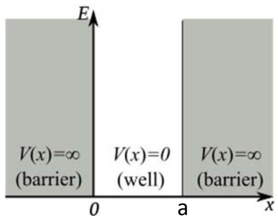
Particle in a 1-Dimensional box



$\Psi = 0$ outside the box

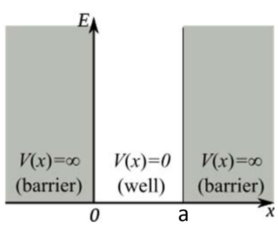
The solution in the well:

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi$$

This must be solved subject to the condition that Ψ be continuous at all points in space

$$\frac{d^2\Psi}{dx^2} + \frac{2mE}{\hbar^2}\Psi = 0$$

Particle in a 1-Dimensional box



$$\frac{d^2\Psi}{dx^2} + \frac{2mE}{\hbar^2}\Psi = 0$$

Using trial method, can find that only exponential function works: $\Psi(x) = \exp(sx)$

$$s^2 = -\frac{2mE}{\hbar^2} \text{ or}$$

$$s = \pm i\frac{\sqrt{2mE}}{\hbar} = \pm ik$$

The general solution:

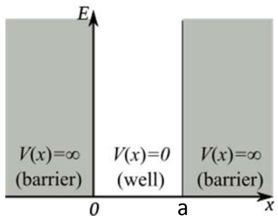
$$\Psi(x) = A_+ \exp(ikx) + A_- \exp(-ikx)$$

or

$$\Psi(x) = C\cos(kx) + D\sin(kx)$$

Particle in a 1-Dimensional box

$$\Psi(x) = C\cos(kx) + D\sin(kx)$$



The singlevalued-ness criteria requires that the function is 0 at x = 0 and at x = a.

The first result means that C = 0

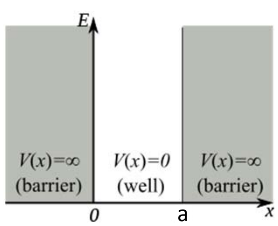
The second gives:

$\sin(ka) = 0$, which is only true if $ka = n\pi$,

where n is a positive integer

Thus:

$$i\frac{\sqrt{2mE}}{\hbar} = ik = i\frac{\pi n}{a} \text{ and } E_n = \frac{n^2h^2}{8ma^2} \text{ (here } \hbar = \frac{h}{2\pi}\text{)}$$



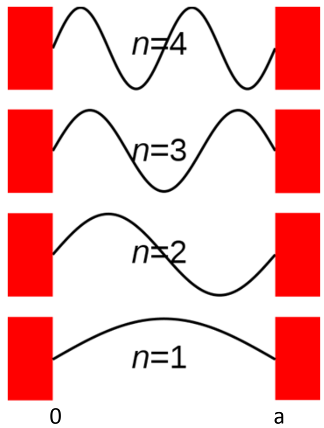
The boundary conditions restrict energy to only have certain values. This is called quantization.

Constant D is not determined by previous conditions but can be found from normalization condition:

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = \int_{0}^{a} \psi^*(x)\psi(x)dx = 1$$

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$$

Particle in a 1-Dimensional box



Particle in a 3-Dimensional box

Simple extension:

$$0 \le x \le a;\ 0 \le y \le b;\ 0 \le z \le c$$

$H = H_x + H_y + H_z$ such that

$$H_x \psi_x = E_x \psi_x$$

$$H_y \psi_y = E_y \psi_y$$

$$H_z \psi_z = E_z \psi_z$$

$$E = E_x + E_y + E_z$$

$$\psi = \psi_x(x)\psi_y(y)\psi_z(z)$$

$$\psi(x,y,z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

Particle in a
3-Dimensional box
The concept of degeneracy, g:
Let's make a=b=c (cubic box)

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

but if a = b = c, then:

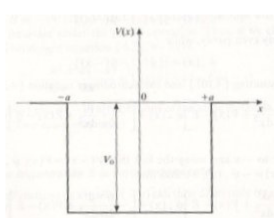
$$E = E_x + E_y + E_z = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

(2,2,1) (2,1,2) (1,2,2)

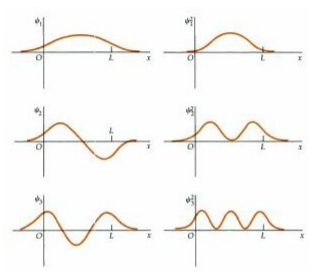
(2,1,1) (1,2,1) (1,1,2)

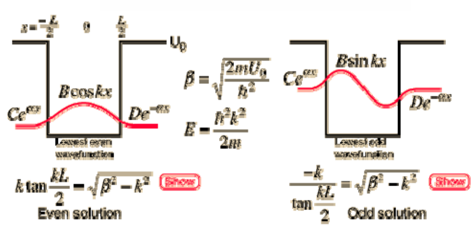
(1,1,1)

Particle in a finite depth box

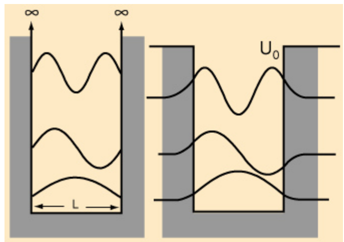


$$V(x) = \begin{cases} -V_0 & |x| < L \\ 0 & |x| > L \end{cases}$$

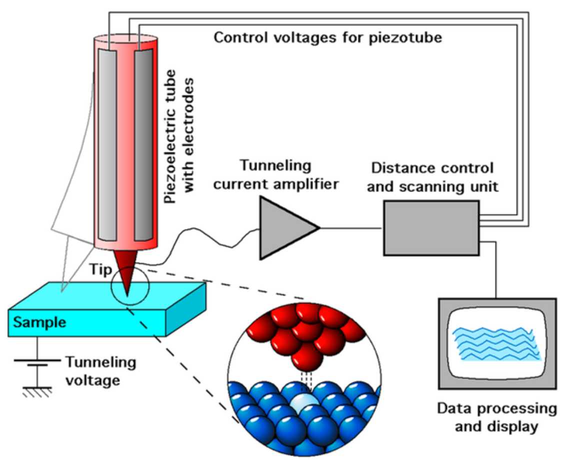




Comparison of finite and infinite potential



Finite potential and tunneling:
Scanning tunneling microscopy



Finite potential and tunneling:
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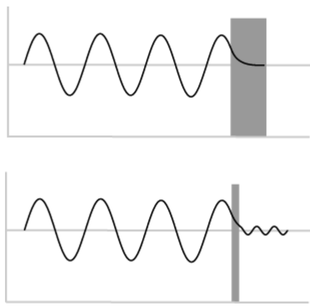


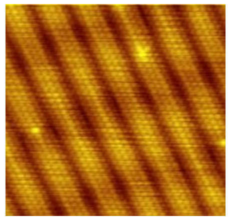
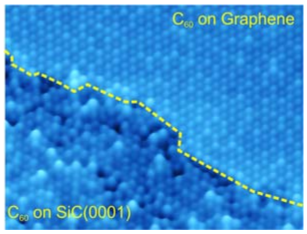
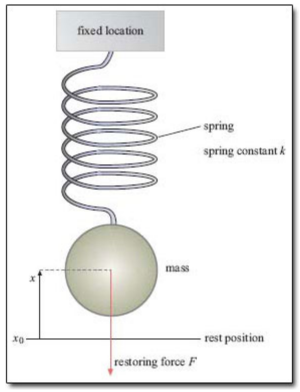


Image of reconstruction on a clean Gold(100) surface



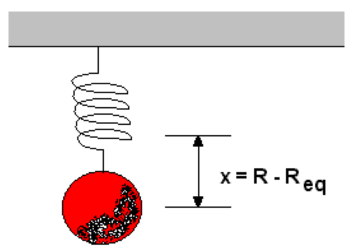
The 1-D Harmonic Oscillator

Quantum mechanical Harmonic Oscillator:
Model for Vibrational motion



The 1-D harmonic oscillator Hamiltonian

- Particle (mass m) attached to a spring of force constant, k



- Potential energy depends on position as a Hooke's-law spring

$$V = \frac{k}{2}(r - r_{eq})^2 = \frac{k}{2}x^2$$

$$H = \frac{p^2}{2m} + \frac{k}{2}x^2$$

Classical solution of the 1-D harmonic oscillator

- Solve for trajectories for constant energy
- Fundamental frequency, ω_0
- Oscillatory motion
- Maximum displacements are classical turning points
  - E = V(x_{max})

$$x(t) = \sqrt{\frac{2E}{m\omega_0^2}}\cos\omega_0 t$$

$$p(t) = -\sqrt{2mE}\sin\omega_0 t$$

$$\omega_0 = \sqrt{\frac{k}{m}}$$

$$x_{\max} = \pm\sqrt{\frac{2E}{m\omega_0^2}}$$

Quantum 1-D harmonic oscillator

- **Schroedinger's equation**

$$H\Psi = E\Psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + \frac{k}{2}x^2\Psi = E\Psi$$

- **Convenient to make dimensionless equation**

$$\frac{d^2\Psi}{dy^2} - y^2\Psi + \varepsilon\Psi = 0$$

$$y = \frac{x}{\alpha} \qquad \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4} \qquad \varepsilon = \frac{2}{\hbar\omega_0}E$$

- **Hermite's associated differential equation**

1-D harmonic-oscillator wave functions and energies

- Wavefunctions

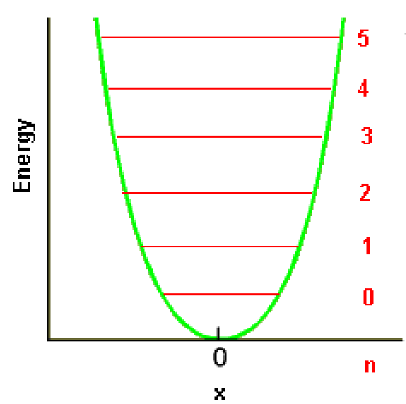
$$\Psi_\upsilon(x) = A_\upsilon H_\upsilon(x/\alpha)\exp\left(-\frac{x^2}{2\alpha^2}\right) \qquad \upsilon = 0, 1, 2, 3, \ldots$$

- Energy eigenvalues

$$E_\upsilon = \left(\upsilon + \frac{1}{2}\right)\hbar\omega_0 = \left(\upsilon + \frac{1}{2}\right)h\nu_0$$

Energy levels

- The 1-D harmonic oscillator has equally spaced energy states
- Energy spacing depends on the fundamental frequency
- Energy levels are nondegenerate
  - One state per level



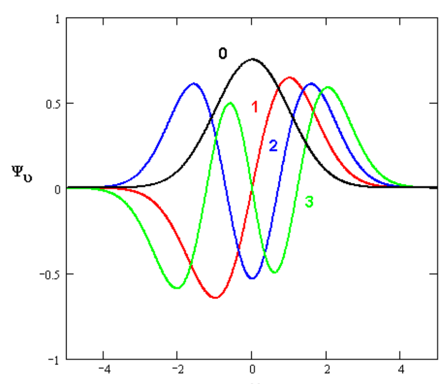
Harmonic-oscillator wave functions

- Harmonic-oscillator wave functions are related to the Hermite polynomials
- Hermite polynomials are well-known sets of functions

υ	$H_\upsilon(y)$	Symmetry
0	1	Even
1	2y	Odd
2	$4y^2 - 2$	Even
3	$8y^3 - 12y$	Odd

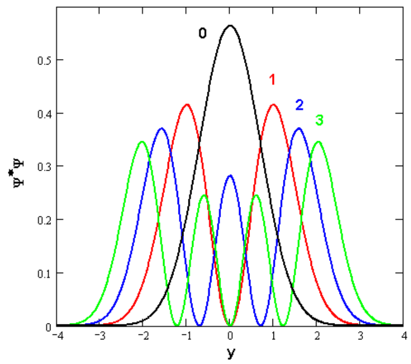
Wave functions

- Hermite polynomials multiplied by a Gaussian function
- Note alternation in symmetry about x = 0
  - Even
  - Odd

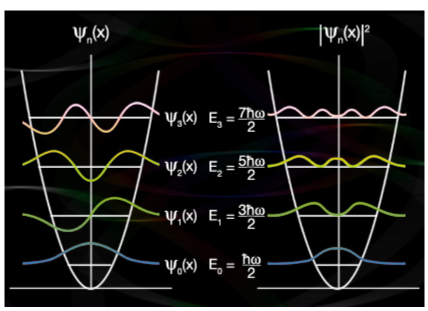


Probability Functions

- The square of the wave function gives the probability density at each position
- Finite possibility the particle is outside of the classical turning points



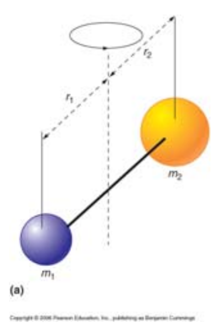
Quantum mechanical Harmonic Oscillator:
Model for Vibrational motion

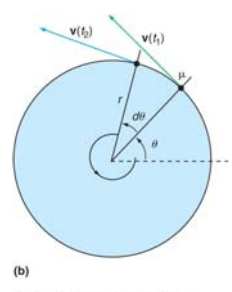


Angular Momentum and the Rigid Rotor

Classical rigid rotor

- Rigid rotor model: A particle of mass m fixed to a massless rod





Classical rigid rotor

- Physical observables:
  angular velocity

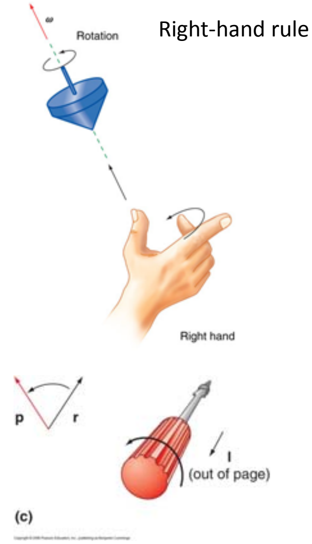
$$|\omega| = \frac{d\theta}{dt}$$

  angular acceleration

$$\alpha = \frac{d|\omega|}{dt} = \frac{d^2\theta}{dt^2}$$

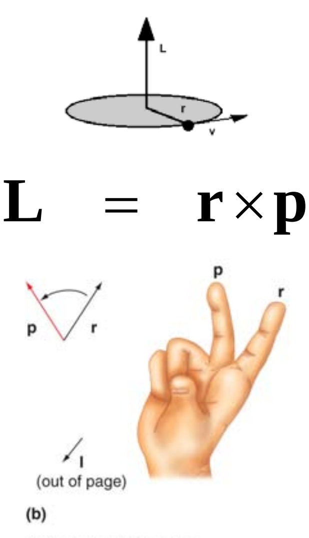
  kinetic energy

$$E_{kin} = \frac{1}{2}mv^2 = \frac{1}{2}\mu r^2\omega^2 = \frac{1}{2}I\omega^2$$



Angular momentum

- Vector property that describes circular motion of a particle or a system of particles
- Rigid rotor model: A particle of mass m fixed to a massless rod
- Examples
  - Swinging a bucket of water
  - Movement of the Earth around the Sun



$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

Classical angular momentum

- Linear motion (Newton's 2nd Law)

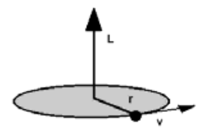
$$\mathbf{F} = m\mathbf{a} = \frac{d\mathbf{p}}{dt}$$

- Angular motion

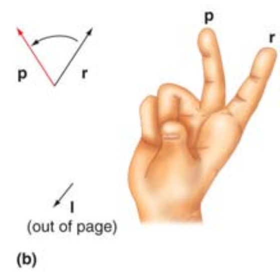
$$\mathbf{L} = \mathbf{r} \times \mathbf{p};$$

$$L = pr\sin\phi = \mu vr\sin\phi$$

$$E = \frac{p^2}{2\mu} = \frac{l^2}{2\mu r^2} = \frac{l^2}{2I}$$



$$\mathbf{L} \quad = \quad \mathbf{r} \times \mathbf{p}$$



Classical constant-angular-momentum problem

- Solve for trajectories for constant angular momentum
- Frequency, ω, must be constant
- *r* must be constant
- Constant **L** is provided by the fact that *r* and ω are constant

$$\mathbf{L} \quad = \quad \text{constant} \quad = \quad mr^2\omega\mathbf{k}$$

$$\mathbf{r}(t) \quad = \quad r\left(\mathbf{i}\cos\omega t \quad + \quad \mathbf{j}\sin\omega t\right)$$

$$\mathbf{p}(t) \quad = \quad mr\omega\left(-\mathbf{i}\sin\omega t \quad + \quad \mathbf{j}\cos\omega t\right)$$

Quantum angular-momentum operators

- Vector definitions

$$\mathbf{L} = L_x\mathbf{i} + L_y\mathbf{j} + L_z\mathbf{k}$$
$$L^2 = \mathbf{L}\bullet\mathbf{L} = L_x^2 + L_y^2 + L_z^2$$

- Expression by correspondence

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \quad \hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \quad \hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$
$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

- Form of operators with a fixed *r*

$$\hat{\mathbf{L}} = -i\hbar\mathbf{r}\times\nabla$$
$$\hat{L}^2 = -\hbar^2(\mathbf{r}\times\nabla)\bullet(\mathbf{r}\times\nabla)$$

Quantum angular momentum

- Commutators of operators

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z \quad \text{and cyclic permutations}$$
$$\left[\hat{L}^2, \hat{L}_i\right] = 0$$

- Can have common set of eigenstates of L^2 and any one component

$$\hat{L}^2\Psi_{km} = k\hbar^2\Psi_{km}$$
$$\hat{L}_z\Psi_{km} = m\hbar\Psi_{km}$$

Operators in spherical co-ordinates

- Natural system for describing angular motion is spherical co-ordinates
- L_z depends only on ϕ
  - Suggests that the wave functions may be written as a product

$$
\begin{aligned}
\hat{L}_x &= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)\\
\hat{L}_y &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)\\
\hat{L}_z &= -i\hbar\frac{\partial}{\partial\phi}\\
\hat{L}^2 &= -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)
\end{aligned}
$$

$$\Psi_{km}(\theta,\phi) = \Theta_{km}(\theta)\Phi_m(\phi)$$

Differential equations for angular-momentum eigenstates

- The *z* component yields a simple differential equation for Φ_m
- The square of the angular momentum yields an equation for Θ_{km} ($\equiv$ P(cosθ))
  - Legendre's associated differential equation
  - Depend on a quantum number, ℓ
- Solutions are a complete set called the spherical harmonic functions

$$-i\hbar\frac{\partial\Phi_m}{\partial\phi} = m\hbar\Phi_m$$

$$-\left(\frac{\partial^2\Theta_{km}}{\partial\theta^2} + \cot\theta\frac{\partial\Theta_{km}}{\partial\theta} - \frac{m^2}{\sin^2\theta}\Theta_{km}\right) = k\Theta_{km}$$

$$Y_{\ell m}(\theta,\phi) = A_{\ell m}P_\ell^{|m|}(\cos\theta)\Phi_m(\phi)$$

where

$$k = \ell(\ell+1) \quad \text{and} \quad \ell = 0, 1, 2, \ldots$$

Angular-momentum wave functions

- Functions of ϕ are exponentials

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}\exp(im\phi)$$

- Legendre polynomials

ℓ	|m|	$P_\ell^{\|m\|}$
0	0	1
1	0	$\cos\theta$
1	1	$\sin\theta$
2	0	$3\cos^2\theta - 1$
2	1	$\sin\theta\cos\theta$
2	2	$\sin^2\theta$

- Should look familiar, as these are the angular parts of hydrogenic wave functions

Quantum rigid rotor

- Hamiltonian $$\hat{H} = \frac{1}{2mr_0^2}\hat{L}^2$$
- The Hamiltonian commutes with L^2 and L_z
  - The three operators have a complete set of eigenstates in common

$$\hat{H}Y_{\ell m}(\theta,\phi) = E_{\ell m}Y_{\ell m}(\theta,\phi)$$

$$\frac{1}{2mr_0^2}\hat{L}^2 Y_{\ell m}(\theta,\phi) = \frac{1}{2mr_0^2}\ell(\ell+1)\hbar^2 Y_{\ell m}(\theta,\phi)$$

$$E_{\ell m} = \frac{\hbar^2}{2mr_0^2}\ell(\ell+1)$$

Spherical harmonics

$$Y_0^0(\theta,\varphi)=\frac{1}{2}\sqrt{\frac{1}{\pi}}$$

$$Y_1^{-1}(\theta,\varphi)=\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta \quad =\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x-iy)}{r}$$

$$Y_1^{0}(\theta,\varphi)=\frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\cos\theta \quad =\frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\frac{z}{r}$$

$$Y_1^{1}(\theta,\varphi)=\frac{-1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta \quad =\frac{-1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x+iy)}{r}$$

$$Y_2^{-2}(\theta,\varphi)=\frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{-2i\varphi}\cdot\sin^2\theta \quad =\frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)^2}{r^2}$$

$$Y_2^{-1}(\theta,\varphi)=\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta\cdot\cos\theta \quad =\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)z}{r^2}$$

$$Y_2^{0}(\theta,\varphi)=\frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot(3\cos^2\theta-1) \quad =\frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot\frac{(2z^2-x^2-y^2)}{r^2}$$

$$Y_2^{1}(\theta,\varphi)=\frac{-1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta\cdot\cos\theta \quad =\frac{-1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)z}{r^2}$$

$$Y_2^{2}(\theta,\varphi)=\frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{2i\varphi}\cdot\sin^2\theta \quad =\frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)^2}{r^2}$$

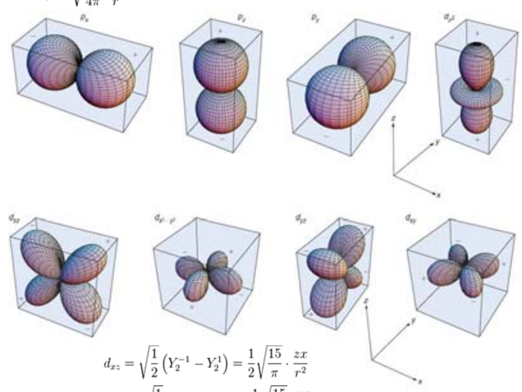
$$p_x=\sqrt{\frac{1}{2}}\left(Y_1^{-1}-Y_1^{1}\right)=\sqrt{\frac{3}{4\pi}}\cdot\frac{x}{r}$$

$$p_y=i\sqrt{\frac{1}{2}}\left(Y_1^{-1}+Y_1^{1}\right)=\sqrt{\frac{3}{4\pi}}\cdot\frac{y}{r}$$

$$p_z=Y_1^{0}=\sqrt{\frac{3}{4\pi}}\cdot\frac{z}{r}$$

$$d_{z^2}=Y_2^0=\frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot\frac{-x^2-y^2+2z^2}{r^2}$$

$$d_{x^2-y^2}=\sqrt{\frac{1}{2}}\left(Y_2^{-2}+Y_2^{2}\right)=\frac{1}{4}\sqrt{\frac{15}{\pi}}\cdot\frac{x^2-y^2}{r^2}$$



$$d_{xz}=\sqrt{\frac{1}{2}}\left(Y_2^{-1}-Y_2^{1}\right)=\frac{1}{2}\sqrt{\frac{15}{\pi}}\cdot\frac{zx}{r^2}$$

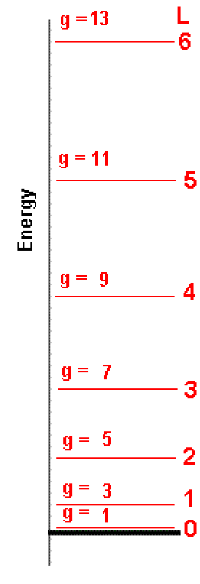
$$d_{yz}=i\sqrt{\frac{1}{2}}\left(Y_2^{-1}+Y_2^{1}\right)=\frac{1}{2}\sqrt{\frac{15}{\pi}}\cdot\frac{yz}{r^2}$$

$$d_{xy}=i\sqrt{\frac{1}{2}}\left(Y_2^{-2}-Y_2^{2}\right)=\frac{1}{2}\sqrt{\frac{15}{\pi}}\cdot\frac{xy}{r^2}$$

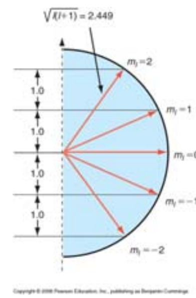
Grotrian diagram for the rigid rotor

- Rigid rotor's energies determined by the quantum number, ℓ
- Each energy level is degenerate
  - States with different values of *m* have the same energy

$$g_\ell = 2\ell+1$$



Spatial quantization of angular momentum

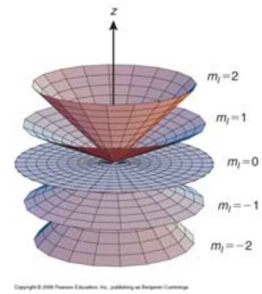


- L_x, L_y, L_z cannot be known simultaneously- do not commute
- Can only know |L| and one component, L_z
- $L = L_x + L_y + L_z$ cannot lie along z;

$$L^2 - L_Z^2 = L_X^2 + L_Y^2 = l(l+1)\hbar^2 - m_l^2\hbar^2$$

circle terminating the cone at its open end

- All the possible magnitudes of L are quantized
- The vector can have only certain orientations in space



Spin

- Goudschmidt and Uehlenbeck proposed electronic "intrinsic angular momentum" to explain spectroscopic anomalies
- Fundamental property of particle called spin
  - Often labeled **I** or **S**
  - Acts like other quantum angular momenta
  - Integer or half-integer values
- Dirac theory of an electron
  - Consequence of relativistic motion of electron

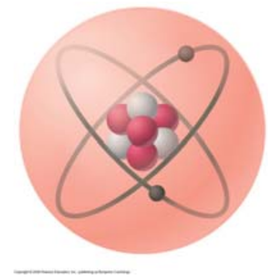
PRINCIPAL SPIN QUANTUM NUMBERS OF PARTICLES	
Electron	**½**
Proton	**½**
Neutron	**½**
Deuteron	**1**
^{12}C	**0**
^{13}C	**½**
^{23}Na	**½**
^{27}Al	**5/2**
^{63}Cu and ^{65}Cu	**3/2**

Hydrogen Atom

Hydrogen atom in quantum mechanics- electron moving about a proton located at the origin of the coordinate system

Coulomb potential

$$U=-\frac{e^2}{4\pi\varepsilon_0|\mathbf{r}|}=-\frac{e^2}{4\pi\varepsilon_0 r}$$



Centrosymmetric potential, use spherical polar coordinates to formulate the ***Schrödinger equation***:

$$-\frac{h^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial\varphi^2}\right]-\frac{e^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

Hydrogen Atom: Solving the Schrödinger Equation

Separation of variables- since U(r) does not depend on the angles:

$$\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)$$

Solution of the Schrödinger equation greatly simplified:

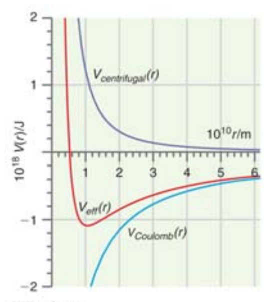
$$-\frac{h^2}{2m_e}\Theta(\theta)\Phi(\phi)\frac{d}{dr}\left[r^2\frac{dR(r)}{dr}\right]+\frac{1}{2m_e r^2}R(r)\hat{l}^2\Theta(\theta)\Phi(\phi)-\Theta(\theta)\Phi(\phi)\left[\frac{e^2}{4\pi\varepsilon_0 r}\right]R(r)=ER(r)\Theta(\theta)\Phi(\phi)$$

Know that $\hat{l}^2\Theta(\theta)\Phi(\phi)=\hbar^2 l(l+1)\Theta(\theta)\Phi(\phi)$

can remove angular dependence from the Schrödinger equation:

$$-\frac{h^2}{2m_e}\frac{d}{dr}\left[r^2\frac{dR(r)}{dr}\right]+\left[\frac{\hbar^2 l(l+1)}{2m_e r^2}-\frac{e^2}{4\pi\varepsilon_0 r}\right]R(r)=ER(r)$$

Effective potential, centrifugal + Coulomb



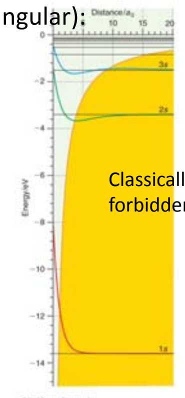
Hydrogen Atom: Eigenvalues and Eigenfunctions of Total Energy

Energy- appears only in the radial equation (not angular):

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2}, \quad n = 1, 2, 3, 4, \ldots$$

Bohr radius:

$$a_0 = -\frac{\varepsilon_0^2 h^2}{\pi m_e e^2}, \quad a_0 = 0.529 \times 10^{-10}\, m$$



Energy taking Bohr radius into account:

$$E_n = -\frac{e^4}{8\pi\varepsilon_0 a_0 n^2} = -\frac{2.179\times 10^{-18} J}{n^2} = -\frac{13.60 eV}{n^2}, \quad n = 1, 2, 3, 4, \ldots$$

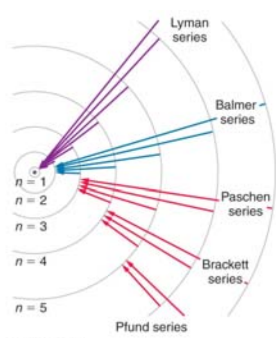
Hydrogen Atom: Atomic Emission Spectra

Experimental frequencies of H atom emission spectra:

$$\nu = \left| \frac{1}{h}\left(E_{initial} - E_{final}\right) \right|$$

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2}, \quad n = 1, 2, 3, 4, \ldots$$

$$\nu = \left| \frac{\mu e^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{n_{initial}^2} - \frac{1}{n_{final}^2}\right) \right|$$



$$\mu = \frac{m_e m_p}{m_e + m_p}$$

Reduced mass

$$\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$$

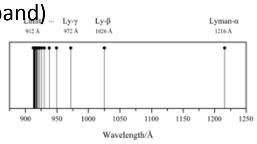
Wave number

$$\frac{m_e e^4}{8\varepsilon_0^2 h^3 c} = 109,677.581\ cm^{-1}$$

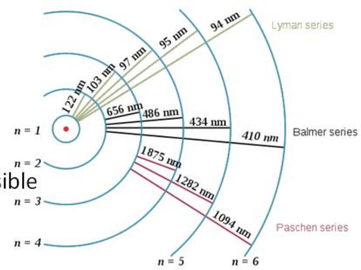
Rydberg constant

Hydrogen Atom: Atomic Emission Spectra

Lyman series (n'=1, UV band)



Balmer series (n'=2, visible band)



Paschen series (n' = 3, IR band)
Brackett series (n' = 4)
Pfund series (n' = 5)
Humphreys series (n' = 6)

Hydrogen Atom: Eigenvalues and Eigenfunctions of Total Energy

Eigenfunctions:

$$\psi_{n,l,m_l}(r,\theta,\phi) = \underbrace{R_{nl}(r)}_{\text{radial}}\underbrace{\left(\Theta(\theta)\Phi(\phi)\right)_{n,l,m_l}}_{\text{Spherical harmonics}} = R_{nl}(r)Y_l^{m_l}(\theta,\phi)$$

Quantum numbers:

$$n = 1,\ 2,\ 3,\ 4,\ \ldots$$
$$l = 0,\ 1,\ 2,\ 3,\ \ldots,\ n-1$$
$$m_l = 0,\ \pm1,\ \pm2,\ \pm3,\ \ldots,\ \pm l$$

Hydrogen Atom: Orbitals

Eigenfunctions:

$$n=1,\ l=0,\ m_l=0\quad \psi_{100}(r)=\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}e^{-r/a_0}$$

$$n=2,\ l=0,\ m_l=0\quad \psi_{200}(r)=\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$$

$$n=2,\ l=1,\ m_l=0\quad \psi_{210}(r,\theta,\phi)=\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\cos\theta$$

$$n=2,\ l=1,\ m_l=\pm1\quad \psi_{211}(r,\theta,\phi)=\frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\sin\theta e^{\pm\phi}$$

$$n=3,\ l=2,\ m_l=0\quad \psi_{320}(r,\theta,\phi)=\frac{1}{81\sqrt{6\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0^2}\right)e^{-r/3a_0}\left(3\cos^2\theta-1\right)$$

l=0 – s orbital
l=1 – p orbitals
l=2 – d orbitals
l=3 – f orbitals

Degeneracy in energy levels: n^2

Hydrogen Atom: Orbitals

To visualize orbitals- normalize the eigenfunctions and make linear combinations

$$N^2\int \psi^*(\tau)\psi(\tau)\,d\tau=1;\qquad N^2\int_0^{\pi}\sin\theta\,d\theta\int_0^{2\pi}d\phi\int_0^{\infty}\psi^*_{n,l,m_l}(R,\theta,\phi)\,\psi_{n,l,m_l}(R,\theta,\phi)=1$$

$$\psi_{2p_x}(r,\theta,\phi)=\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\sin\theta\cos\phi$$

$$\psi_{2p_y}(r,\theta,\phi)=\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\sin\theta\sin\phi$$

$$\psi_{2p_z}(r,\theta,\phi)=\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\cos\phi$$

$$\psi_{3p_x}(r,\theta,\phi)=\frac{\sqrt{2}}{81\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6\frac{r}{a_0}-\frac{r^2}{a_0^2}\right)e^{-r/3a_0}\sin\theta\cos\phi$$

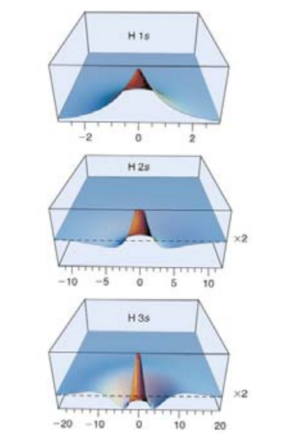
$$\psi_{3p_y}(r,\theta,\phi)=\frac{\sqrt{2}}{81\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6\frac{r}{a_0}-\frac{r^2}{a_0^2}\right)e^{-r/3a_0}\sin\theta\sin\phi$$

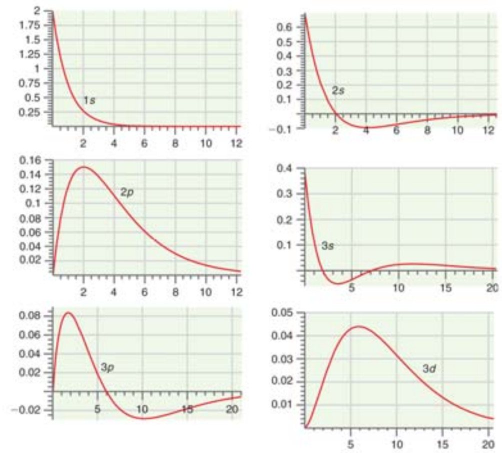
$$\psi_{3p_z}(r,\theta,\phi)=\frac{\sqrt{2}}{81\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6\frac{r}{a_0}-\frac{r^2}{a_0^2}\right)e^{-r/3a_0}\cos\phi$$

Hydrogen Atom: Orbitals

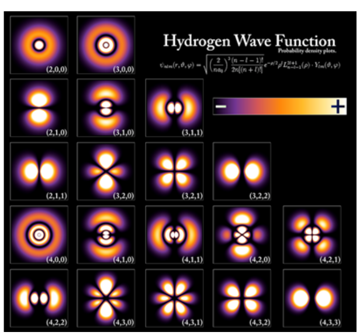
3D orbital contour plots

Radial wave function vs. r





Hydrogen Atom: Orbitals

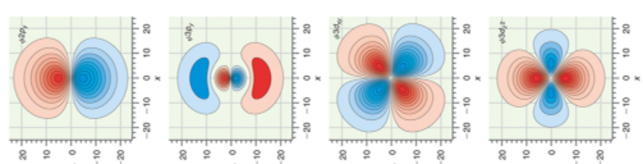


2D orbital contour plots:

R(r) - $n - l - 1$ nodal surfaces

$Y_l^m(\theta,\phi) - l$ nodal surfaces

R(r) $Y_l^m(\theta,\phi) - n - 1$ nodes
(same as in particle in the box and harmonic oscillator)



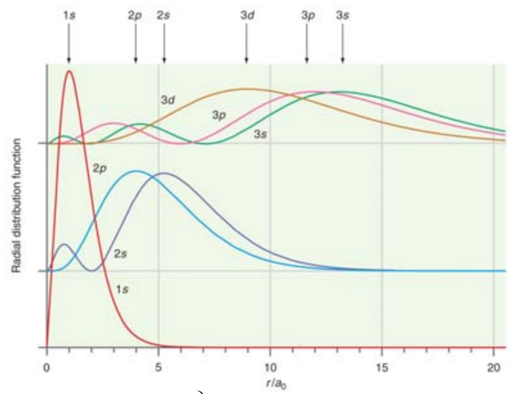
Hydrogen Atom: Radial Distribution Function

What is the probability of finding an electron at a particular value of r regardless of θ and ϕ?

Integrate probability density

$$\psi^2_{nlm_l}(r,\theta,\phi)\; r^2 \sin\theta \;\; dr \quad d\theta$$

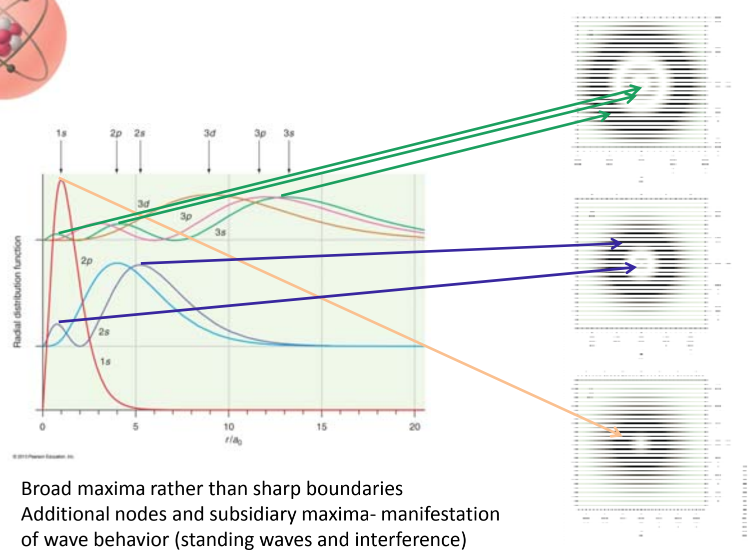
over all values of θ and ϕ



Radial distribution function:

$$P_{nl}(r)\,dr = \left\{ \int_0^{2\pi} d\phi \int_0^{\pi} \left[Y_l^{m_l}(\theta,\phi)\right]^* \left[Y_l^{m_l}(\theta,\phi)\right] \sin\theta\, d\theta \right\} r^2 R_{nl}^2(r)\,dr = r^2 R_{nl}^2(r)\,dr$$

Hydrogen Atom: The Validity of the Shell Model



- Broad maxima rather than sharp boundaries
- Additional nodes and subsidiary maxima- manifestation of wave behavior (standing waves and interference)