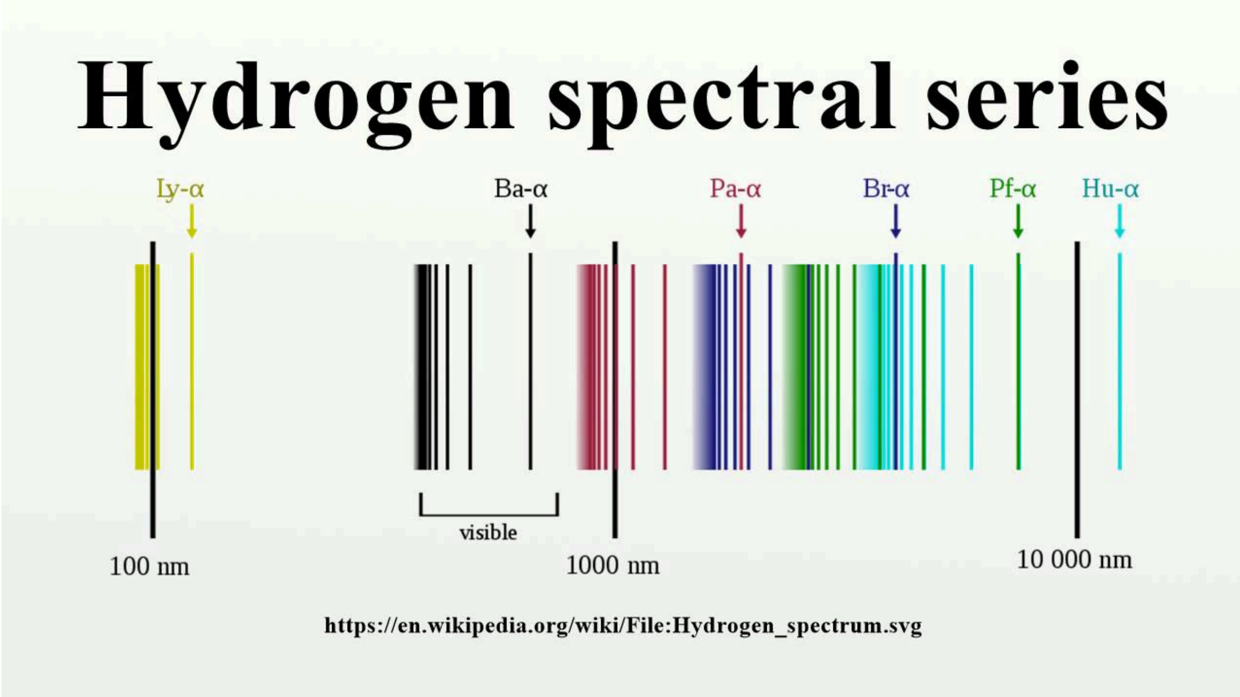
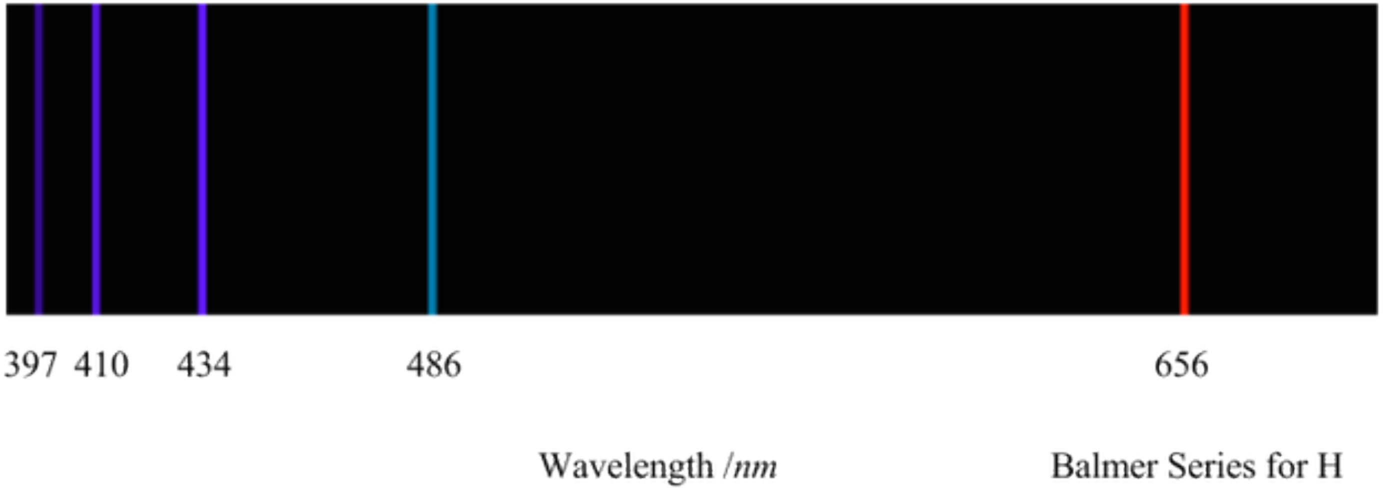
one-electron atoms

2018/3/15



https://franklyandjournal.wordpress.com/2016/07/18/hydrogen-spectrum/

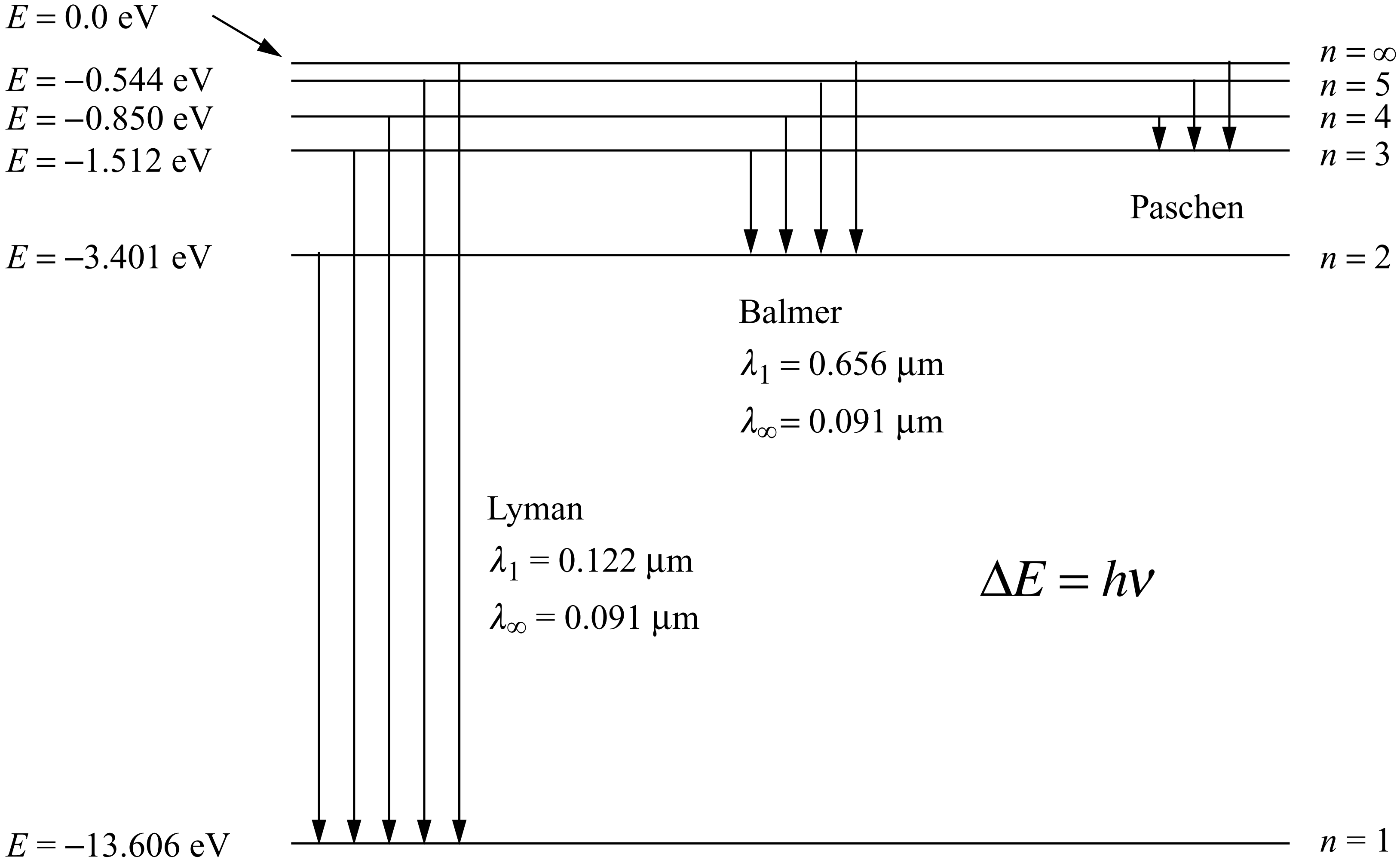


$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

Rydberg constant

$$R_H = 10967757.6 \pm 1.2\ \mathrm{m}^{-1}$$

Photon emission spectra of excited hydrogen

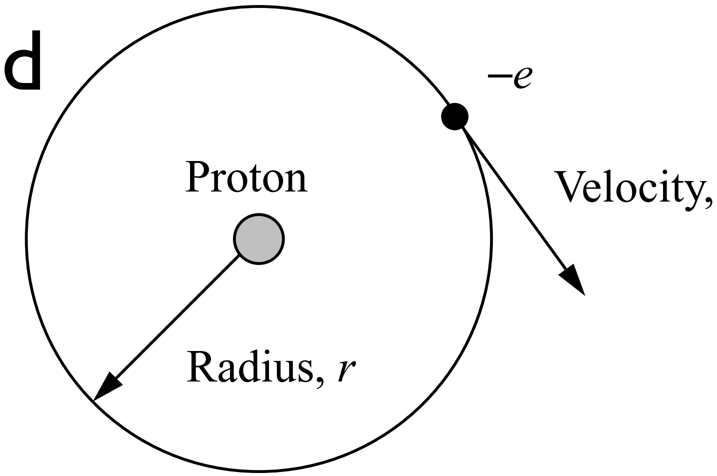


Quantization of angular momentum

- Bohr postulate, 1913
- for circular orbit, angular momentum takes on values of

$$L = n\hbar$$

- Atoms are observed stable and the total energy remains constant



Bohr's model

- The forces are balanced $$\frac{Ze^2}{4\pi\varepsilon_0 r^2} = m\frac{v^2}{r}$$

- apply quantization condition $$mvr = n\hbar$$

$$\frac{Ze^2}{4\pi\varepsilon_0} = mv^2 r = \frac{n^2\hbar^2}{mr}$$

- orbit radius

$$r = 4\pi\varepsilon_0 \frac{n^2\hbar^2}{mZe^2}$$

$$r = 5.3\times10^{-11}\,\mathrm{m} \quad (Z = 1)$$ Bohr radius

Bohr's model

- energy of circular orbits

$$K = \frac{1}{2} m v^2$$

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r} = -2K$$

- Quantization of energy

$$E = K + V = -\frac{V}{2} = -\frac{Ze^2}{8\pi\varepsilon_0 r} = -\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2}$$

atomic structure

- A dimensionless "magic" constant relating h, c, e and ε_0

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \sim \frac{1}{137}$$

- in terms of α

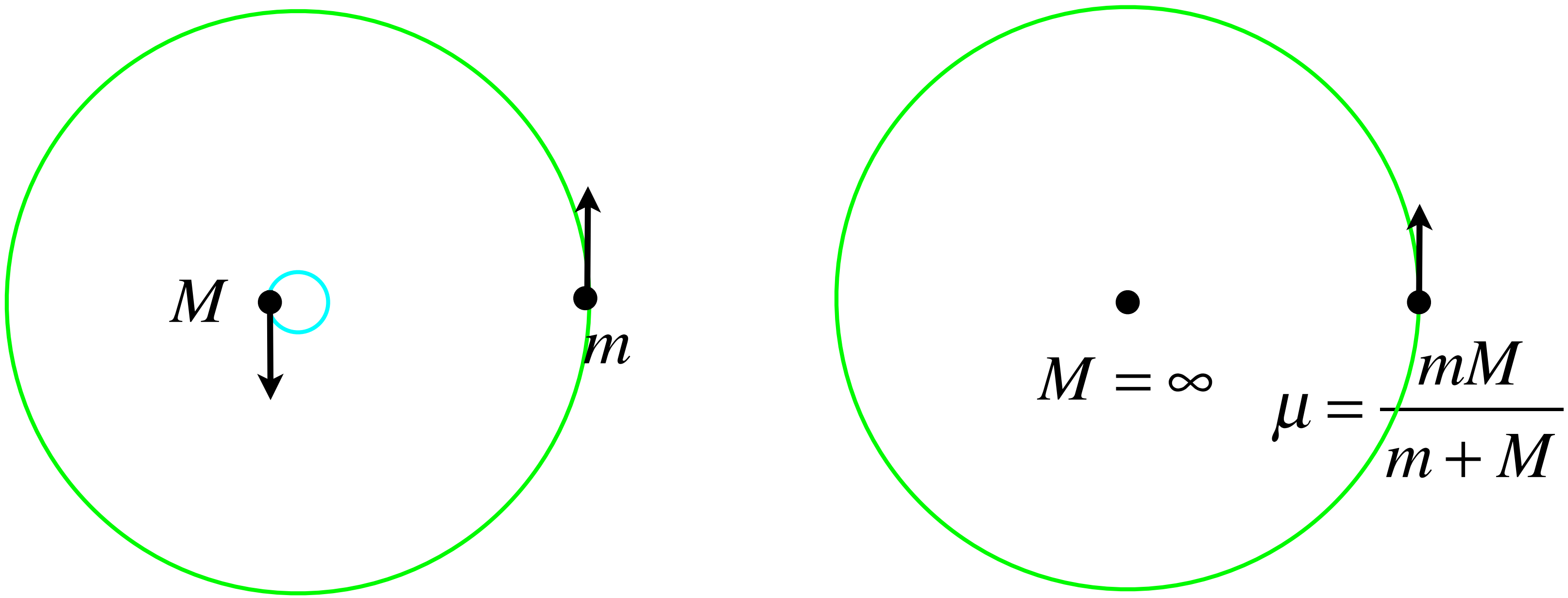
$$E = -\frac{1}{2}\frac{mZ^2\alpha^2 c^2}{n^2} = -R_y \frac{Z^2}{n^2}$$

$$r = \frac{\hbar}{mcZ\alpha} n^2 = \frac{n^2}{Z} a_0$$

- Rydberg energy $R_y = \frac{1}{2} m\alpha^2 c^2 = 13.6 \text{ eV}$
- Bohr radius a_0 =0.053 nm

reduced mass

- the one-electron atom contains two particles



Sommerfeld rule

- For any physical system in which the coordinate are periodic functions of time, there exists a quantum condition for each coordinate

$$\oint p_q dq = n_q h$$

- When choosing the angular coordinate

$$\oint p_q dq \rightarrow \oint L d\theta \qquad\qquad L = n\hbar$$

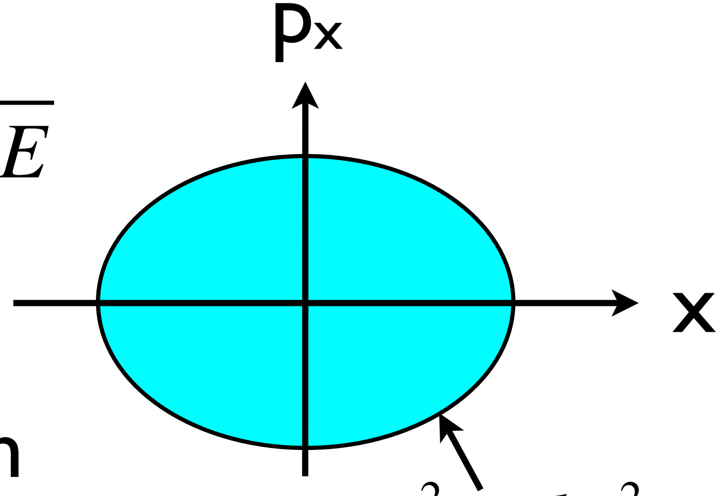
application to SHO

- the SHO is a periodic motion.
- With constant energy, it goes in an elliptical trajectory in phase space
- The quantum condition requires that elipse area is *nh*
- area= $\pi x_0 p_0 = \pi \sqrt{2E/k}\sqrt{2mE}$

$$= 2\pi E/\omega$$

- We get energy quantization

$$E = n\hbar\omega$$

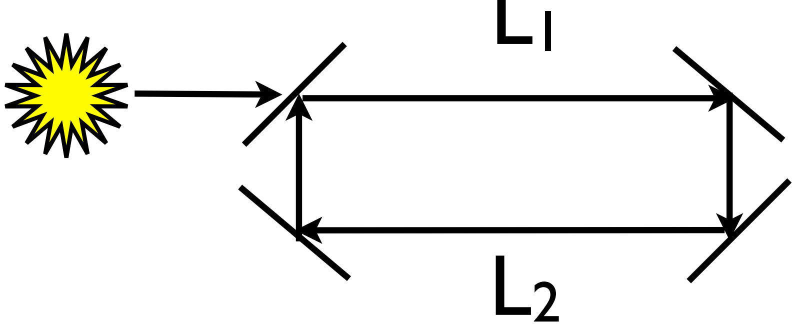


$$E = \frac{p^2}{2m} + \frac{kx^2}{2}$$

interpretation of the rule

- It describes the standing wave condition

$$\phi_1 + \phi_2 = 2n\pi \qquad \frac{L_1}{\lambda} + \frac{L_2}{\lambda} = n$$



- If velocity changes

$$\frac{L_1}{\lambda_1} + \frac{L_2}{\lambda_2} = n$$

- Apply de Broglie postulate

$$p_1 L_1 + p_2 L_2 = nh \qquad \sum_i p_i L_i = nh$$

Schrodinger equation in 3D

- in 3D system $$H = \frac{\mathbf{p}^2}{2\mu} + V(\mathbf{r})$$
- μ mass
- momentum operator in 3D

$$\mathbf{p} = (p_x, p_y, p_z) = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}, \frac{\hbar}{i}\frac{\partial}{\partial z} \right)$$

- Schrodinger equation

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right]\psi(x,y,z) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z)$$

Central potential

- central potential problem

$$V(\mathbf{r}) = V(r)$$

separable in spherical coordinate

- kinetic energy in spherical coordinate

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right] = -\frac{\hbar^2}{2\mu}\nabla^2$$

$$\nabla^2 \to \frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2}+\cot\theta\frac{\partial}{\partial \theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right)$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

Easy way to memorize

$$\frac{\partial}{\partial x}=\frac{\partial r}{\partial x}\frac{\partial}{\partial r}+\frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta}+\frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}$$

$$\frac{\partial^2}{\partial x^2}=\frac{\partial}{\partial x}\left(\frac{\partial r}{\partial x}\frac{\partial}{\partial r}+\frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta}+\frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}\right)$$

$$=\left(\frac{\partial r}{\partial x}\right)^2\frac{\partial^2}{\partial r^2}+\left(\frac{\partial\theta}{\partial x}\right)^2\frac{\partial^2}{\partial\theta^2}+\left(\frac{\partial\phi}{\partial x}\right)^2\frac{\partial^2}{\partial\phi^2}+\frac{\partial^2 r}{\partial x^2}\frac{\partial}{\partial r}+\frac{\partial^2\theta}{\partial x^2}\frac{\partial}{\partial\theta}+\frac{\partial^2\phi}{\partial x^2}\frac{\partial}{\partial\phi}$$

$$+2\frac{\partial r}{\partial x}\frac{\partial\theta}{\partial x}\frac{\partial}{\partial r}\frac{\partial}{\partial\theta}+2\frac{\partial\theta}{\partial x}\frac{\partial\phi}{\partial x}\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi}+2\frac{\partial r}{\partial x}\frac{\partial\phi}{\partial x}\frac{\partial}{\partial r}\frac{\partial}{\partial\phi}$$

2nd derivative terms

$$\nabla^2=\left[\left(\frac{\partial r}{\partial x}\right)^2+\left(\frac{\partial r}{\partial y}\right)^2+\left(\frac{\partial r}{\partial z}\right)^2\right]\frac{\partial^2}{\partial r^2}+\left[\left(\frac{\partial\theta}{\partial x}\right)^2+\left(\frac{\partial\theta}{\partial y}\right)^2+\left(\frac{\partial\theta}{\partial z}\right)^2\right]\frac{\partial^2}{\partial\theta^2}+\left[\left(\frac{\partial\phi}{\partial x}\right)^2+\left(\frac{\partial\phi}{\partial y}\right)^2+\left(\frac{\partial\phi}{\partial z}\right)^2\right]\frac{\partial^2}{\partial\phi^2}$$

$$+\left[\frac{\partial^2 r}{\partial x^2}+\frac{\partial^2 r}{\partial y^2}+\frac{\partial^2 r}{\partial z^2}\right]\frac{\partial}{\partial r}+\left[\frac{\partial^2\theta}{\partial x^2}+\frac{\partial^2\theta}{\partial y^2}+\frac{\partial^2\theta}{\partial z^2}\right]\frac{\partial}{\partial\theta}+\left[\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}+\frac{\partial^2\phi}{\partial z^2}\right]\frac{\partial}{\partial\phi}$$

1st derivative terms

$$+2\left[\frac{\partial r}{\partial x}\frac{\partial\theta}{\partial x}+\frac{\partial r}{\partial y}\frac{\partial\theta}{\partial y}+\frac{\partial r}{\partial z}\frac{\partial\theta}{\partial z}\right]\frac{\partial}{\partial r}\frac{\partial}{\partial\theta}+2\left[\frac{\partial\theta}{\partial x}\frac{\partial\phi}{\partial x}+\frac{\partial\theta}{\partial y}\frac{\partial\phi}{\partial y}+\frac{\partial\theta}{\partial z}\frac{\partial\phi}{\partial z}\right]\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi}+2\left[\frac{\partial r}{\partial x}\frac{\partial\phi}{\partial x}+\frac{\partial r}{\partial y}\frac{\partial\phi}{\partial y}+\frac{\partial r}{\partial z}\frac{\partial\phi}{\partial z}\right]\frac{\partial}{\partial r}\frac{\partial}{\partial\phi}$$

cross terms =0

$$\frac{\partial r}{\partial x} = \sin\theta\cos\phi$$

$$\frac{\partial r}{\partial y} = \sin\theta\cos\phi$$

$$\frac{\partial r}{\partial z} = -\cos\theta$$

$$\frac{\partial \theta}{\partial x} = \frac{\cos\theta\cos\phi}{r}$$

$$\frac{\partial \theta}{\partial y} = \frac{\cos\theta\sin\phi}{r}$$

$$\frac{\partial \theta}{\partial z} = -\frac{\sin\theta}{r}$$

$$\frac{\partial \phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta}$$

$$\frac{\partial \phi}{\partial y} = \frac{\cos\phi}{r\sin\theta}$$

$$\frac{\partial \phi}{\partial z} = 0$$

2nd derivative terms

$$\left(\frac{\partial r}{\partial x}\right)^2 + \left(\frac{\partial r}{\partial y}\right)^2 + \left(\frac{\partial r}{\partial z}\right)^2 = \sin^2\theta\cos^2\phi + \sin^2\theta\cos^2\phi + \cos^2\theta = 1$$

$$\left(\frac{\partial \theta}{\partial x}\right)^2 + \left(\frac{\partial \theta}{\partial y}\right)^2 + \left(\frac{\partial \theta}{\partial z}\right)^2 = \frac{\cos^2\theta\cos^2\phi}{r^2} + \frac{\cos^2\theta\sin^2\phi^2}{r} + \frac{\sin^2\theta}{r^2} = \frac{1}{r^2}$$

$$\left(\frac{\partial \phi}{\partial x}\right)^2 + \left(\frac{\partial \phi}{\partial y}\right)^2 + \left(\frac{\partial \phi}{\partial z}\right)^2 = \frac{\sin^2\phi}{r^2\sin^2\theta} + \frac{\cos^2\phi}{r^2\sin^2\theta} = \frac{1}{r^2\sin^2\theta}$$

cross terms

$$\frac{\partial r}{\partial x}\frac{\partial \theta}{\partial x} + \frac{\partial r}{\partial y}\frac{\partial \theta}{\partial y} + \frac{\partial r}{\partial z}\frac{\partial \theta}{\partial z} = \frac{\sin\theta\cos\theta\cos^2\phi}{r} + \frac{\sin\theta\cos\theta\sin^2\phi}{r} - \frac{\sin\theta\cos\theta}{r} = 0$$

$$\frac{\partial r}{\partial x}\frac{\partial \phi}{\partial x} + \frac{\partial r}{\partial y}\frac{\partial \phi}{\partial y} + \frac{\partial r}{\partial z}\frac{\partial \phi}{\partial z} = -\sin\theta\cos\phi\frac{\sin\phi}{r\sin\theta} + \sin\theta\cos\phi\frac{\cos\phi}{r\sin\theta} = 0$$

$$\frac{\partial \theta}{\partial x}\frac{\partial \phi}{\partial x} + \frac{\partial \theta}{\partial y}\frac{\partial \phi}{\partial y} + \frac{\partial \theta}{\partial z}\frac{\partial \phi}{\partial z} = \frac{\cos\theta\cos\phi}{r}\frac{\sin\phi}{r\sin\theta} + \frac{\cos\theta\sin\phi}{r}\frac{\cos\phi}{r\sin\theta} = 0$$

1st derivative terms

$$\frac{\partial^2 r}{\partial x^2} = \frac{y^2 + z^2}{r^2}$$

$$\frac{\partial^2 r}{\partial y^2} = \frac{x^2 + z^2}{r^2}$$

$$\frac{\partial^2 r}{\partial z^2} = \frac{x^2 + y^2}{r^2}$$

$$\frac{\partial^2 r}{\partial x^2} + \frac{\partial^2 r}{\partial y^2} + \frac{\partial^2 r}{\partial z^2} = \frac{2}{r}$$

$$\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} + \frac{\partial^2 \theta}{\partial z^2} = \frac{\cos\theta}{r^2 \sin\theta}$$

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\cot\theta \frac{\partial}{\partial \theta}$$

$$= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{\hbar^2 r^2} L^2$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

Schrodinger equation

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\phi)+V(r)\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

radial part

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+V(r)\psi(r,\theta,\phi)$$

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

angular parts contain in this term

Separation of variables

- separation of variables

$$\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$$

$$-\frac{\hbar^2}{2\mu}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]+V(r)RY$$
$$=ERY$$

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{r^2Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{r^2Y\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]+V(r)=E$$

separation constant

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2\mu r^2}{\hbar^2}(V-E)$$

$$+\frac{1}{Y\sin\theta}\left[\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]=0$$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2\mu r^2}{\hbar^2}(V-E)=l(l+1)$$

$$\frac{1}{Y\sin\theta}\left[\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]=-l(l+1)$$

Here we choose the constant to be $l(l+1)$

Angular equation

$$\sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} = -l(l+1)\sin^2\theta Y$$

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

$$\boxed{\frac{1}{\Theta}\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + l(l+1)\sin^2\theta} + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = 0$$

$$\frac{1}{\Theta}\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + l(l+1)\sin^2\theta = m^2$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$$

Here we choose the constant to be m^2

φ equation

- equation for φ $$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi$$
- boundary condition $$\Phi(\phi + 2\pi) = \Phi(\phi)$$
- solution $\Phi = e^{im\phi}$ $m = 0, \pm 1, \pm 2 \cdots$

θ equation

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + l(l+1)\sin^2\theta\Theta = m^2\Theta$$

- let $x = \cos\theta$ $\qquad \frac{d}{dx} = -\frac{1}{\sin\theta}\frac{d}{d\theta}$

$$\frac{d}{dx}\left[\left(1-x^2\right)\frac{d\Theta}{dx}\right] + l(l+1)\Theta = m^2\Theta$$

- The solutions are special functions, called associated Legendre functions

$$\Theta(\theta) = P_l^m(\cos\theta)$$

Legendre polynomials

- Associated Legendre functions can be generated from Legendre polynomials P_l

$$P_l^m(x) = \left(1 - x^2\right)^{m/2} \left(\frac{d}{dx}\right)^m P_l(x) \qquad m > 0 \qquad P_l^{-m}(x) = P_l^m(x)$$

- Legendre polynomials are

$$P_l(x) = \frac{1}{2^l l!} \left(\frac{d}{dx}\right)^l \left(x^2 - 1\right)^l$$

called Rodrigues formula

- It is easy to check $P_l(x)$ satisfies

$$\frac{d}{dx}\left[\left(1-x^2\right)\frac{dP_l}{dx}\right]+l\left(l+1\right)P_l=0$$

$$\left[\left(1-x^2\right),\frac{d}{dx}\right]=2x$$

$$\left[A,BC\right]=\left[A,B\right]C+B\left[A,C\right]$$

$$\left[\left(1-x^2\right),\left(\frac{d}{dx}\right)^l\right]=\left[\left(1-x^2\right),\left(\frac{d}{dx}\right)^{l-1}\right]\left(\frac{d}{dx}\right)+\left(\frac{d}{dx}\right)^{l-1}\left[\left(1-x^2\right),\left(\frac{d}{dx}\right)\right]$$

$$=\left[\left(1-x^2\right),\left(\frac{d}{dx}\right)^{l-1}\right]\left(\frac{d}{dx}\right)+2x\left(\frac{d}{dx}\right)^{l-1}+2\left(l-1\right)\left(\frac{d}{dx}\right)^{l-2}$$

$$=2lx\left(\frac{d}{dx}\right)^{l-1}+\left(l-1\right)l\left(\frac{d}{dx}\right)^{l-2}$$

$$=2l\left(\frac{d}{dx}\right)^{l-1}x-\left(l-1\right)l\left(\frac{d}{dx}\right)^{l-2}$$

$$\left[A,B^n\right]=n\left[A,B\right]B^{n-1}$$

$$x\left(\frac{d}{dx}\right)^{l-1}=\left(\frac{d}{dx}\right)^{l-1}x-\left(l-1\right)\left(\frac{d}{dx}\right)^{l-2}$$

$$\text{if }\left[A,B\right]=\text{constant}$$

$$\frac{d}{dx}\left[\left(1-x^2\right)\frac{d}{dx}\right]\frac{d^l}{dx^l}=\frac{d}{dx}\frac{d^{l+1}}{dx^{l+1}}\left(1-x^2\right)+\frac{d}{dx}\left[2\left(l+1\right)\left(\frac{d}{dx}\right)^l x-l\left(l+1\right)\left(\frac{d}{dx}\right)^{l-1}\right]$$

$$=\frac{d^{l+2}}{dx^{l+2}}\left(1-x^2\right)+2\left(l+1\right)\left(\frac{d}{dx}\right)^{l+1}x-l\left(l+1\right)\left(\frac{d}{dx}\right)^l$$

$$\frac{d}{dx}\left[\left(1-x^2\right)\frac{d}{dx}\right]\frac{d^l}{dx^l}\left(1-x^2\right)^l=\frac{d^{l+2}}{dx^{l+2}}\left(1-x^2\right)^{l+1}+2\left(l+1\right)\left(\frac{d}{dx}\right)^{l+1}x\left(1-x^2\right)^l-l\left(l+1\right)\left(\frac{d}{dx}\right)^l\left(1-x^2\right)^l$$

$$=-2\left(l+1\right)\left(\frac{d}{dx}\right)^{l+1}x\left(1-x^2\right)^l+2\left(l+1\right)\left(\frac{d}{dx}\right)^{l+1}x\left(1-x^2\right)^l-l\left(l+1\right)\left(\frac{d}{dx}\right)^l\left(1-x^2\right)^l$$

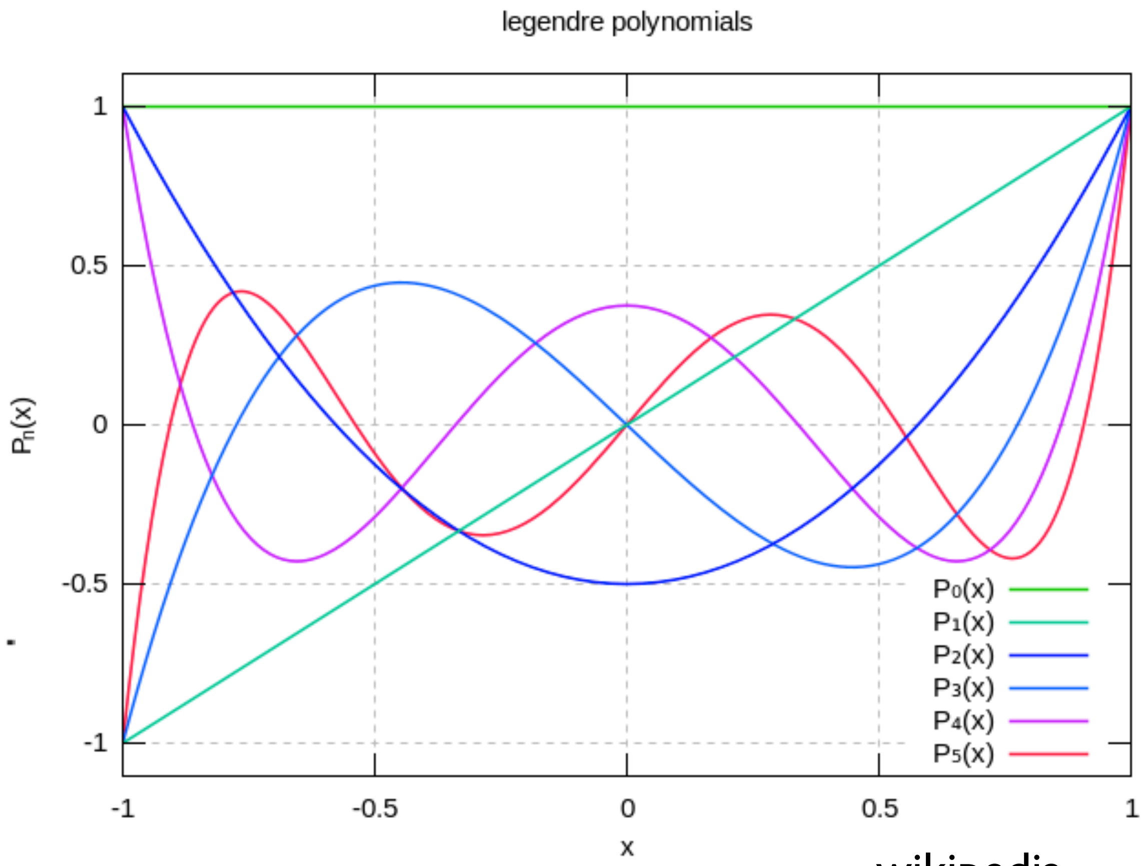
$$=-l\left(l+1\right)\left(\frac{d}{dx}\right)^l\left(1-x^2\right)^l$$

limitations on *l* and *m*

- *l* should be non-negative integers $l = 0, 1, 2, \cdots$
- if $|m| > l$ $P_l^m(x) = 0$
- possible values of $m = -l, -l+1, \cdots, 0, \cdots l-1, l$

Legendre polynomials

$$P_0(x) = 1$$
$$P_1(x) = x$$
$$P_2(x) = \tfrac{1}{2}(3x^2 - 1)$$
$$P_3(x) = \tfrac{1}{2}(5x^3 - 3x)$$
$$P_4(x) = \tfrac{1}{8}(35x^4 - 30x^2 + 3)$$
$$P_5(x) = \tfrac{1}{8}(63x^5 - 70x^3 + 15x)$$
$$P_6(x) = \tfrac{1}{16}(231x^6 - 315x^4 + 105x^2 - 5).$$



wikipedia

$$P_0^0(\cos\theta) = 1$$

$$P_1^0(\cos\theta) = \cos\theta$$

$$P_1^1(\cos\theta) = -\sin\theta$$

$$P_2^0(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_2^1(\cos\theta) = -3\cos\theta\sin\theta$$

$$P_2^2(\cos\theta) = 3\sin^2\theta$$

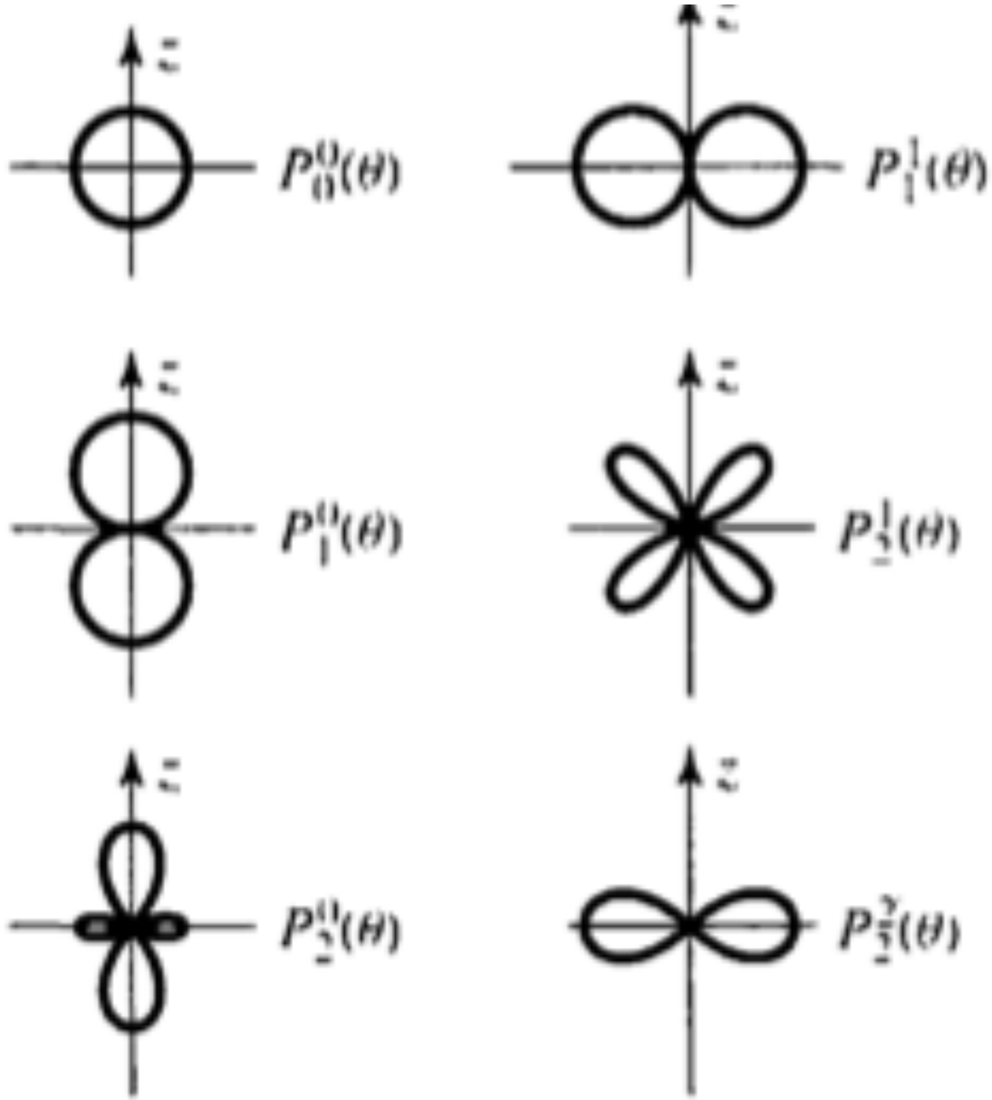
$$P_3^0(\cos\theta) = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$$

$$P_3^1(\cos\theta) = -\frac{3}{2}(5\cos^2\theta - 1)\sin\theta$$

$$P_3^2(\cos\theta) = 15\cos\theta\sin^2\theta$$

$$P_3^3(\cos\theta) = -15\sin^3\theta$$

$$P_4^0(\cos\theta) = \frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3)$$



Spherical harmonics

- normalized wavefunctions *Y* are called spherical harmonics

$$\int |Y|^2 \sin\theta \, d\theta \, d\phi = 1$$

$$Y_{lm}(\theta,\phi) = (-1)^m \left[\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos\theta) e^{im\phi}$$

- *l*: azimuthal quantum number
- *m*:magnetic quantum number

Hydrogen atom

- attractive Coulomb potential

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

- Differential equation

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{l(l+1)}{r^2}\right]R_{nl}(r)-\frac{Ze^2}{4\pi\varepsilon_0 r}R_{nl}(r)=ER_{nl}(r)$$

$$\left[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{2\mu}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{\hbar^2 l(l+1)}{2\mu r^2}\right)\right]R_{nl}(r)=0$$

Scaling

- choose the scaling factor for length

$$E < 0 \qquad \frac{1}{x_0} = \frac{\sqrt{8\mu|E|}}{\hbar} = \frac{\sqrt{-8\mu E}}{\hbar}$$

- dimensionless length $\rho = \frac{r}{x_0} = \frac{\sqrt{-8\mu E}}{\hbar} r$

$$\left[\frac{1}{x_0^2}\frac{\partial^2}{\partial\rho^2} + \frac{1}{x_0^2}\frac{2}{\rho}\frac{\partial}{\partial\rho} + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 x_0 \rho} - \frac{\hbar^2 l(l+1)}{2\mu x_0^2 \rho^2}\right)\right]R(\rho) = 0$$

$$\left[\frac{\partial^2}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial}{\partial\rho} - \frac{1}{4} + \frac{2\mu}{\hbar^2}\frac{x_0 Ze^2}{4\pi\varepsilon_0 \rho} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0$$

$$\left[\frac{\partial^2}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial}{\partial\rho} - \frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0$$

Characteristic length

- characteristic(eigen) length

$$\lambda = \frac{2\mu}{\hbar^2}\frac{x_0 Ze^2}{4\pi\varepsilon_0} = \frac{2\mu}{\hbar^2}\frac{Ze^2}{4\pi\varepsilon_0}\frac{\hbar}{\sqrt{-8\mu E}}$$

$$= \frac{Ze^2}{4\pi\varepsilon_0\hbar}\sqrt{\frac{\mu}{-2E}}$$

$$= Z\alpha\sqrt{\frac{\mu c^2}{-2E}}$$

$$x_0 = \frac{\hbar^2 4\pi\varepsilon_0\lambda}{2\mu Ze^2} = \frac{a_0\lambda}{2Z}$$

- fine structure constant

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 c\hbar} = \frac{1}{137}$$

asymptotic behavior

- when $\rho \to \infty$

$$\left[\frac{\partial^2}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial}{\partial\rho} - \frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0$$

$$\longrightarrow \quad \left[\frac{\partial^2}{\partial\rho^2} - \frac{1}{4}\right]R(\rho) = 0$$

$$R(\rho) \to e^{-\rho/2}$$

- in general $\quad R(\rho) = e^{-\rho/2}G(\rho)$

asymptotic behavior

- when $\rho \to 0$

$$\left[\frac{\partial^2}{\partial\rho^2}+\frac{2}{\rho}\frac{\partial}{\partial\rho}-\frac{1}{4}+\frac{\lambda}{\rho}-\frac{l(l+1)}{\rho^2}\right]R(\rho)=0$$

$$\longrightarrow \quad \left[\frac{\partial^2}{\partial\rho^2}+\frac{2}{\rho}\frac{\partial}{\partial\rho}-\frac{l(l+1)}{\rho^2}\right]R(\rho)=0$$

$$R(\rho)\propto\rho^s$$

$$s(s-1)+2s-l(l+1)=0 \qquad s(s+1)=l(l+1)$$

$s=l$ or $s=-l-1$

asymptotic behavior

- differential equation for G

$$\left[\frac{\partial^2}{\partial\rho^2}+\frac{2}{\rho}\frac{\partial}{\partial\rho}-\frac{1}{4}+\frac{\lambda}{\rho}-\frac{l(l+1)}{\rho^2}\right]e^{-\rho/2}G(\rho)$$

$$=e^{-\rho/2}\frac{\partial^2 G}{\partial\rho^2}-e^{-\rho/2}\frac{\partial G}{\partial\rho}+\frac{1}{4}e^{-\rho/2}G$$

$$+e^{-\rho/2}\frac{2}{\rho}\frac{\partial G}{\partial\rho}-e^{-\rho/2}\frac{1}{\rho}G+\left[-\frac{1}{4}+\frac{\lambda}{\rho}-\frac{l(l+1)}{\rho^2}\right]e^{-\rho/2}G$$

$$\frac{\partial^2 G}{\partial\rho^2}-\frac{\partial G}{\partial\rho}+\frac{2}{\rho}\frac{\partial G}{\partial\rho}-\frac{1}{\rho}G+\left[\frac{\lambda}{\rho}-\frac{l(l+1)}{\rho^2}\right]G=0$$

$$\frac{\partial^2 G}{\partial\rho^2}-\left(1-\frac{2}{\rho}\right)\frac{\partial G}{\partial\rho}+\left[\frac{\lambda-1}{\rho}-\frac{l(l+1)}{\rho^2}\right]G=0$$

asymptotic behavior

- owing to the behavior of R at small ρ

$$G(\rho) \propto \rho^l = \rho^l H(\rho)$$

$$\frac{\partial^2}{\partial \rho^2}\rho^l H(\rho) - \left(1-\frac{2}{\rho}\right)\frac{\partial}{\partial \rho}\rho^l H(\rho) + \left[\frac{\lambda-1}{\rho} - \frac{l(l+1)}{\rho^2}\right]\rho^l H(\rho) = 0$$

$$\rho^l \frac{\partial^2 H}{\partial \rho^2} + \frac{2l}{\rho}\rho^l \frac{\partial H}{\partial \rho} + \rho^l \frac{l(l-1)}{\rho^2} H - \left(1-\frac{2}{\rho}\right)\frac{\partial H}{\partial \rho} - \left(1-\frac{2}{\rho}\right)\frac{l}{\rho}\rho^l H + \left[\frac{\lambda-1}{\rho} - \frac{l(l+1)}{\rho^2}\right]\rho^l H = 0$$

$$\frac{\partial^2 H}{\partial \rho^2} + \left(\frac{2l+2}{\rho} - 1\right)\frac{\partial H}{\partial \rho} + \frac{\lambda - l - 1}{\rho} H = 0$$

- We will take the similar approach with that in Chapter IV to discuss the possible eigenvalues

power series expansion

- Here we consider the approach of power series expansion for the differential equation

$$\frac{\partial^2 H}{\partial \rho^2}+\left(\frac{2l+2}{\rho}-1\right)\frac{\partial H}{\partial \rho}+\frac{\lambda-l-1}{\rho}H=0$$

- assuming $H(\rho)=\sum_k a_k \rho^k$

$$\frac{dH}{d\rho}=\sum_k k a_k \rho^{k-1} \qquad \frac{d^2 H}{d\rho^2}=\sum_k k(k-1)a_k \rho^{k-2}$$

$$\sum_k k(k-1)a_k\rho^{k-2}+\sum_k\left(\frac{2l+2}{\rho}-1\right)ka_k\rho^{k-1}+\frac{\lambda-l-1}{\rho}\sum_k a_k\rho^k=0$$

$$\sum_k\left[k(k-1)+k(2l+2)\right]a_k\rho^{k-2}+\sum_k(\lambda-l-1-k)a_k\rho^{k-1}=0$$

recursion formula

- rearrange the order

$$\sum_k (k+1)(k+2l+2)a_{k+1}\rho^{k-1} + \sum_k (\lambda - l - 1 - k)a_k\rho^{k-1} = 0$$

- The coefficients

$$(k+1)(k+2l+2)a_{k+1} + (\lambda - l - 1 - k)a_k = 0$$

$$\frac{a_{k+1}}{a_k} = \frac{k+l+1-\lambda}{(k+1)(k+2l+2)}$$

recursion formula

- when *k* is large, it behaves as $\frac{a_{k+1}}{a_k} \to \frac{1}{k}$

$$a_k \approx \left(\frac{1}{k}\right)\left(\frac{1}{k-1}\right)\left(\frac{1}{k-2}\right)\cdots \simeq \frac{1}{k!}C$$

$$H(\rho) = \sum_k a_k \rho^k \simeq C \sum_k \frac{1}{k!} \rho^k = Ce^{\rho}$$

in general cases, $R(\rho) = e^{-\frac{\rho}{2}} \rho^l H(\rho) \sim C\rho^l e^{\rho} e^{-\frac{\rho}{2}} = C\rho^l e^{\frac{\rho}{2}}$

diverges when ρ is large

termination of series

- we want a reasonable solution which is finite at infinite ρ $\quad a_{k+1} = 0$ for some *k*

$$k + l + 1 - \lambda = 0 \qquad k = 0,1,2\cdots$$

- It restricts the value of λ $\qquad \lambda = (1+l),(2+l)\cdots$

$$\lambda = k + l + 1 = n$$

- n is called principle quantum number

- some properties

$$\lambda = n = Z\alpha\sqrt{\frac{\mu c^2}{-2E}}$$

$$k \geq 0 \qquad n \geq l + 1$$

$$E = -\mu c^2 \frac{Z^2\alpha^2}{2n^2}$$

Numerical method-1

- another way of scaling, Bohr radius $a_0 = \frac{\hbar^2 4\pi\varepsilon_0}{\mu e^2}$
- rewrite the equation $\rho = \frac{r}{a_0}$

$$-\frac{\hbar^2}{2\mu}\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right]R_{nl}(r)-\frac{Ze^2}{4\pi\varepsilon_0 r}R_{nl}(r)=ER_{nl}(r)$$

$$\left[-\frac{d^2}{dr^2}-\frac{2}{r}\frac{d}{dr}+\frac{l(l+1)}{r^2}\right]R_{nl}(r)-\frac{2\mu Ze^2}{4\pi\varepsilon_0\hbar^2 r}R_{nl}(r)=\frac{2\mu}{\hbar^2}ER_{nl}(r)$$

$$\left[-\frac{\partial^2}{\partial\rho^2}-\frac{2}{\rho}\frac{\partial}{\partial\rho}-\frac{2Z}{\rho}+\frac{l(l+1)}{\rho^2}\right]R(\rho)=\frac{2\mu a_0^2}{\hbar^2}ER(\rho)$$

Numerical method-2

- normalization condition

$$\int \left|\rho R(\rho)\right|^2 d\rho = \int |f|^2 d\rho = 1 \qquad f = \rho R(\rho)$$

- The equation for *f*

$$-\frac{\partial^2}{\partial \rho^2} f(\rho) - \left[\frac{2Z}{\rho} - \frac{l(l+1)}{\rho^2}\right] f(\rho) = \lambda f(\rho)$$

$$\lambda = \frac{2\mu a_0^2}{\hbar^2} E = \frac{E}{R_y} \qquad R_y = \frac{\mu e^4}{8\varepsilon_0^2 h^2}$$

Numerical method-3

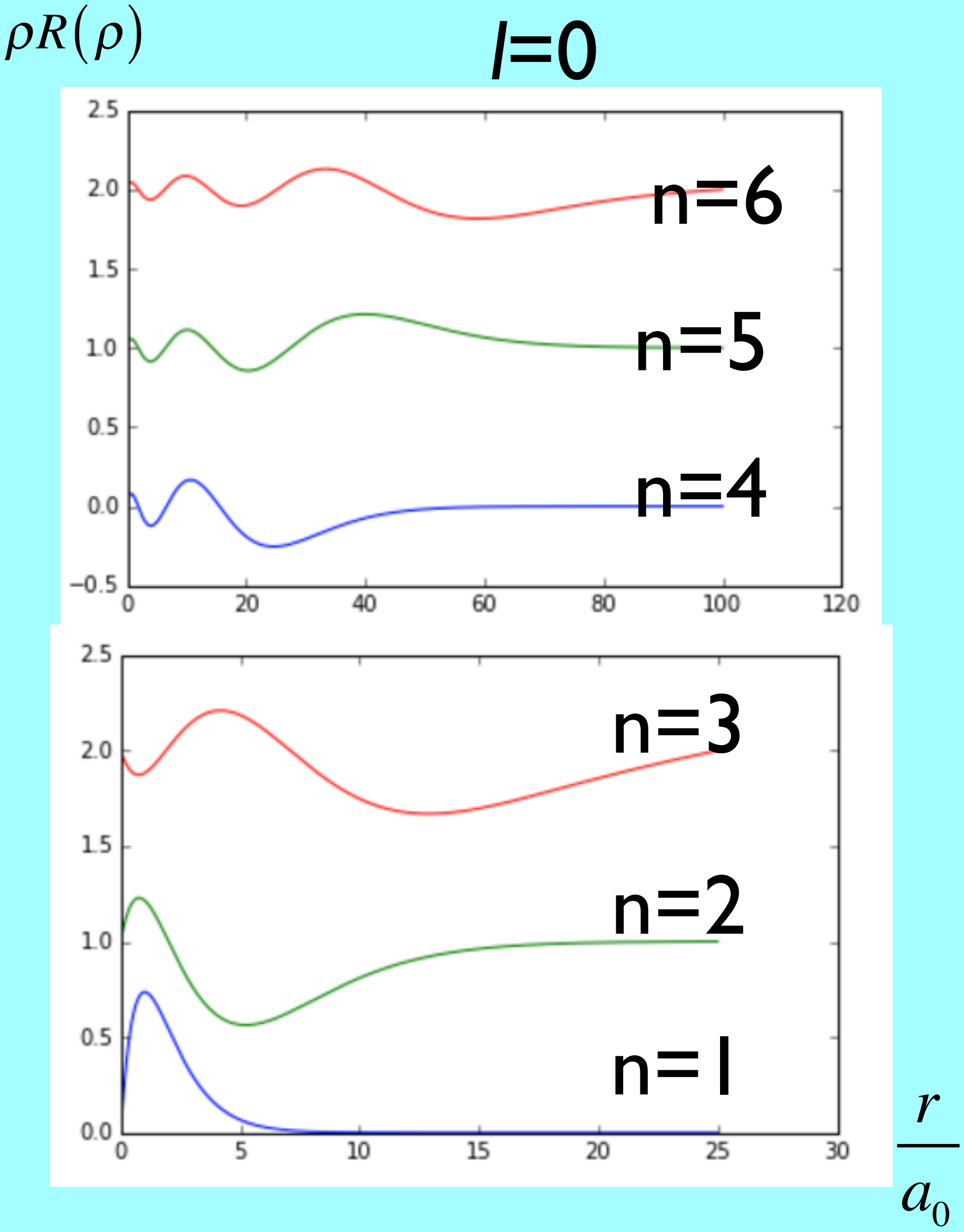
- Define the hermitian operator satisfying

$$\hat{O}|f\rangle = \lambda|f\rangle \qquad \hat{O} = -\frac{\partial^2}{\partial\rho^2} - \frac{2Z}{\rho} + \frac{l(l+1)}{\rho^2}$$

- If write the solution with a column vector with linearly spaced coordinate $\rho_{j+1} - \rho_j = \Delta\rho$

$$f(\rho) = \begin{pmatrix} \rho_1 R(\rho_1) \\ \rho_2 R(\rho_2) \\ \rho_3 R(\rho_3) \\ \vdots \\ \rho_N R(\rho_N) \end{pmatrix} \qquad \frac{d^2}{d\rho^2} = \frac{1}{(\Delta\rho)^2} \begin{pmatrix} -2 & 1 & 0 & & 0 \\ 1 & -2 & 1 & \cdots & 0 \\ 0 & 1 & -2 & & 0 \\ & \vdots & & \ddots & 1 \\ 0 & 0 & 0 & 1 & 2 \end{pmatrix}$$

Numerical method-4



eigenvalues

-0.99937578~ 1
-0.2499605 ~ 1/4
-0.10921206 ~1/9
-0.06246099 ~1/16
-0.03998396 ~1/25
-0.0277305 ~1/36
-0.01921007 ~1/49

mass difference

- the mass of a deutron(1p1n) is twice of a proton
- Eigenenergy and transition frequency scale as

$$\mu = \frac{mM}{m+M} = \frac{m}{1+\frac{m}{M}}$$

- small difference of transition energies for a deuterium(epn) and a hydrogen(ep)

$$\mu_D \simeq m_e\left(1-\frac{m_e}{2m_p}\right) \qquad \mu_H \simeq m_e\left(1-\frac{m_e}{m_p}\right)$$

Proton size puzzle

- to study the spectrum of a muonic hydrogen (μp)
- muon mass ~ 270 m_e
- a muon orbits much closer than an electron to the hydrogen nucleus, where it is consequently much more sensitive to the size of the proton.

LETTERS

The size of the proton

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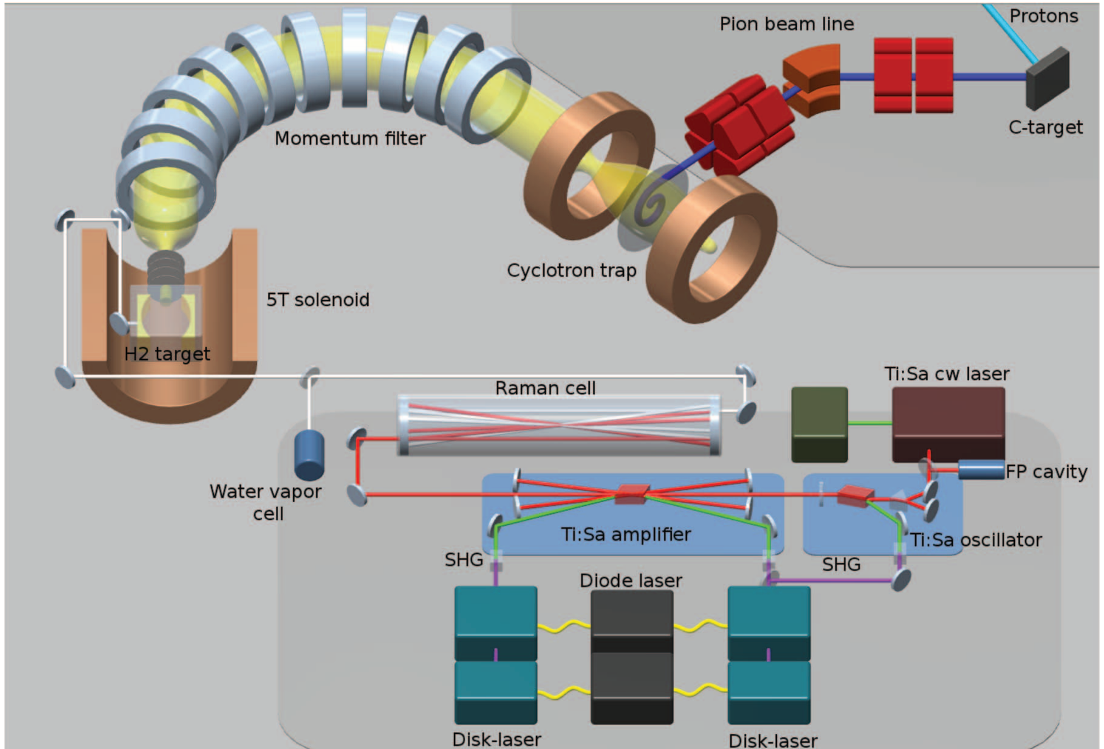


degeneracy

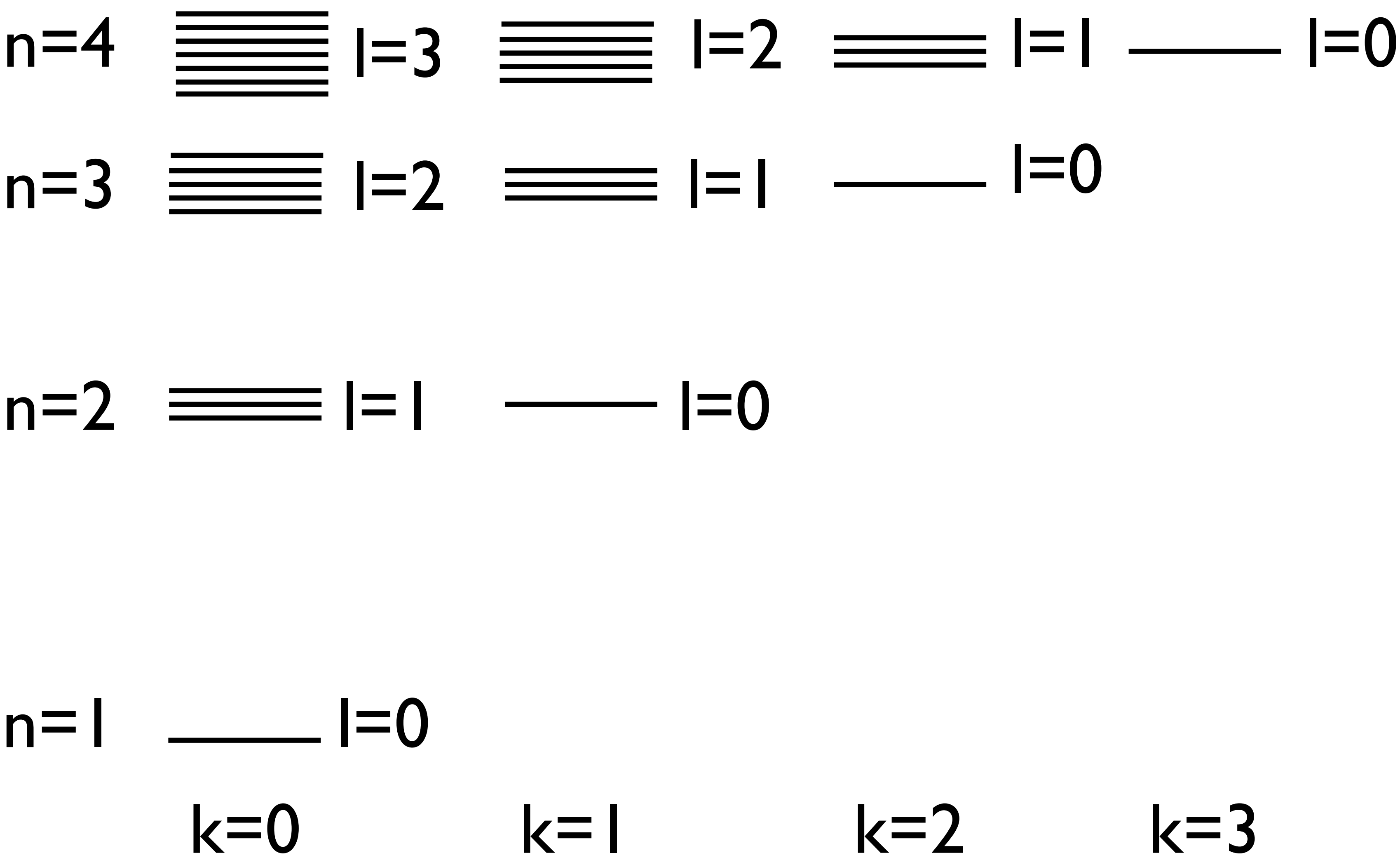
- energy only depends on n

$$n = k + l + 1$$

- since k is an integer, the number of possible k is n (from l=0, 1, ...n-1)
- for each l, there are $2l+1$ states (m=-l, ...l)
- total degeneracy

$$\sum_{l=0}^{n-1} 2l + 1 = n^2$$

spectrum



ground state

- n=1, l=0 (k=0)

$$\frac{a_{k+1}}{a_k} = \frac{k+l}{(k+1)(k+2l+2)}$$

- only a_0 exists

radial

$$H(\rho) = 1$$

$$R(\rho) = e^{-\rho/2}$$

angular

$$Y_{00} = \text{cosntant}$$

1st excited state

- *n*=2, *l*=0 (*k*=1)

$$\frac{a_{k+1}}{a_k} = \frac{k+l-1}{(k+1)(k+2l+2)}$$

$$a_0 = 1$$

$$a_1 = -\frac{1}{2}$$

$$a_2 = 0$$

radial

$$H(\rho) = 1 - \frac{\rho}{2}$$

angular

$$Y_{00}$$

- *n*=2, *l*=1 (*k*=0)

radial

$$H(\rho) = 1$$

angular

$$Y_{11}, Y_{10}, Y_{1-1}$$

2nd excited state

- n=3, l=0 (k=2)

$$a_0 = 1$$
$$a_1 = -1$$
$$a_2 = \frac{1}{6}$$
$$a_3 = 0$$

$$\frac{a_{k+1}}{a_k} = \frac{k+l-2}{(k+1)(k+2l+2)}$$

radial

$$H(\rho) = 1 - \rho + \frac{\rho^2}{6}$$

angular

$$Y_{00}$$

- n=3, l=1 (k=1)

$$a_0 = 1$$
$$a_1 = -\frac{1}{4}$$
$$a_2 = 0$$

$$H(\rho) = 1 - \frac{\rho}{4}$$

$$Y_{11}, Y_{10}, Y_{1-1}$$

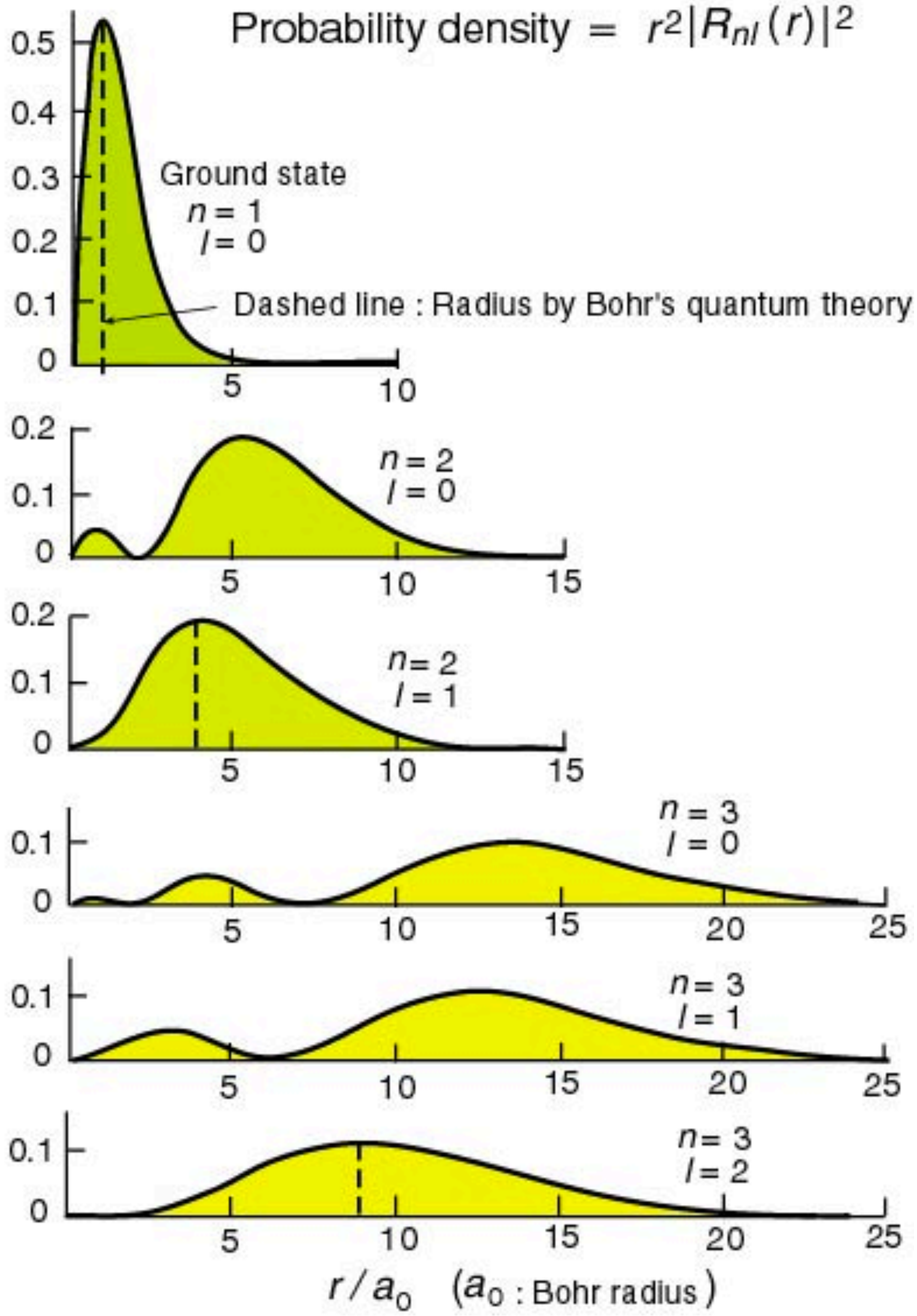
associate Lagurre polynomials

- The radial eigenfunctions are called associate Lagurre polynomials

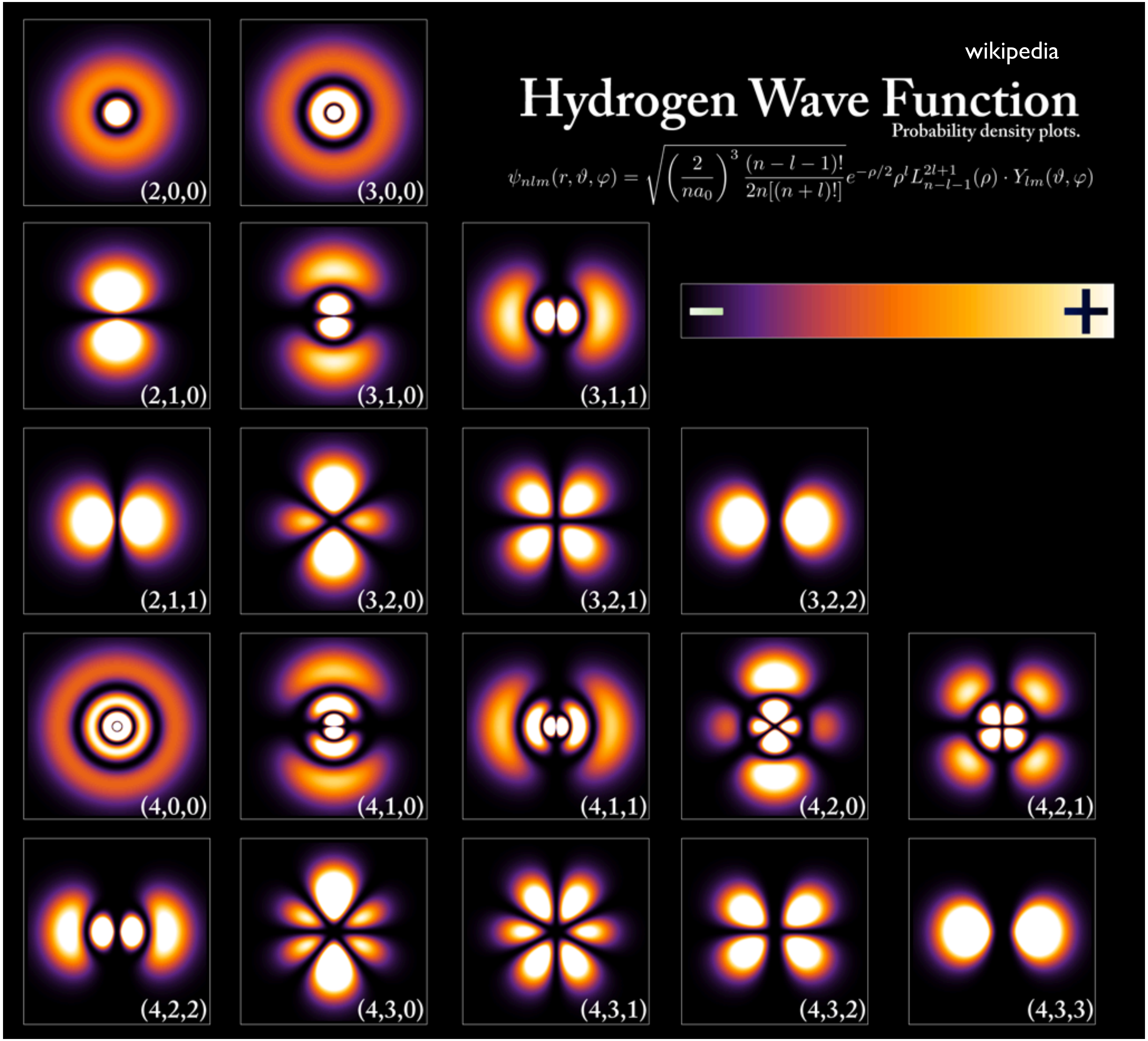
$$H(\rho) = L_{n-l-1}^{(2l+1)}(\rho)$$

$$L_n^{\alpha}(\rho) = \sum_{m=0} \begin{pmatrix} n+\alpha \\ n-m \end{pmatrix} \frac{(-\rho)^m}{m!}$$

n	l	m_l	$R(r)$	$\Theta(\theta)$	$\Phi(\phi)$
1	0	0	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	0	0	$\frac{1}{(2a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	1	0	$\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\sqrt{\frac{3}{2}} \cos\theta$	$\frac{1}{\sqrt{2\pi}}$
2	1	±1	$\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\mp\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	0	0	$\frac{2}{(3a_0)^{3/2}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
3	1	0	$\frac{8}{9\sqrt{2}(3a_0)^{3/2}} \left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right) e^{-r/3a_0}$	$\sqrt{\frac{3}{2}} \cos\theta$	$\frac{1}{\sqrt{2\pi}}$
3	1	±1	$\frac{8}{9\sqrt{2}(3a_0)^{3/2}} \left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right) e^{-r/3a_0}$	$\mp\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	2	0	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\sqrt{\frac{5}{8}}(3\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}$
3	2	±1	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\mp\sqrt{\frac{15}{4}} \sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	2	±2	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{\sqrt{15}}{4} \sin^2\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$



http://ne.phys.kyushu-u.ac.jp/seminar/MicroWorld2_E/2Part3_E/2P32_E/hydrogen_atom_E.htm


wikipedia
Hydrogen Wave Function
Probability density plots.
$\psi_{nlm}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{lm}(\vartheta,\varphi)$
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