<Lecture 3 Appendix – Hydrogen atom SE>

$$\boxed{\hat{H}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{4\pi\varepsilon_0 r}\psi = E\psi}$$ SE

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

$$\Rightarrow -\frac{\hbar^2}{2mr^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \left[\frac{e^2}{4\pi\varepsilon_0 r} + E\right]\psi = 0$$

$\times\ 2mr^2$, substitute $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$, $\div RY$

$$\Rightarrow \underbrace{-\frac{\hbar^2}{R(r)}\left[\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)R(r)\right]}_{= -\hbar^2 \ell(\ell+1)} \underbrace{- \frac{\hbar^2}{Y(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]}_{= \hbar^2\ell(\ell+1)} = 0$$

✓ Blue part : Separation of variables again $Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$

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

$\times\sin^2\theta$, $Y = \Theta\Phi$, $\div\Theta\Phi$

$$\longrightarrow \underbrace{\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \ell(\ell+1)\sin^2\theta}_{= m^2} + \underbrace{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}_{= -m^2} = 0$$

– ϕ part: Note that azimuthal angle is periodic $\Rightarrow$ $\Phi(\phi)$ should be identical with $\Phi(\phi+2\pi)$ ↗ Boundary Condition

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \Rightarrow \Phi(\phi) = e^{im\phi} \text{ or } e^{-im\phi} \quad \text{(special solution)}$$

$$\boxed{\text{From the B.C., } \begin{cases}\Phi(\phi) = e^{\pm im\phi} \\ \Phi(\phi+2\pi) = e^{\pm im\phi \pm im2\pi}\end{cases} \Rightarrow e^{\pm 2\pi i m} = 1 = \cos 2\pi m \pm i\sin 2\pi m \quad \Rightarrow m = 0, \pm1, \pm2, \cdots}$$

– θ part : Let $x = \cos\theta$. Then $\begin{cases} dx = -\sin\theta\, d\theta \Rightarrow \frac{dx}{d\theta} = -\sin\theta \\ 0 \le \theta \le \pi \Rightarrow -1 \le x \le 1\end{cases}$

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

$$\hookrightarrow \sin\theta\frac{d}{dx}\frac{dx}{d\theta}\left(\sin\theta\frac{dx}{d\theta}\frac{d\Theta}{dx}\right) + \ell(\ell+1)\Theta\cdot(1-x^2) = m^2\Theta$$

$$\hookrightarrow \sin^2\theta\frac{d}{dx}\left(\sin^2\theta\frac{d\Theta}{dx}\right) + \ell(\ell+1)\Theta(1-x^2) = m^2\Theta$$

$\div\sin^2\theta$ (equal to $\div(1-x^2)$)

$$\hookrightarrow \frac{d}{dx}\left((1-x^2)\frac{d\Theta}{dx}\right) + \left[\ell(\ell+1) - \frac{m^2}{1-x^2}\right]\Theta = 0$$

$$\hookrightarrow \boxed{(1-x^2)\frac{d^2\Theta}{dx^2} - 2x\frac{d\Theta}{dx} + \left[\ell(\ell+1) - \frac{m^2}{1-x^2}\right]\Theta = 0}$$ Well-known DE

Associated Legendre polynomials

From Wikipedia, the free encyclopedia

In mathematics, the **associated Legendre polynomials** are the canonical solutions of the **general Legendre equation**

$$(1-x^2)\frac{d^2}{dx^2}P_\ell^m(x) - 2x\frac{d}{dx}P_\ell^m(x) + \left[\ell(\ell+1) - \frac{m^2}{1-x^2}\right]P_\ell^m(x) = 0,$$

$\therefore\ \Theta(\theta) = P_\ell^m(x)$, Associated Legendre Polynomials

$$\begin{cases}\ell = 0, 1, 2, \cdots \\ m = 0, \pm1, \cdots, \pm\ell\end{cases}$$ (quantization condition from the DE)

Reparameterization in terms of angles [edit]

These functions are most useful when the argument is reparameterized in terms of angles, letting $x = \cos\theta$:

$$P_\ell^m(\cos\theta) = (-1)^m (\sin\theta)^m \frac{d^m}{d(\cos\theta)^m}\left(P_\ell(\cos\theta)\right)$$

Using the relation $(1-x^2)^{1/2} = \sin\theta$, the list given above yields the first few polynomials, parameterized this way, as:

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

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

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

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

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

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

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

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

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

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

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

$P_4^1(\cos\theta) = -\frac{5}{2}(7\cos^3\theta - 3\cos\theta)\sin\theta$

$P_4^2(\cos\theta) = \frac{15}{2}(7\cos^2\theta - 1)\sin^2\theta$

$P_4^3(\cos\theta) = -105\cos\theta\sin^3\theta$

$P_4^4(\cos\theta) = 105\sin^4\theta$

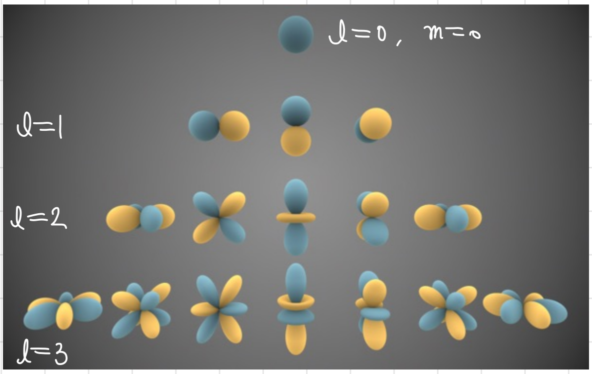
✓ Associated Legendre polynomials!

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

$= P_\ell^m(x)\, e^{im\phi}$. (some normalization factor)

is called spherical harmonics,

$$Y_\ell^m(\theta,\phi) = (-1)^m \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\; P_\ell^{|m|}(\cos\theta)\, e^{im\phi}$$



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✓ Orthogonality

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\;\; Y_\ell^m(\theta,\phi)^* \, Y_n^k(\theta,\phi) = \langle \ell, m | n, k\rangle = \delta_{\ell n}\delta_{mk}$$

✓ Digression. $|m| \le \ell$ using Angular Momentum

Since rotational kinetic energy is $\hat{K} = \frac{1}{2}I\omega^2 = \frac{\hat{L}^2}{2I}$ ($I = mr^2$; moment of inertia of an electron)

$$\Rightarrow -\frac{\hbar^2}{2mr^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] = \frac{\hat{L}^2}{2mr^2}$$

$$\boxed{\therefore\; \hat{L}^2 = -\hbar^2\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]}$$

$$\boxed{\hat{L}^2 Y_\ell^m(\theta,\phi) = -\hbar^2\left[\cancel{\frac{\partial}{\partial r}\left(r^2\frac{\partial Y_\ell^m}{\partial r}\right)} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_\ell^m}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y_\ell^m}{\partial\phi^2}\right] = \hbar^2\ell(\ell+1)Y_\ell^m(\theta,\phi)}$$ (From the sep. of var.)

(Y has no r-dependence)

✓ z-component of angular momentum, $\hat{L}_z$

Since $\vec{L} = \vec{r}\times\vec{p}$, $L_z = xp_y - yp_x$ (classically) $\longrightarrow \hat{L}_z = x\left(-i\hbar\frac{\partial}{\partial y}\right) - y\left(-i\hbar\frac{\partial}{\partial x}\right) = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

In spherical coordinates, ($x = r\sin\theta\cos\phi$ and $y = r\sin\theta\sin\phi$)

$$\begin{cases} \dfrac{\partial}{\partial y} = \dfrac{\partial}{\partial r}\dfrac{\partial r}{\partial y} + \dfrac{\partial}{\partial\theta}\dfrac{\partial\theta}{\partial y} + \dfrac{\partial}{\partial\phi}\dfrac{\partial\phi}{\partial y} = \sin\theta\sin\phi\dfrac{\partial}{\partial r} + \dfrac{\cos\theta\sin\phi}{r}\dfrac{\partial}{\partial\theta} + \dfrac{\cos\phi}{r\sin\theta}\dfrac{\partial}{\partial\phi} \\ \dfrac{\partial}{\partial x} = \dfrac{\partial}{\partial r}\dfrac{\partial r}{\partial x} + \dfrac{\partial}{\partial\theta}\dfrac{\partial\theta}{\partial x} + \dfrac{\partial}{\partial\phi}\dfrac{\partial\phi}{\partial x} = \sin\theta\cos\phi\dfrac{\partial}{\partial r} + \dfrac{\cos\theta\cos\phi}{r}\dfrac{\partial}{\partial\theta} - \dfrac{\sin\phi}{r\sin\theta}\dfrac{\partial}{\partial\phi} \end{cases}$$

$$\Rightarrow \hat{L}_z = -i\hbar\left[+\cos^2\phi\frac{\partial}{\partial\phi} + \sin^2\phi\frac{\partial}{\partial\phi}\right] = -i\hbar\frac{\partial}{\partial\phi}$$ (only ϕ-dep.)

$\Rightarrow \hat{L}_z Y_\ell^m(\theta,\phi) = -i\hbar \cdot im\, Y_\ell^m(\theta,\phi) = m\hbar\, Y_\ell^m(\theta,\phi)$, $\boxed{\hat{L}_z^2 Y_\ell^m(\theta,\phi) = m^2\hbar^2 Y_\ell^m(\theta,\phi)}$

↳ differentiation on $\Phi(\phi) = e^{im\phi}$

✱✱ Therefore

$$(\hat{L}^2 - \hat{L}_z^2)Y_\ell^m(\theta,\phi) = [\ell(\ell+1) - m^2]\hbar^2 Y_\ell^m(\theta,\phi) = \underbrace{(\hat{L}_x^2 + \hat{L}_y^2)Y_\ell^m(\theta,\phi)}_{\ge 0}$$

$\therefore\; \ell(\ell+1) \ge m^2$, $|m| \le \ell$ $\blacksquare$

✓ Spherical coordinates

$$\begin{cases} dx = \sin\theta\cos\phi\, dr + \cos\theta\cos\phi\,(r\,d\theta) - \sin\phi\,(r\sin\theta\, d\phi) \\ dy = \sin\theta\sin\phi\, dr + \cos\theta\sin\phi\,(r\,d\theta) + \cos\phi\,(r\sin\theta\, d\phi) \\ dz = \cos\theta\, dr - \sin\theta\,(r\,d\theta) \end{cases} \Rightarrow \begin{bmatrix} dx \\ dy \\ dz \end{bmatrix} = \begin{bmatrix} \sin\theta\cos\phi & \cos\theta\cos\phi & -\sin\phi \\ \sin\theta\sin\phi & \cos\theta\sin\phi & \cos\phi \\ \cos\theta & -\sin\theta & 0 \end{bmatrix} \begin{bmatrix} dr \\ r\,d\theta \\ r\sin\theta\, d\phi \end{bmatrix}$$

Reverse into

$$\begin{bmatrix} dr \\ r\,d\theta \\ r\sin\theta\, d\phi \end{bmatrix} = \begin{bmatrix} \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \\ \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0 \end{bmatrix} \begin{bmatrix} dx \\ dy \\ dz \end{bmatrix}$$

$$\Rightarrow \frac{\partial r}{\partial x} = \sin\theta\cos\phi,\quad \frac{\partial r}{\partial y} = \sin\theta\sin\phi,\quad \frac{\partial\theta}{\partial x} = \frac{\cos\theta\cos\phi}{r},\quad \frac{\partial\theta}{\partial y} = \frac{\cos\theta\sin\phi}{r},\quad \frac{\partial\phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta},\quad \frac{\partial\phi}{\partial y} = \frac{\cos\phi}{r\sin\theta}$$

✓ Red part : radial part — Series expansion

$$-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \left[\frac{e^2}{4\pi\varepsilon_0 r} + E\right]R(r) + \frac{\hbar^2 l(l+1)}{2mr^2}R(r) = 0$$

Step 1. $u(r) = rR(r)$ transformation. Then

$$\begin{cases} \frac{d^2u}{dr^2} = \frac{d}{dr}\cdot\frac{du}{dr} = \frac{d}{dr}\left(R + r\frac{dR}{dr}\right) = \frac{dR}{dr} + \frac{dR}{dr} + r\frac{d^2R}{dr^2} = r\frac{d^2R}{dr^2} + 2\frac{dR}{dr} \\ \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{1}{r^2}\left(2r\frac{dR}{dr} + r^2\frac{d^2R}{dr^2}\right) = \frac{1}{r}\left(r\frac{d^2R}{dr^2} + 2\frac{dR}{dr}\right) = \frac{1}{r}\frac{d^2u}{dr^2} \end{cases}$$

$\times r$

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \underbrace{\left[-\frac{e^2}{4\pi\varepsilon_0 r} + \underbrace{\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}}_{\text{centrifugal term}}\right]}_{\text{effective potential}} u = Eu}$$

effective potential

centrifugal term (due to the orbital motion)

Step 2. Substitutions $\boxed{K = \frac{\sqrt{-2mE}}{\hbar},\quad \rho = Kr,\quad \rho_0 = \frac{me^2}{2\pi\varepsilon_0\hbar^2 K}}$

$\times\left(-\frac{2m}{\hbar^2}\right)$

$$K^2\frac{d^2u}{d(Kr)^2} + \left[\frac{me^2}{2\pi\varepsilon_0\hbar\cdot\rho/K} - \frac{l(l+1)}{\rho^2/K^2}\right]u = \underbrace{-\frac{2mE}{\hbar^2}}_{K^2} u$$

$\div K^2$

$$\frac{d^2u}{d\rho^2} + \left[\frac{\rho_0}{\rho} - \frac{l(l+1)}{\rho^2}\right]u = u, \qquad \boxed{\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u}$$

Step 3. Asymptotic behaviors

① $\rho\to\infty$ limit : $\rho^{-1}, \rho^{-2} \to 0$

$$\frac{d^2u}{d\rho^2} \doteq u, \qquad u(\rho) = \cancel{Ae^{\rho}} + Be^{-\rho} \qquad \therefore\ u(\rho) \propto e^{-\rho}$$

$\to\infty$ as $\rho\to\infty$

② $\rho\to 0$ limit : ρ^{-2} term dominates

$$\frac{d^2u}{d\rho^2} \doteq \frac{l(l+1)}{\rho^2}u$$

✓ Try $u(\rho) = \rho^k$. Then $k(k-1)\rho^{k-2} = \frac{l(l+1)}{\rho^2}\rho^k \Rightarrow k(k-1) = l(l+1)$

$\therefore\ u(\rho) = \rho^{l+1}$ or $\cancel{\rho^{-l}}$ $\to\infty$ as $\rho\to 0$, $u(\rho) \propto \rho^{l+1}$

$$\Rightarrow \boxed{u(\rho) = e^{-\rho}\rho^{l+1}v(\rho)}$$

Step 4. Yield equation about $v(\rho)$

$$\begin{cases} \dfrac{du}{d\rho} = -e^{-\rho}\rho^{l+1}v + \dfrac{l+1}{\rho}\cdot e^{-\rho}\rho^{l+1}v + e^{-\rho}\rho^{l+1}\dfrac{dv}{d\rho} = e^{-\rho}\rho^{l+1}\left[\left(\dfrac{l+1}{\rho}-1\right)v + \dfrac{dv}{d\rho}\right] \\ \dfrac{d^2u}{d\rho^2} = \left[-e^{-\rho}\rho^{l+1} + \dfrac{l+1}{\rho}e^{-\rho}\rho^{l+1}\right]\left[\left(\dfrac{l+1}{\rho}-1\right)v + \dfrac{dv}{d\rho}\right] + e^{-\rho}\rho^{l+1}\left[\dfrac{d^2v}{d\rho^2} + \dfrac{dv}{d\rho}\left(\dfrac{l+1}{\rho}-1\right) - \dfrac{l+1}{\rho^2}v\right] \end{cases}$$

$$= \cancel{e^{-\rho}\rho^{l+1}}\left[\frac{d^2v}{d\rho^2} + \frac{dv}{d\rho}\left(\frac{l+1}{\rho}-1-1+\frac{l+1}{\rho}\right) + v\left(\cancel{-\frac{l+1}{\rho^2}}\cancel{+1} - \frac{l+1}{\rho} + \cancel{\frac{(l+1)^2}{\rho^2}} - \frac{l+1}{\rho}\right)\right]$$

$$= \left[\cancel{1} - \frac{\rho_0}{\rho} + \cancel{\frac{l(l+1)}{\rho^2}}\right]\cdot \cancel{e^{-\rho}\rho^{l+1}}v$$

$$\Rightarrow \frac{d^2v}{d\rho^2} + 2\left(\frac{l+1}{\rho}-1\right)\frac{dv}{d\rho} + \frac{\rho_0-2l-2}{\rho}v = 0, \quad \boxed{\rho\frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0}$$

Step 5. Take series expansion of $v(\rho)$

Let $v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j = c_0 + c_1\rho + c_2\rho^2 + \cdots$

$$\begin{cases} \dfrac{dv}{d\rho} = c_1 + 2c_2\rho^1 + 3c_3\rho^2 + \cdots = \sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j = \sum_{j=0}^{\infty} j c_j \rho^{j-1} \\ \dfrac{d^2v}{d\rho^2} = 2\cdot 1\, c_2 + 3\cdot 2 c_3\rho + \cdots = \sum_{j=0}^{\infty}(j+1)j\, c_{j+1}\rho^{j-1} \end{cases}$$

$$\Rightarrow \sum_{j=0}^{\infty}\rho^j \underbrace{\left[(j+1)j\,c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(l+1)]c_j\right]}_{=0} = 0$$

↳ Recurrence relation $c_{j+1} = \dfrac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}c_j$

Step 6. "Stopping condition"

Suppose that this series expansion does not end as $j\to\infty$. Then $\begin{cases} c_{j+1} \sim \dfrac{2}{j}c_j \\ c_j \sim \dfrac{2^j}{j!}c_0 \end{cases}$

$\Rightarrow v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j \doteqdot \sum_{j=0}^{\infty}\dfrac{(2\rho)^j}{j!} = e^{2\rho} \to \infty$ as $\rho\to\infty$

$\Rightarrow$ This is contradiction.

$\Rightarrow$ Therefore, the power series must be truncated at some point.

√ Suppose that $c_N = 0$ and $c_{N-1} \neq 0$ for some N.

$$c_N = \frac{2(N+l)-\rho_0}{N(N+2l+1)}c_{N-1} = 0 \qquad \therefore \rho_0 = 2(N+l)$$

Define n (principal quantum number) $\equiv N+l$. Since $N \geq 1$, $l = 0, 1, \cdots, n-1$. Moreover,

$$\rho_0 = 2n = \frac{me^2}{2\pi\varepsilon_0\hbar^2 K} \Rightarrow K^2 = \left(\frac{me^2}{4\pi\varepsilon_0\hbar^2}\right)^2\cdot\frac{1}{n^2} = -\frac{2mE}{\hbar^2}$$

$$\boxed{\therefore E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\cdot\frac{1}{n^2} \qquad n = 1, 2, 3, \cdots)}$$ Hydrogen atomic orbital energy level