscillator
  - like having spring constant that doesn't change
  - describes motion in center-of-mass coordinates
  - classically, energy moves between *KE* and *PE*
    - equilibrium point (x=0); can be stationary, no *KE* or *PE*

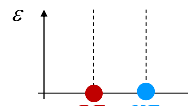
diatomic example



$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

- Schrödinger Eq. $\nabla^2\psi + \frac{2m}{\hbar^2}(\varepsilon - V)\psi = 0$
- V=?
  - related to force $dV/dx = -F$
  - from classical mechanics for k=const. spring attached to mass m $F = -kx \quad \therefore V = ½\, kx^2$
    - relate to frequency, $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$

$$\Rightarrow V = 2\pi^2 m \nu^2 x^2$$



$\varepsilon = PE + KE$

in center-of-mass system

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad V = 2\pi^2 \mu \nu^2 x^2$$

for diatomic $r = r_e + x$ = internuclear spacing

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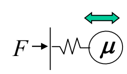
HO (1-D): Solutions

- Schrodinger Eqn. for HO

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



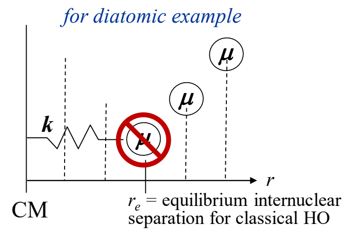
- B.C. and constraint $\psi \to 0$ as $x \to \pm\infty$ $\quad \int_{-\infty}^{\infty} \psi\psi^* dx = 1$
- Let $\rho \equiv 2\pi x\sqrt{\frac{\mu\nu}{h}} \Rightarrow \frac{d^2\psi}{d\rho^2} + \left(\frac{2\varepsilon}{h\nu} - \rho^2\right)\psi = 0$ i.e., $y'' + (a - x^2)y = 0$
- Solution can be found by a transformation into Hermite's ODE
- Result
  - **eigenvalues** $\boxed{\varepsilon_v = h\nu(\text{v}+1/2)}$
  - **quantum numbers** v = 0, 1, 2, …
  - **eigenfunctions** $\psi_v = \left[\left(\frac{2\mu\nu}{h}\right)^{1/2}\frac{1}{2^v v!}\right]^{1/2} e^{-\rho^2/2} H_v(\rho)$

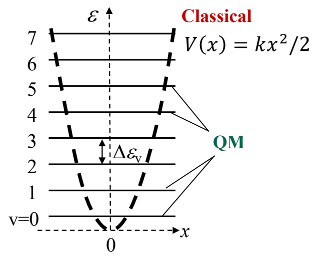
Hermite Polynomial of order v $\quad H_v(\rho) = (-1)^v e^{\rho^2}\frac{d^v}{d\rho^v}\left(e^{-\rho^2}\right)$

$H_0 = 1; H_1 = 2\rho; H_2 = 4\rho^2 - 2$
$H_3 = 8\rho^3 - 12\rho$

HO (1-D): Energy

- Discrete energy states are equally spaced
  - $\varepsilon_v = h\nu(v+½) \Rightarrow \varepsilon_{v+1} - \varepsilon_v \equiv \Delta\varepsilon_v = h\nu$
- All states have same vibrational frequency, ν
  - but max/min separation increases with energy ε_v
- Lowest energy state (v=0) is vibrating
  - can't be at rest like classical HO





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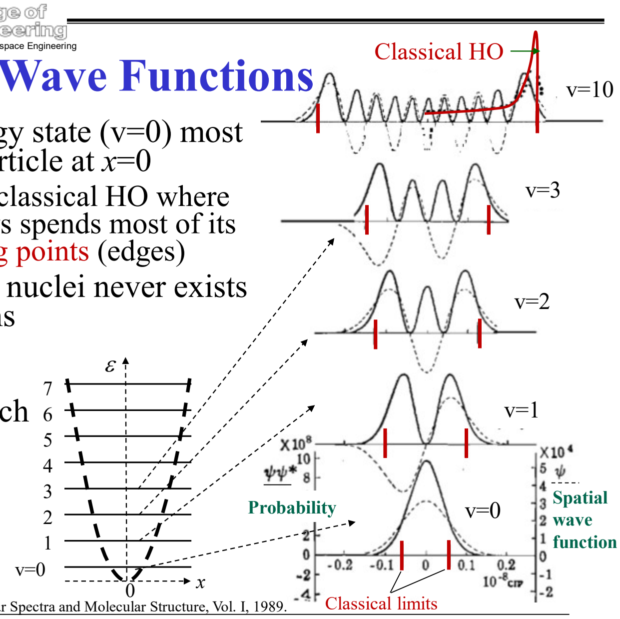
HO (1-D): Wave Functions

- For lowest energy state (v=0) most likely to find particle at x=0
  - in contrast to classical HO where particle always spends most of its time at turning points (edges)
- For other states, nuclei never exists at some locations
- For high v, QM results do (on average) approach classical results



G. Herzberg, Molecular Spectra and Molecular Structure, Vol. I, 1989.

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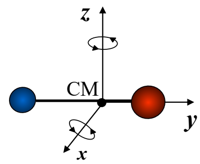
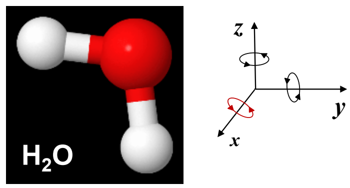
Molecular Rotations

- In addition to translation and vibrations, multi-atom molecules can also rotate about their center-of-mass
- Linear molecules
  - 2 orthogonal axes of rotation



- Nonlinear molecules
  - 3 orthogonal axes of rotation

rotation about 1 axis



https://commons.wikimedia.org/wiki/File:Water_molecule_rotation_animation_large.gif

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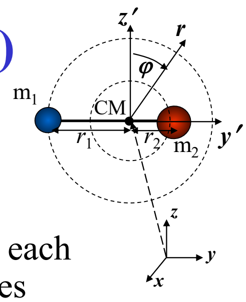
Rigid Rotor (Linear)



- 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

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

- SOV

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

- Get

$$\nabla^2 F + \frac{2m_{tot}\varepsilon_{tr}}{\hbar^2}F = 0$$

already solved = translational motion of "total" particle

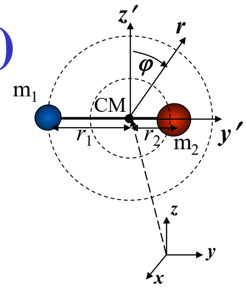
$$\nabla^2\psi_{tr} + \frac{2m\varepsilon_{tr}}{\hbar^2}\psi_{tr} = 0$$

$$\frac{d^2\Phi}{r^2 d\varphi^2} + \frac{2\mu\varepsilon_{rot}}{\hbar^2}\Phi = 0$$

looks like 1-D translating particle with $m \rightarrow \mu$, $x \rightarrow r\varphi$

$$\frac{d^2X}{dx^2} + \frac{2m\varepsilon_x}{\hbar^2}X = 0$$

Rigid Rotor (Linear)



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

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

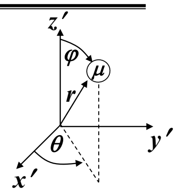
$$\varepsilon_{rot,n_\varphi} = \frac{h^2}{2\mu}\frac{n_\varphi^2}{r^2} = \frac{h^2 n_\varphi^2}{2I} \qquad n_\varphi = 0,1,2,3,\ldots$$

$r = r_1 + r_2$

$2I \longleftarrow$ moment of inertia, μr^2

- However, this solution was for a rotor confined to rotate **only** in a fixed plane (parallel to y-z plane)

3-D (Linear) Rigid Rotor



- For more general case, can write Schrödinger Eqn. in polar coordinates with CM translation removed

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \underbrace{\cancel{\frac{\partial \psi}{\partial r}}}_{0,\ \text{rigid}}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{1}{r^2\sin\theta}\frac{\partial^2}{\partial\varphi^2}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{2\mu\varepsilon_{rot}}{\hbar^2}\psi = 0$$

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

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

  - each term must be same, equal to a constant ($\equiv -m^2$)
- Solutions
  - $\Phi \qquad \Phi_m(\varphi) = \dfrac{1}{\sqrt{2\pi}}e^{im\varphi} \qquad m = 0, \pm 1, \pm 2, \pm 3, \ldots$ **to satisfy periodicity BC $\Phi(0)=\Phi(2\pi)$**

for $\int_0^{2\pi} \Phi\Phi^* d\varphi = 1$

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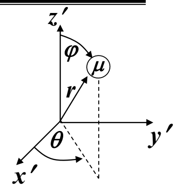
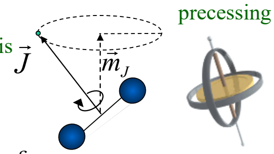
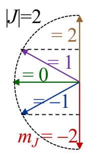
3-D (Linear) Rigid Rotor



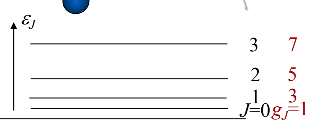
- Θ solution
  - eigenfunctions
$$\Theta_{J,m}(\theta)=\left[\frac{2J+1}{2}\frac{(J-|m|)!}{(J+|m|)!}\right]^{1/2} P_J^{|m|}(\cos\theta)$$
Associated Legendre Functions
  - eigenvalues
$$\boxed{\varepsilon_J = J(J+1)\frac{\hbar^2}{2I}} \qquad J=0,1,2,...$$
$$|m|\le J \qquad m=0,\pm1,\pm2,...\pm J$$
- So for 3-D rigid rotor
  - each energy level has discrete energy $\varepsilon_J \propto J(J+1)/I$
    - J=rotational (ang. mom.) quantum #
    - for large J, $\varepsilon_J \propto J^2$ like the planar rotor
  - there are $2J+1=g_J$ different states with same energy, $m= -J,-J+1,\ldots, J$
    - m=magnetic quantum #

ang. mom. ⊥ internuclear axis





each quantized m_J state has different J angle wrt arbitrary direction; will have different ε in mag. field



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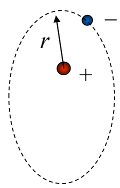
Electronic Energy



- 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)

radial or principal — magnetic — azimuthal or orbital ang. mom., like J