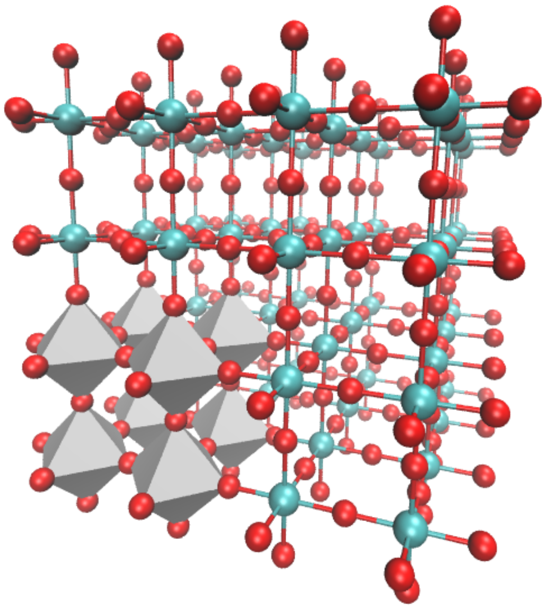
Solutions of Analytically Solvable Systems



Prof. Lee M. Thompson

Translational Motion

Unbound particle traveling in one dimension

- Potential can be set at zero

$$\hat{H} = \hat{K} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

- Time independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi \Rightarrow \frac{d^2}{dx^2}\psi = -\frac{2mE}{\hbar^2}\psi$$

- This is a second order differential equation where λ is imaginary
  - The general solution is

$$\psi = C\cos\left(\left\{\frac{2mE}{\hbar^2}\right\}^{\frac{1}{2}} x\right) + D\sin\left(\left\{\frac{2mE}{\hbar^2}\right\}^{\frac{1}{2}} x\right)$$

  - Energy of particle

$$k = \left\{\frac{2mE}{\hbar^2}\right\}^{\frac{1}{2}} \rightarrow E = \frac{k^2\hbar^2}{2m}$$

- No boundary conditions for a free particle
- Wavefunction corresponds to uniform probability distribution
- Energy of the particle is not quantized as particle is not bound

Translational Motion

Unbound particle traveling in one dimension

- Momentum of particle prepared in state where *D=0*

$$\hat{p}\psi = -i\hbar\frac{d}{dx}\psi = -i\hbar\frac{d}{dx}(C\cos(kx)) = ik\hbar C\sin(kx)$$

- Wavefunction is not an eigenfunction of momentum but using Euler identity can be written

$$\psi = \frac{1}{2}Ce^{ikx} + \frac{1}{2}Ce^{-ikx}$$

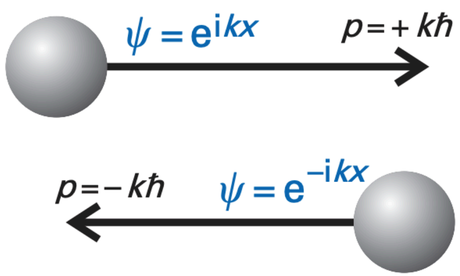
- To understand the significance, look at each term separately

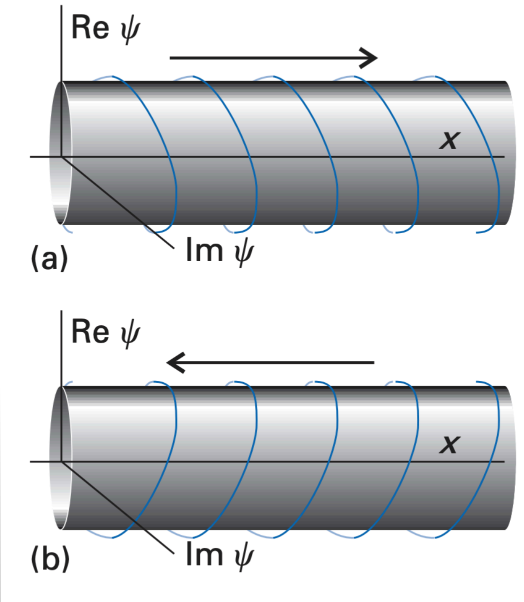
$$\hat{p}\psi = -i\hbar\frac{d}{dx}\left(\frac{1}{2}Ce^{ikx}\right) = \hbar k\frac{1}{2}Ce^{ikx} = \hbar k\psi$$

$$\hat{p}\psi = -i\hbar\frac{d}{dx}(\frac{1}{2}Ce^{-ikx}) = -\hbar k\frac{1}{2}Ce^{-ikx} = -\hbar k\psi$$

- Wavefunction is superposition of particle traveling with equal magnitude momentum in opposite directions

$$\psi = Ae^{ikx} + Be^{-ikx}$$





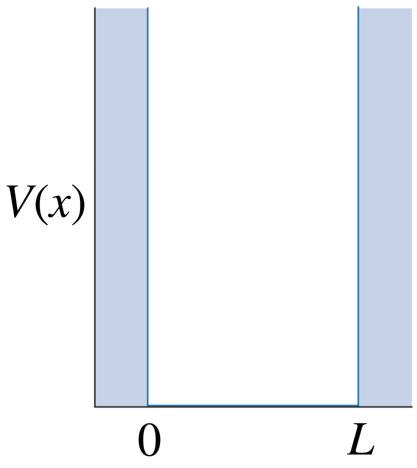
Translational Motion

Particle traveling in one dimensional box

- Potential constraint added to free particle

$$\hat{H} = \hat{K} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \qquad V(x) = \begin{cases} 0 & \text{for } 0 \le x \le L \\ \infty & \text{otherwise} \end{cases}$$

- Due to infinite potential, wavefunction is zero at boundaries and Hamiltonian within box is that of free particle
- Thus wavefunction is the general solution but now with boundary conditions to satisfy $\psi(0)=0$ and $\psi(L) = 0$



$$\psi = C\cos\left(\left\{\frac{2mE}{\hbar^2}\right\}^{\frac{1}{2}} x\right) + D\sin\left(\left\{\frac{2mE}{\hbar^2}\right\}^{\frac{1}{2}} x\right)$$

$$\psi(0) = C = 0 \qquad \psi(L) = D\sin\left(\left\{\frac{2mE}{\hbar^2}\right\}^{\frac{1}{2}} L\right) = 0$$

- Only nontrivial solution to $\psi(L)=0$ is $\sin(kL)=0$ which is true at $kL=n\pi$, where n=1,2,3… (n=0 is trivial)

$$\psi(x) = D\sin\left(\frac{n\pi}{L}x\right) \qquad k = \left\{\frac{2mE}{\hbar^2}\right\}^{\frac{1}{2}} \Rightarrow E = \frac{k^2\hbar^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

Translational Motion

Particle traveling in one dimensional box

- Now we need to solve for the constant D
- Use the property of wavefunction normalization

$$\psi(x) = D\sin\left(\frac{n\pi}{L}x\right) \qquad \int_0^L \psi(x)^*\psi(x) = 1$$

Recall trig identities

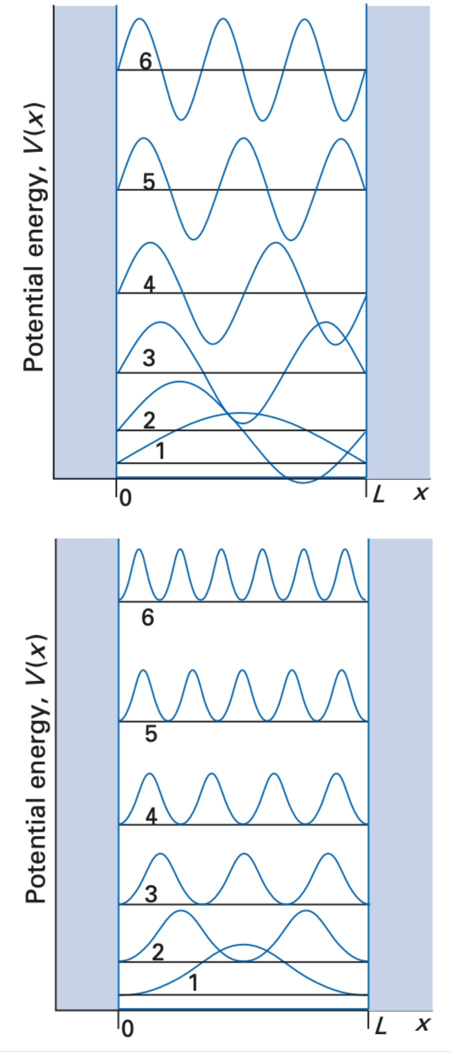
$$\int_0^L D^2\sin^2\left(\frac{n\pi}{L}x\right) = 1 \qquad D^2\int_0^L \frac{1}{2} - \frac{1}{2}\cos\left(\frac{2n\pi}{L}x\right) = 1$$

$$D^2\left[\frac{1}{2}x - \frac{L}{4\pi n}\sin\left(\frac{2n\pi}{L}x\right)\right]_0^L = 1$$

$$D^2\left(\frac{1}{2}L - \frac{L}{4\pi n}\sin(2n\pi) - \frac{1}{2}0 - \frac{L}{4\pi n}\sin\left(\frac{2n\pi}{L}0\right)\right) = 1$$

$$\frac{1}{2}D^2L = 1 \qquad D = \sqrt{\frac{2}{L}}$$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) \qquad E_n = \frac{n^2h^2}{8mL^2}$$



Translational Motion

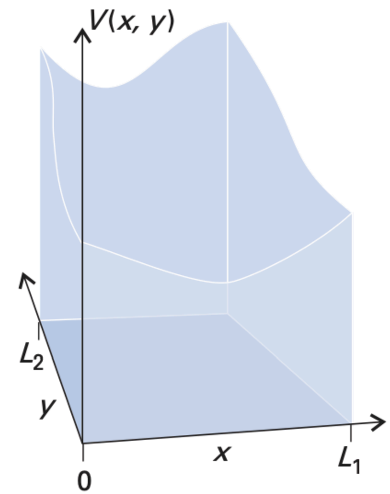
Particle traveling in two dimensional box

- Potential constraint added to free particle

$$\hat{H} = \hat{K} + \hat{V} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + V(x) \qquad V(x) = \begin{cases} 0 & \text{for } 0 \le x \le L \text{ and } 0 \le y \le L \\ \infty & \text{otherwise} \end{cases}$$

- Again, wavefunction is zero at boundaries and Schrödinger equation in differential equation form is

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi = -\frac{2mE}{\hbar^2}\psi$$



- Try separation of variables to solve the equation (as we did for space and time in the last lecture) $\psi(x, y) = \psi_x(x)\psi_y(y)$

$$\psi_y(y)\frac{\partial^2\psi_x(x)}{\partial x^2} + \psi_x(x)\frac{\partial^2\psi_y(y)}{\partial y^2} = -\frac{2mE}{\hbar^2}\psi_x(x)\psi_y(y)$$

$$\frac{1}{\psi_x(x)}\frac{\partial^2\psi_x(x)}{\partial x^2} + \frac{1}{\psi_y(y)}\frac{\partial^2\psi_y(y)}{\partial y^2} = -\frac{2mE}{\hbar^2}$$

$$\frac{\partial^2}{\partial x^2}\psi_x(x) = -\frac{2mE_x}{\hbar^2}\psi_x(x) \qquad \frac{\partial^2}{\partial y^2}\psi_y(y) = -\frac{2mE_y}{\hbar^2}\psi_y(y) \qquad E_x + E_y = E$$

Translational Motion

Particle traveling in two dimensional box

- Separated solutions are the same as particle in one dimensional box so using $\psi(x,y)=\psi_x(x)\psi_y(y)$ and $E_x+E_y=E$

$$\psi(x,y)=\sqrt{\frac{2}{L_x}}\sin\left(\frac{n_x\pi}{L_x}x\right)\sqrt{\frac{2}{L_y}}\sin\left(\frac{n_y\pi}{L_y}y\right)=\frac{2}{\sqrt{L_xL_y}}\sin\left(\frac{n_x\pi}{L_x}x\right)\sin\left(\frac{n_y\pi}{L_y}y\right)$$

$$E_{n_xn_y}=\frac{n_x^2h^2}{8mL_x^2}+\frac{n_y^2h^2}{8mL_y^2}\quad n_x=1,2,3\ldots\quad n_y=1,2,3\ldots$$

- Systematic degeneracy occurs when $L_x=L_y$

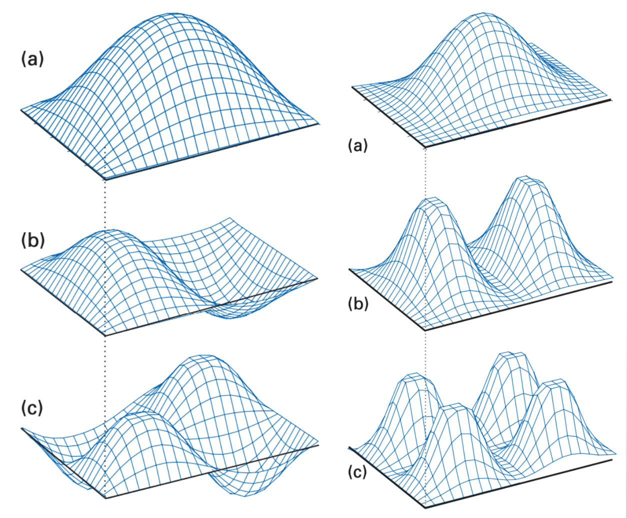
$$E_{n_xn_y}=\frac{h^2}{8mL^2}(n_x^2+n_y^2)$$

e.g.

$$E_{2,1}=E_{1,2}=\frac{5h^2}{8mL^2}$$

corresponding to rotation of $\pi/2$

- If $L_x \neq L_y$ degeneracy is still possible but it is **accidental**



Vibrational Motion

Particle traveling in harmonic potential

- Potential is that of a parabola

$$\hat{H} = \hat{K} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \qquad V(x) = \frac{1}{2}kx^2$$

- The Schrödinger equation can be written

$$\frac{d^2}{dx^2}\psi = -\frac{2m}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi$$

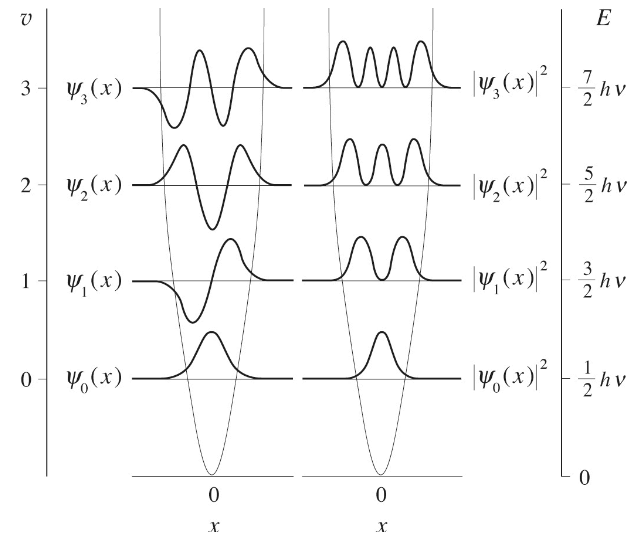
- Right-hand side not a constant so solution more difficult, with solutions

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\omega \qquad \nu = 0,1,2\ldots \qquad \omega = \sqrt{\frac{k}{m}}$$

$$\psi_\nu(x) = N_\nu H_\nu \alpha^{\frac{1}{2}} x e^{-\frac{\alpha x^2}{2}} \qquad N_\nu = \frac{1}{\sqrt{2^\nu \nu!}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \qquad \alpha = \left(\frac{km}{\hbar^2}\right)^{\frac{1}{2}}$$

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} \qquad \psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}}(2\alpha x^2 - 1)e^{-\frac{\alpha x^2}{2}}$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{4}} x e^{-\frac{\alpha x^2}{2}} \qquad \psi_3(x) = \left(\frac{\alpha^3}{9\pi}\right)^{\frac{1}{4}}(2\alpha x^3 - 3x)e^{-\frac{\alpha x^2}{2}}$$



ν	$H_\nu(z)$
0	1
1	$2z$
2	$4z^2 - 2$
3	$8z^3 - 12z$
4	$16z^4 - 48z^2 + 12$
5	$32z^5 - 160z^3 + 120z$
6	$64z^6 - 480z^4 + 720z^2 - 120$
7	$128z^7 - 1344z^5 + 3360z^3 - 1680z$
8	$256z^8 - 3584z^6 + 13440z^4 - 13440z^2 + 1680$

Rotational Motion

Particle traveling on a ring

- Potential is zero on the ring

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \qquad \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$$

- Circular symmetry so easier to transform to use polar coordinates

$$x = r\cos\phi \qquad y = r\sin\phi \qquad \hat{H} = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial \phi^2} \qquad I = mr^2 \qquad \frac{\partial^2}{\partial \phi^2}\Phi = -\frac{2IE}{\hbar^2}\Phi$$

- General solution can be constructed

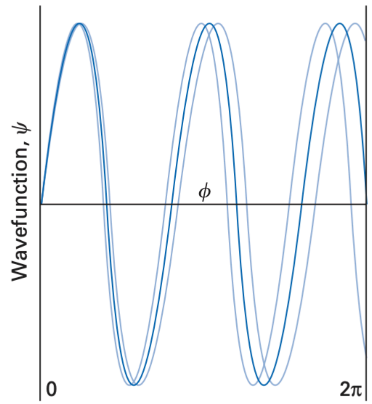
$$\Phi = C\cos\left(\sqrt{\frac{2IE}{\hbar^2}}\phi\right) + D\sin\left(\sqrt{\frac{2IE}{\hbar^2}}\phi\right) \qquad m_l = \sqrt{\frac{2IE}{\hbar^2}}$$

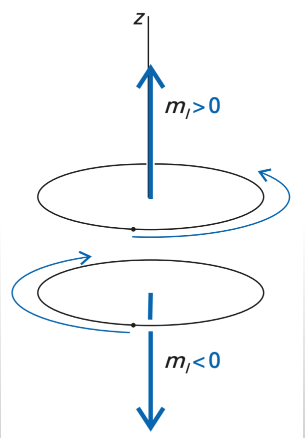
- Boundary conditions stated using periodicity of ring

$$C\cos(m_l\phi) + D\sin(m_l\phi) = C\cos(m_l(\phi + 2\pi)) + D\sin(m_l(\phi + 2\pi))$$

- Boundary conditions satisfied so long as m_l is integer

$$E = \frac{m_l^2\hbar^2}{2I} \qquad m_l = 0, \pm 1, \pm 2\ldots$$





Rotational Motion

Particle traveling on a ring

- Normalization conditions establish unknown constants

$$\int_0^{2\pi} \Phi^*\Phi d\phi = \int_0^{2\pi} C^2\cos^2(m_l\phi) + 2CD\cos(m_l\phi)\sin(m_l\phi) + D^2\sin^2(m_l\phi)d\phi = 1$$

$$= \int_0^{2\pi} C^2\frac{1}{2}(1+\cos(2m_l\phi)) + CD\sin(2m_l\phi) + D^2\frac{1}{2}(1-\cos(2m_l\phi))d\phi$$

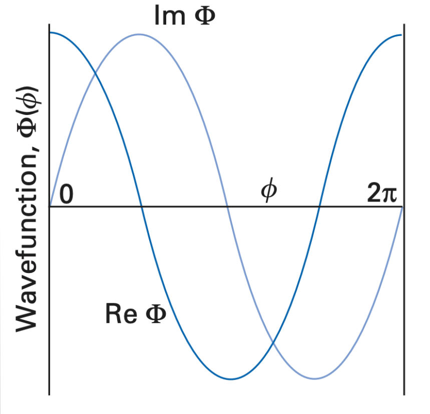
$$= \left[\frac{C^2}{2}\left(\phi + \frac{1}{2m_l}\sin(2m_l\phi)\right) - \frac{CD}{2m_l}\cos(2m_l\phi) + \frac{D^2}{2}\left(\phi - \frac{1}{2m_l}\sin(2m_l\phi)\right)\right]_0^{2\pi}$$

$$= C^2 + D^2 = \frac{1}{\pi}$$

- Setting $C^2 = D^2$ and recalling that D must be complex

$$2C^2 = \frac{1}{\pi} \Rightarrow C = \left(\frac{1}{2\pi}\right)^{\frac{1}{2}} \Rightarrow D = \pm\left(\frac{1}{2\pi}\right)^{\frac{1}{2}} i$$

$$\Phi = \left(\frac{1}{2\pi}\right)^{\frac{1}{2}}\cos(m_l\phi) \pm \left(\frac{1}{2\pi}\right)^{\frac{1}{2}} i\sin(m_l\phi) = \left(\frac{1}{2\pi}\right)^{\frac{1}{2}} e^{\pm i m_l\phi}$$



Rotational Motion

Particle traveling on a sphere

- Potential is zero on the ring

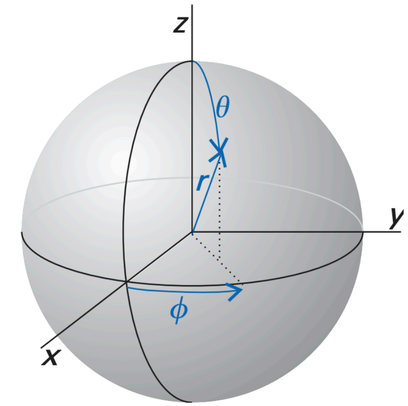
$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m}\hat{\nabla}^2$$

- Use spherical polar coordinates to take advantage of symmetry

$$x = r\cos\theta\sin\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

$$\hat{\nabla}^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2$$

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$



- As fixed radius, only need to account for angular variation

$$\hat{H} = -\frac{\hbar^2}{2I}\Lambda^2 \qquad \Lambda^2\psi = -\frac{2IE}{\hbar^2}\psi$$

- Solution to this equation are the spherical harmonics

$$\Lambda^2 Y(\theta,\phi) = -l(l+1)Y(\theta,\phi)$$

$$l = 0,1,2\ldots \qquad m_l = -l, -l+1,\ldots l$$

l	m_l	$Y_{lm_l}(\theta,\phi)$
0	0	$1/2\pi^{1/2}$
1	0	$\frac{1}{2}(3/\pi)^{1/2}\cos\theta$
	±1	$\mp(3/2\pi)^{1/2}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}(5/\pi)^{1/2}(3\cos^2\theta - 1)$
	±1	$\mp\frac{1}{2}(15/2\pi)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$
	±2	$\frac{1}{4}(15/2\pi)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}(7/\pi)^{1/2}(2 - 5\sin^2\theta)\cos\theta$
	±1	$\mp\frac{1}{8}(21/\pi)^{1/2}(5\cos^2\theta - 1)\sin\theta\, e^{\pm i\phi}$
	±2	$\frac{1}{4}(105/2\pi)^{1/2}\cos\theta\sin^2\theta\, e^{\pm 2i\phi}$
	±3	$\mp\frac{1}{8}(35/\pi)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$

Rotational Motion

Particle traveling on a sphere

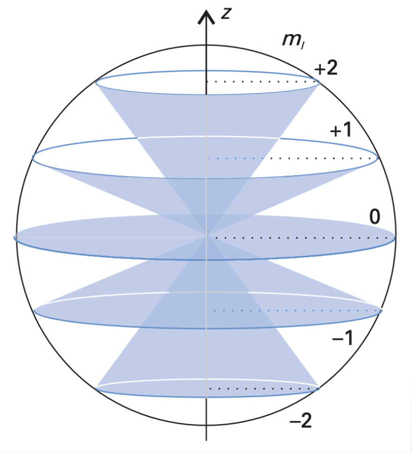
- Comparing the two equations we can determine the energy

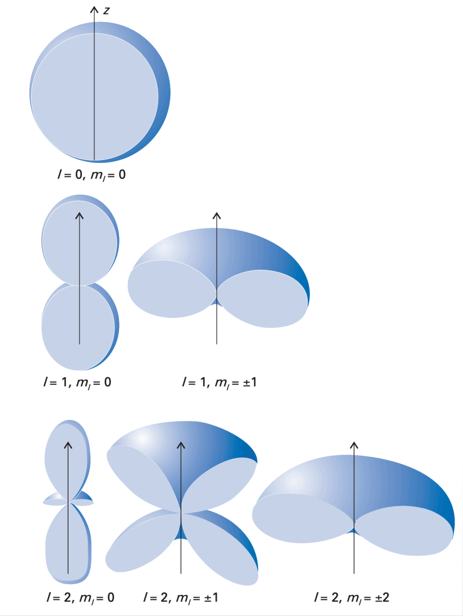
$$\Lambda^2\psi = -\frac{2IE}{\hbar^2}\psi \qquad \Lambda^2 Y(\theta,\phi) = -l(l+1)Y(\theta,\phi) \qquad E_{l,m_l} = l(l+1)\frac{\hbar^2}{2I}$$

- The energy is independent of m_l so as there are $2l+1$ values of m_l for a given value of l, each state is $2l+1$ degenerate
- $Y_{lm_l}(\theta,\phi) = \Theta_{lm_l}(\theta)\Phi_{m_l}(\phi)$
- Rotational energy in classical physics is related to moment of inertia and angular velocity

$$E = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$$

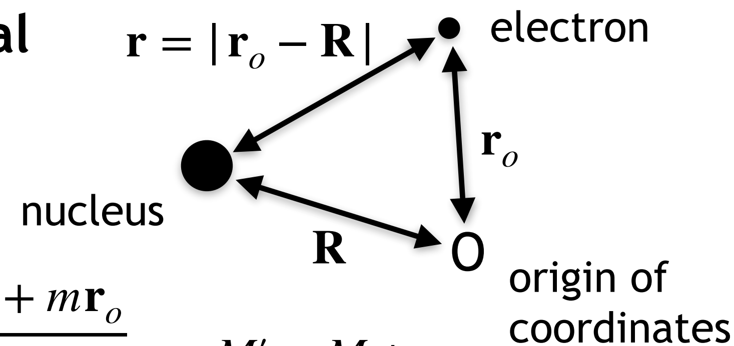
- Where $L = I\omega$ is the angular momentum
- Therefore $L = \sqrt{l(l+1)}\hbar$
- l is the angular momentum quantum number
- $\hat{l}_z Y_{lm_l} = m_l\hbar Y_{lm_l}$ shows m_l is space quantization (see next chapter)





Hydrogen Atoms

Particle traveling in a Coulombic potential



- Hamiltonian for electron-nucleus system

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_o} - \frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r}$$

- Change to center-of-mass coordinates

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} - \frac{\hbar^2}{2M'}\nabla^2_{\mathbf{R}'} - \frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r} \qquad \mathbf{R}' = \frac{M\mathbf{R} + m\mathbf{r}_o}{M'} \qquad M' = M + m$$

- We have terms that depend on translation which can be ignored but unlike for particle on sphere need to consider radial terms

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} - \frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r} \qquad \left(-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} - \frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r}\right)\psi = E\psi \qquad \hat{\nabla}^2_{\mathbf{r}} = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2$$

$$\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2 + \frac{Z\mu e^2}{2\hbar^2\pi\varepsilon_0 r}\right)\psi = -\frac{2\mu E}{\hbar^2}\psi$$

- We can separate variables in wavefunction using $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$

Hydrogen Atoms

Particle traveling in a Coulombic potential

$$\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2 + \frac{Z\mu e^2}{2\hbar^2\pi\varepsilon_0 r}\right)\psi = -\frac{2\mu E}{\hbar^2}\psi \qquad \psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

$$\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2 + \frac{Z\mu e^2}{2\hbar^2\pi\varepsilon_0 r}\right)R(r)Y(\theta,\phi) = -\frac{2\mu E}{\hbar^2}R(r)Y(\theta,\phi)$$

$$Y(\theta,\phi)\frac{1}{r}\frac{\partial^2}{\partial r^2}rR(r) + R(r)\frac{1}{r^2}\Lambda^2 Y(\theta,\phi) + \frac{Z\mu e^2}{2\hbar^2\pi\varepsilon_0 r}R(r)Y(\theta,\phi) = -\frac{2\mu E}{\hbar^2}R(r)Y(\theta,\phi)$$

$$\frac{1}{rR(r)}\frac{\partial^2}{\partial r^2}rR(r) + \frac{1}{Y(\theta,\phi)}\frac{1}{r^2}\Lambda^2 Y(\theta,\phi) + \frac{Z\mu e^2}{2\hbar^2\pi\varepsilon_0 r} = -\frac{2\mu E}{\hbar^2} \qquad u = rR(r)$$

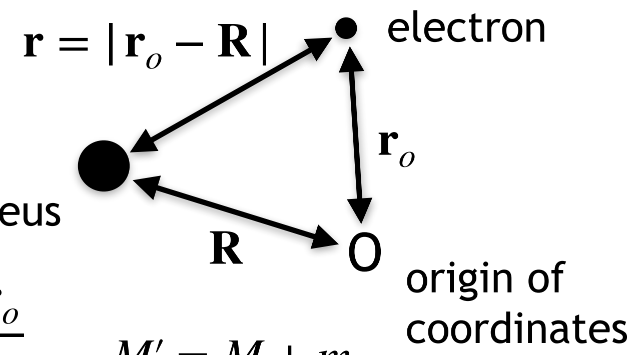
$$\frac{\partial^2}{\partial r^2}u + \frac{1}{Y(\theta,\phi)}\frac{1}{r^2}\Lambda^2 Y(\theta,\phi)u + \frac{Z\mu e^2}{2\hbar^2\pi\varepsilon_0 r}u = -\frac{2\mu E}{\hbar^2}u \qquad \Lambda^2 Y(\theta,\phi) = -l(l+1)Y(\theta,\phi)$$

$$\frac{\partial^2}{\partial r^2}u - \frac{1}{r^2}l(l+1)u + \frac{Z\mu e^2}{2\hbar^2\pi\varepsilon_0 r}u = -\frac{2\mu E}{\hbar^2}u$$

$$\frac{\partial^2}{\partial r^2}u - \left(\frac{2\mu}{\hbar^2}\right)V_{eff}u = -\frac{2\mu E}{\hbar^2}u \qquad V_{eff=} = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Hydrogen Atoms

Particle traveling in a Coulombic potential



- Hamiltonian for electron-nucleus system

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- Change to center-of-mass coordinates

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} - \frac{\hbar^2}{2M'}\nabla^2_{\mathbf{R}'} - \frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r} \qquad \mathbf{R}' = \frac{M\mathbf{R} + m\mathbf{r}_o}{M'} \qquad M' = M + m$$

- We have terms that depend on translation which can be ignored but unlike for particle on sphere need to consider radial terms

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} - \frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r} \qquad \left(-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} - \frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r}\right)\psi = E\psi \qquad \hat{\nabla}^2_{\mathbf{r}} = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2$$

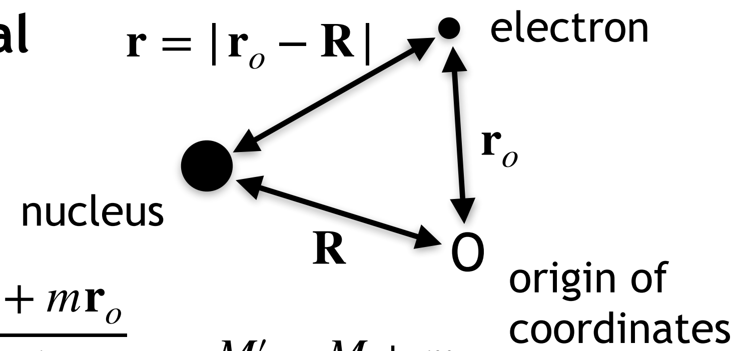
$$\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2 + \frac{Z\mu e^2}{2\hbar^2\pi\varepsilon_0 r}\right)\psi = -\frac{2\mu E}{\hbar^2}\psi$$

- We can separate variables in wavefunction using $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ which after manipulations gives

$$\frac{\partial^2}{\partial r^2}u - \left(\frac{2\mu}{\hbar^2}\right)V_{eff}u = -\frac{2\mu E}{\hbar^2}u \qquad V_{eff=} = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \qquad u = rR(r)$$

Hydrogen Atoms

Particle traveling in a Coulombic potential



- Hamiltonian for electron-nucleus system

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_o} - \frac{Z}{4\pi\varepsilon_0}\frac{e^2}{d}$$

- Change to center-of-mass coordinates

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} - \frac{\hbar^2}{2M'}\nabla^2_{\mathbf{R}'} - \frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r} \qquad \mathbf{R}' = \frac{M\mathbf{R} + m\mathbf{r}_o}{M'} \qquad M' = M + m$$

- We have terms that depend on translation which can be ignored but unlike for particle on sphere need to consider radial terms

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} - \frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r} \qquad \left(-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} - \frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r}\right)\psi = E\psi \qquad \hat{\nabla}^2_{\mathbf{r}} = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2$$

$$\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2 + \frac{Z\mu e^2}{2\hbar^2\pi\varepsilon_0 r}\right)\psi = -\frac{2\mu E}{\hbar^2}\psi$$

Coulombic force

Repulsive term (angular momentum)

- We can separate variables in wavefunction using $\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$ which after manipulations gives

$$\frac{\partial^2}{\partial r^2}u - \left(\frac{2\mu}{\hbar^2}\right)V_{eff}u = -\frac{2\mu E}{\hbar^2}u \qquad V_{eff=} = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \qquad u = rR(r)$$

Hydrogen Atoms

Particle traveling in a Coulombic potential

- Solving the resulting equation gives solutions of the radial part (associated Laguerre functions) with energy a function of principle quantum number **n**

$$E_n = -\left(\frac{Z\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2}\right)\frac{1}{n^2}$$

n	l	Orbital	$R_{nl}(r)$
1	0	1s	$(Z/a)^{3/2}2e^{-\rho/2}$
2	0	2s	$(Z/a)^{3/2}(1/8)^{1/2}(2-\rho)e^{-\rho/2}$
	1	2p	$(Z/a)^{3/2}(1/24)^{1/2}\rho e^{-\rho/2}$
3	0	3s	$(Z/a)^{3/2}(1/243)^{1/2}(6-6\rho+\rho^2)e^{-\rho/2}$
	1	3p	$(Z/a)^{3/2}(1/486)^{1/2}(4-\rho)\rho e^{-\rho/2}$
	2	3d	$(Z/a)^{3/2}(1/2430)^{1/2}\rho^2 e^{-\rho/2}$

$$\rho = \frac{2Z}{na}r \qquad a = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

n	l	m_l	Name
1	0	0	1s
2	0	0	2s
2	1	-1 0 1	2p
3	0	0	3s
3	1	-1 0 1	3p
3	2	-2 -1 0 1 2	3d
4	0	0	4s
4	1	-1 0 1	4p
4	2	-2 -1 0 1 2	4d
4	3	-3 -2 -1 0 1 2 3	4f

Hydrogen Atoms

Particle traveling in a Coulombic potential

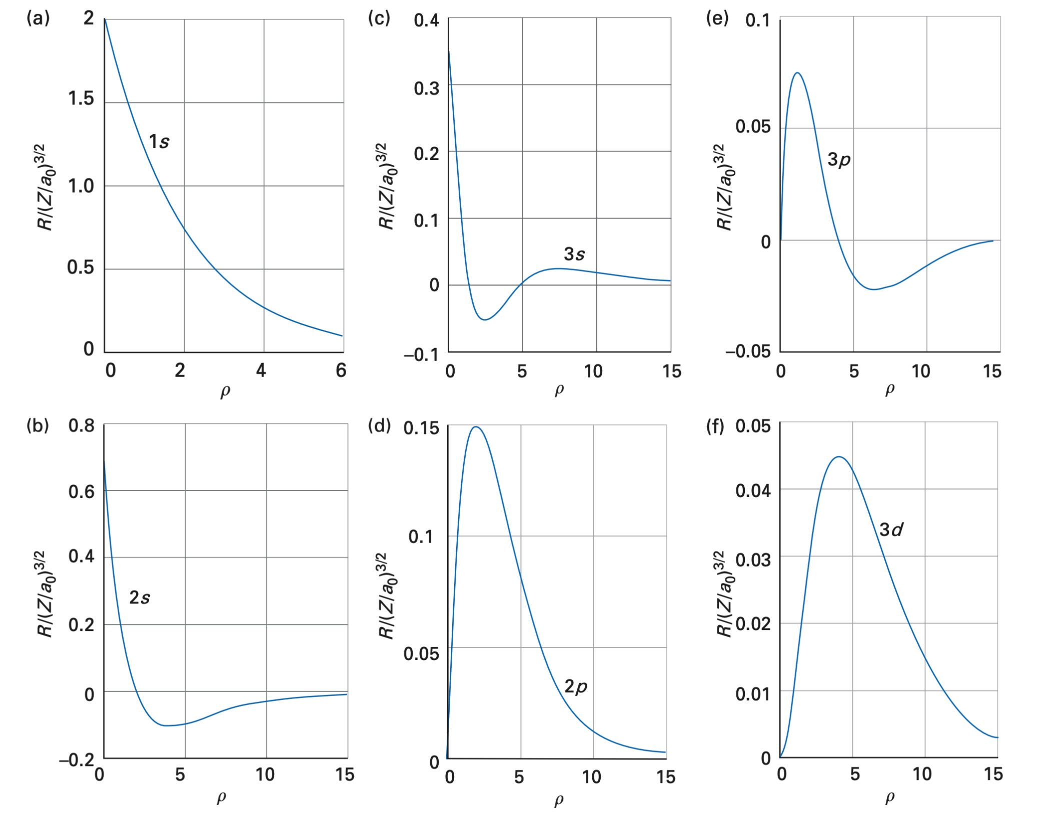
- n is the principle quantum number (n=1,2,…)
  - Specifies the energy and controls range of acceptable values of l (l=0,1,…,n-1)
  - Specifies number of orbitals with principle quantum number n (n^2)
  - Specifies the total number of radial and angular nodes (n-1)

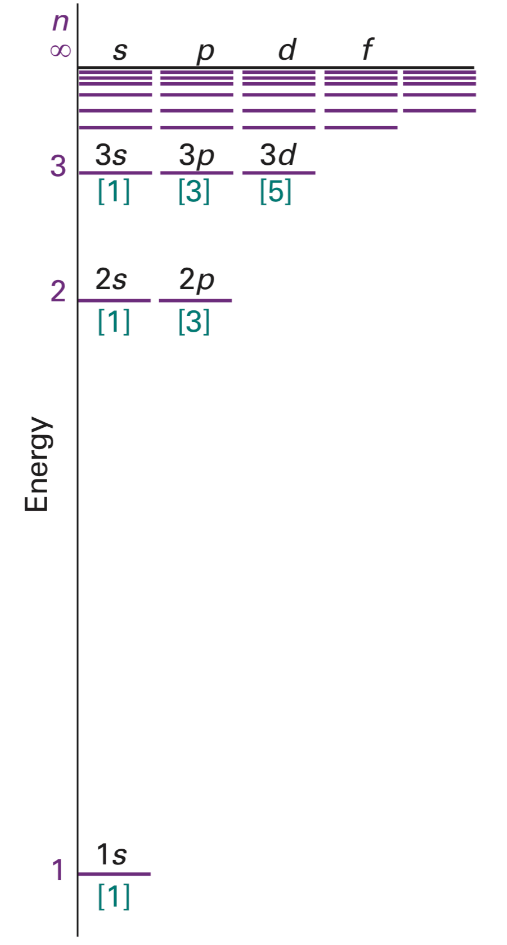
- l is the orbital angular momentum quantum number (l=0,1,…,n-1)
  - Specifies orbital angular momentum ($\sqrt{l(l+1)}\hbar$)
  - Specifies number of orbitals with given n and l (2l+1)
  - Specifies the number of angular nodes (l) and radial nodes (n-l-1)

- ml is the magnetic quantum number
  - Specifies the component of angular momentum along the z axis ($m_l\hbar$)
  - Specifies a one-electron wavefunction for a given n, l and ml,

Hydrogen Atoms

Particle traveling in a Coulombic potential





Summary

- Translational Motion
  - Free particle
  - Particle in one-dimensional box
  - Particle in two-dimensional box
- Vibrational Motion
  - Harmonic oscillator
- Rotational Motion
  - Particle on a ring
  - Particle on a sphere
- Hydrogen atoms
  - Pseudo one-body problems