# DEVELOPMENT AND SOLUTION TO TISE - COULOMB - 3D

To take advantage of the spherical symmetry of the Coulomb ($\frac{-1}{r}$) potential, we have written the TISE as:

(still a partial diff eq in 3 vars)

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

We will do now SEPARATION OF VARIABLES and look for solutions of the form:

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

(we'll see that this allows us to split TISE into 3 ordinary differ. eq's)

Thus TISE becomes:

$$-\frac{\hbar^2}{2\mu}\underbrace{\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R\Theta\Phi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial R\Theta\Phi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 R\Theta\Phi}{\partial\varphi^2}\right]}_{\nabla^2 R\Theta\Phi}+V(r)R\Theta\Phi=E R\Theta\Phi$$

doing partial derivatives and using $\frac{\partial R}{\partial r}=\frac{dR}{dr}$ ... (by definition: $R$ is function of $r$ only):

$$-\frac{\hbar^2}{2\mu}\left[\frac{\Theta\Phi}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R\Phi}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{R\Theta}{r^2\sin^2\theta}\frac{d^2\Phi}{d^2\varphi}\right]+V(r)\cdot R\Theta\Phi=E R\Theta\Phi$$

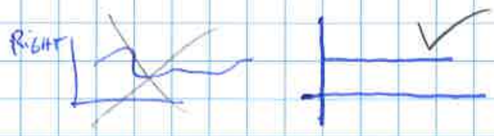
To separate this eq. into 2 independent sides, we $\times\ \dfrac{-2\mu r^2\sin^2\theta}{R\Theta\Phi\,\hbar^2}$

$\Longrightarrow$

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

Reordering terms we get to:

$$\underbrace{\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}}_{\text{DOES NOT DEPEND ON } \theta, r} = \underbrace{-\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta\left[E-V(r)\right]}_{\text{DOES NOT DEPEND ON } \varphi}$$


(have to be = for all $r,\theta,\varphi$)

Because the two sides of the equation depend on different variables, they both have to be constant and equal to the same ("separation") CONSTANT.

We'll take this constant $\overset{(*)}{=} -m_\ell^2$ so the left side becomes:

$$\boxed{\frac{d^2\Phi}{d\varphi^2} = -m_\ell^2\,\Phi}$$

EQ. I($\varphi$)

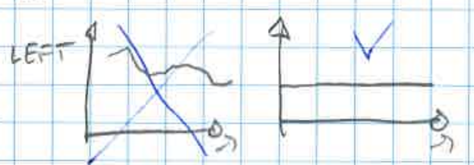
(*) for "convenience", we'll see why.

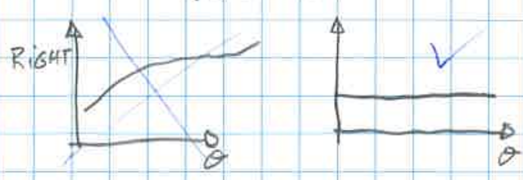
Dividing the right side by $\sin^2\theta$:

$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2\left[E-V(r)\right] = -\frac{m_\ell^2}{\sin^2\theta}$$

Reordering/transposing terms:

$$\underbrace{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left[E-V(r)\right]}_{\text{DEPENDS ON } r \text{ ONLY}} = \underbrace{\frac{m_\ell^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)}_{\text{DEPENDS ON } \theta \text{ ONLY}}$$




Again, because each side of the equation depends on a different variable, and they have to be = for any $(r,\theta)$, BOTH SIDES MUST EQUAL A CONSTANT.

We'll take this ~~separation~~ constant $= \ell(\ell+1)$

(again for convenience, we'll see why. SOMEONE HAS GONE THROUGH THIS BEFORE!)

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Then we get two more equations, one for $\theta$ and one for $r$:

$$\boxed{-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{m_\ell^2\,\Theta}{\sin^2\theta}=\ell(\ell+1)\Theta} \quad \boxed{\text{EQ. II }(\theta)}$$

$$\boxed{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-V(r)\right]R=\ell(\ell+1)\frac{R}{r^2}} \quad \boxed{\text{EQ. III }(r)}$$

Note that:

- $\Psi=R\Theta\Phi$ works, it has separated the TISE (partial dif. eq.) into THREE ORDINARY DIFF. EQ's (1 var each): I, II, III
- The separation constants $m_\ell$ and $\ell$ have become related in the process (they both appear in EQ II ($\theta$)).
- Recall $E$ was the separation constant of time vs. position (sec 5.5). The separation constants $E$ and $\ell$ are also related, as they both appear in EQ III ($r$).

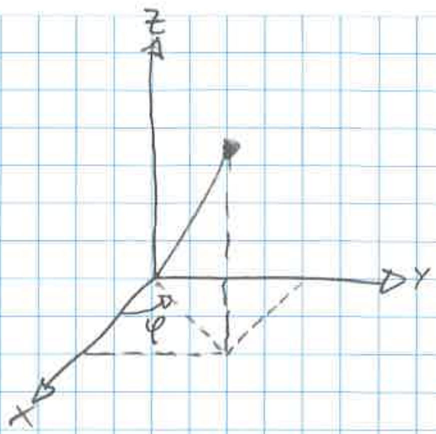
When we solve these three equations we will find that:

- EQ I ($\varphi$) has VALID solutions only for CERTAIN values of $m_\ell$.
- (given the valid $m_\ell$:) EQ II ($\theta$) has VALID solutions only for CERTAIN values of $\ell$.
- (given the valid $\ell$:) EQ III ($r$) has VALID solutions only for CERTAIN values of $E$.

"VALID" $\Longleftrightarrow$ finite, single-valued, continuous.

"CERTAIN" $\Rightarrow$ discrete, integer $\Rightarrow$ QUANTIZATION OF ENERGY (AND ANGULAR MOMENTUM)

$$EQ.\ I(\varphi):\quad \frac{d^2\Phi}{d\varphi^2} = -m_\ell^2\,\Phi$$




This is the simplest of the 3 EQ's.

We'll take the solution $\Phi(\varphi) = e^{i m_\ell \varphi}$

By construction of spherical coordinates: $0 = 2\pi$ (one turn, same place / same angle)

The wave function and thus $\Phi$ MUST BE SINGLE-VALUED:

$$\Phi(0) = \Phi(2\pi) \Rightarrow e^{i m_\ell 0} = e^{i m_\ell 2\pi} \Rightarrow 1 = \cos(2\pi m_\ell) + i\,\mathrm{sen}(2\pi m_\ell)$$

real part: $1 = \cos(2\pi m_\ell)$

imaginary: $0 = \mathrm{sen}(2\pi m_\ell)$

$$\boxed{\begin{array}{c} m_\ell = 0, \pm 1, \pm 2, \ldots \\ \text{or} \\ |m_\ell| = 0, 1, 2, 3, \ldots \end{array}}$$

Notation: the corresponding VALID (single-val) solutions are subscripted:

(I.1) $$\boxed{\Phi_{m_\ell}(\varphi) = e^{i m_\ell \varphi} \quad ; \quad |m_\ell| = 0, 1, 2, 3 \ldots}$$

And $m_\ell$ is what we call a QUANTUM NUMBER.

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To solve EQ. II ($\theta$), we first change to the independent variable: $z = \cos\theta$ $\left(\sin\theta = \sqrt{1-z^2};\ \sin^2\theta = 1-z^2;\ \frac{d}{d\theta} = -\sqrt{1-z^2}\,\frac{d}{dz}\right)$

$$\Rightarrow \frac{d}{dz}\left[(1-z^2)\frac{d\Theta}{dz}\right] + \left[l(l+1) - \frac{m_l^2}{1-z^2}\right]\Theta = 0 \qquad \text{II.1}$$

This beast is called the ASSOCIATED LEGENDRE DIFFERENTIAL EQUATION.
(the Legendre differential equation is the $m_l = 0$ case)

It's solutions are the ASSOCIATED LEGENDRE FUNCTIONS:

$$\Theta_{lm_l}(z) = (1-z^2)^{\frac{|m_l|}{2}} \frac{d^{|m_l|} P_l(z)}{dz^{|m_l|}} \qquad \text{II.2}$$

where $P_l(z)$ are the LEGENDRE POLYNOMIALS, which satisfy a somewhat simpler differential equation, the LEGENDRE DIFFERENTIAL EQ:

$$(1-z^2)\frac{d^2 P_l}{dz^2} - 2z\frac{dP_l}{dz} + l(l+1)P_l = 0 \qquad \text{II.3}$$

Indeed if we differentiate II.3 $|m_l|$ times with respect to $z$ we get:

$$(1-z^2)\frac{d^{|m_l|+2} P_l}{dz^{|m_l|+2}} - 2z(|m_l|+1)\frac{d^{|m_l|+1} P_l}{dz^{|m_l|+1}} + \left[l(l+1) - |m_l|(|m_l|+1)\right]\frac{d^{|m_l|} P_l}{dz^{|m_l|}} = 0$$

(where we've applied chain rule a bunch of times and regrouped terms)

II.4, from $P_l$ equation (II.3)

Take II.1 now and plug in this form for $\Theta$:

$$\Theta_{\ell m_\ell} = (1-z^2)^{|m_\ell|/2}\,\Gamma \quad \Longrightarrow$$

$$(1-z^2)\frac{d^2\Gamma}{dz^2} - 2(|m_\ell|+1)\,z\frac{d\Gamma}{dz} + \Big[\ell(\ell+1) - |m_\ell|(|m_\ell|+1)\Big]\Gamma = 0$$

(II.5), from $\Theta_{\ell m_\ell}$ equation (II.1)

COMPARING II.4 AND II.5 $\Longrightarrow \Gamma = \dfrac{d^{|m_\ell|}P_\ell}{dz^{|m_\ell|}}$ ;

- which proves the relation between solutions to the ASSOCIATED LEGENDRE ($\Theta_{\ell m_\ell}$) AND LEGENDRE ($P_\ell$) EQUATIONS (II.1 & II.3, respectively)
- In other words, we just proved that if $P_\ell$ are good solutions (to a simpler eq.), $\Theta_{\ell m_\ell}$ are also good solutions (to our original eq.).
- Now let's find $P_\ell$ by solving II.3 with the POWER SERIES method:

$$P_\ell(z) = \sum_{k=0}^{\infty} a_k z^k$$

Plugging this into II.3 and gathering terms with the same power of z yields:

$$\sum_{k=0}^{\infty}\Big[\big[\ell(\ell+1)-k(k+1)\big]z^k a_k + k(k-1)a_k z^{k-2}\Big] = 0 \qquad \left(\frac{dP}{dz} = \sum k a_k z^{k-1},\quad \frac{d^2P}{dz^2} = \sum k(k-1)a_k z^{k-2}\right)$$

Write a few terms and regroup coefficients of the same powers of z:

$k=0$ : $[\ell(\ell+1)-k(k+1)]\,z^0 a_0 + 0$

$k=1$ : $[\ell(\ell+1)-k(k+1)]\,z^1 a_1 + 0$

$k=2$ : $[\ell(\ell+1)-k(k+1)]\,z^2 a_2 + k(k-1)\,a_2 z^0$

$k=3$ : $[\ell(\ell+1)-k(k+1)]\,z^3 a_3 + k(k-1)\,a_3 z^1$

...

$$\boxed{k(k-1)a_k \text{ TURNS INTO } (j+2)(j+1)a_{j+2}}$$

→ We can rewrite the series as:

$$\sum_{j=0}^{\infty} \{ \underbrace{a_{j+2}(j+2)(j+1) + a_j[l(l+1) - j(j+1)]}_{\text{COEFFICIENT OF } z^j} \} z^j = 0$$

Because this sum has to be $=0$ for any $z$, ALL COEFFICIENTS MUST VANISH.

⇒ We thereby get to the RECURSION RELATION:

$$\boxed{a_{j+2} = a_j \frac{j(j+1) - l(l+1)}{(j+2)(j+1)}} \qquad \text{II.6}$$

Index 'jumps' by 2: | setting $a_0$ will set all the even powers.
SERIES SPLIT IN TWO: | setting $a_1$ will set all the odd powers.

- NOW is when we have to impose that the solutions are valid, i.e., that the wave functions derived from them are {finite, single-val, continuous}.
- Because the coefficients do not necessarily vanish when $j \to \infty$ ($a_{j+2} \to a_j$), the infinite series will not converge.
- For instance, at $z=1$ we have a sum of infinite terms so that

$$\Psi \propto \Theta \propto P_l \to \infty \quad \text{at } z=1 \text{ if the series is infinite (NO GOOD)}$$

TO PREVENT THIS UNPHYSICAL BEHAVIOR WE HAVE TO TRUNCATE THE SERIES:

AND
- We set one of the two arbitrary constants to 0 ($a_0 = 0$ OR $a_1 = 0$)
- We REQUIRE THAT $l$ IS INTEGER: $l = 0, 1, 2, 3 \ldots$

Because the j's in the recursion relation are integers, this will make ALL TERMS $j > l$ VANISH:

$$a_{j+2} = \frac{j(j+1) - l(l+1)}{(j+2)(j+1)} a_j$$

e.g. $l=3$, $a_0=0$, $\boxed{a_1=3}$ gives $\boxed{a_3 = -5}$ and $a_5 = a_7 = a_9 = \cdots = 0$, $a_2 = a_4 = \cdots = a_6 = 0$

e.g. $l=2$, $\boxed{a_0=1}$, $a_1=0$ gives $\boxed{a_2 = -3}$ and the rest $=0$

$\Rightarrow$ THUS THE LEGENDRE POLYNOMIALS ARE OF DEGREE $l$.

$$\boxed{P_0 = 1,\ P_1 = z,\ P_2 = 1 - 3z^2,\ P_3 = 3z - 5z^3,\ \ldots}$$

AND THAT YIELDS THE <u>ASSOC. LEGENDRE FUNCTIONS</u>, OUR SOLUTIONS!! (VIA EQ II.2 WHICH RELATES THEM):

$$\boxed{\begin{aligned}
&\Theta_{00} = 1 \qquad\qquad (\text{II}.7)\\
&\Theta_{10} = z \ ; \ \Theta_{1\pm1} = (1-z^2)^{1/2}\\
&\Theta_{20} = 1-3z^2 \ ; \ \Theta_{2\pm1} = (1-z^2)^{1/2} z \ ; \ \Theta_{2\pm2} = 1-z^2\\
&\Theta_{30} = 3z - 5z^3 \ ; \ \Theta_{3\pm1} = (1-z^2)^{1/2}(1-5z^2),\ \Theta_{3\pm2} = (1-z^2)z,\ \Theta_{3\pm3} = (1-z^2)^{3/2}
\end{aligned}}$$

- NOTE: Because $P_l$ are of $l$-th degree and $\Theta_{lm_l}$ contains their $|m_l|$-th derivative (II.2): $|m_l|$ can't be $> l$, i.e., $\boxed{m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l}$

$\Rightarrow$ WE HAVE TWO QUANTUM NUMBERS NOW, AND RELATED.

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Now let's get to the radial part of the TISE, EQ. III($r$).

- Changing to a new indep. variable $\rho = 2\beta r$
- Defining $\beta^2 = \frac{2\mu E}{\hbar^2}$
- Defining $\gamma = \frac{\mu Z e^2}{4\pi\epsilon_0 \hbar^2 \beta}$

the radial equation becomes:

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2 \frac{dR}{d\rho}\right) + \left[-\frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2} + \frac{\gamma}{\rho}\right] R = 0 \qquad \text{III.1}$$

This can't be solved with the power series method yet (would give a recursion relation with >2 coeff.), but if we take the limit $\rho \to \infty$: $\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2 \frac{dR}{d\rho}\right) = \frac{R}{4}$

we can see that has a solution $R(\rho) = e^{-\rho/2}$.

That suggests we look for solutions of the form:

$$R(\rho) = e^{-\rho/2} F(\rho) \qquad \text{III.2}$$

(analogous to "educated guess" in II.2)

Plugging that form into III.1 and rearranging:

$$\frac{d^2F}{d\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{dF}{d\rho} + \left[\frac{\gamma - 1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right] F = 0 \qquad \text{III.3}$$

We can now attempt the power series solution in a more gral. form:

$$F(\rho) = \rho^s \sum_{k=0}^{\infty} a_k \rho^k \qquad \left(\begin{array}{c}\text{This form with } \rho^s \text{ makes} \\ \text{sure that } F \text{ is finite at } \rho=0\end{array}\right)$$

Similar to what we did with the polar eq., we find derivatives of this series and plug them into III.3 to get:

$$\sum \left\{ \left[(s+k)(s+k+1) - \ell(\ell+1)\right] a_k \rho^{s+k-2} - (s+k+1-\gamma) a_k \rho^{s+k-1} \right\} = 0$$

regrouping terms with the same power of $\rho$:

$$\underbrace{\left[s(s+1)-\ell(\ell+1)\right]}_{0} a_0 \rho^{s-2} + \sum_{j=0}^{\infty} \left\{ \underbrace{\left[(s+j+1)(s+j+2)-\ell(\ell+1)\right] a_{j+1} - (s+j+1-\gamma) a_j}_{0} \right\} \rho^{s+j-1} = 0$$

All coefficients must be zero so we have to satisfy these two relations:

$$\boxed{s(s+1) - \ell(\ell+1) = 0} \qquad \text{INDICIAL EQ.} \qquad \text{III.4}$$

$$\boxed{a_{j+1} = \frac{s+j+1-\gamma}{(s+j+1)(s+j+2)-\ell(\ell+1)}\, a_j} \qquad \text{RECURSION REL.} \qquad \text{III.5}$$

III.4 has two roots $\left\{ \begin{array}{ll} \boxed{s=\ell} & \checkmark \\ s=-(\ell+1) & \times \quad \text{NOT GOOD BECAUSE WE NEED } s \geq 0 \end{array}\right.$

(to keep $F$ finite at $\rho=0$)

$$\boxed{\Rightarrow a_{j+1} = \frac{j+\ell+1-\gamma}{(j+\ell+1)(j+\ell+2)-\ell(\ell+1)}\, a_j} \qquad \text{III.5}'$$

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In principle, a priori, $\gamma$ can take any value.

However, $F(\rho)$ AND $R(\rho)$ will diverge if the series is infinite, when $\rho \to \infty$.

- AGAIN WE NEED TO TRUNCATE THE SERIES to impose "good" (finite) behavior for $F, R, \Psi$.
- REQUIRING THAT $\gamma = n$ IS INTEGER keeps only $n-(l+1)$ terms in the series.

$\boxed{\text{with } n = l+1, l+2, l+3 \ldots}$ $(j = 0, 1, 2 \ldots)$

(III.5' $= 0$ : $j_{max} + l + 1 = \gamma = n \Rightarrow j_{max} = n-(l+1)$)

e.g.
- $n=2$, $l=0$: $\boxed{a_0 = 2}$ $\left\{ \boxed{a_1 = \frac{-1}{2}\, 2 = -1} \right.$, $a_2 = a_3 = \cdots = 0$
- $n=3$, $l=1$, $a_0 = 4$ $\Rightarrow$ $\boxed{a_1 = \frac{0+1+1-3}{(0+1+1)(0+1+2)-1\cdot 2} a_0 = -\frac{1}{4} a_0 = -1}$, $a_2 = a_3 = \cdots = 0$

$\Rightarrow$ THUS $F(\rho)$ are polynomials of order $n-1$. (see definition)

$\Rightarrow$ QUANTUM NUMBERS $n$ & $l$ related: $\boxed{l = 0, 1 \ldots n-1}$

$\Rightarrow$ From the definition of $\gamma, \beta$:

$\boxed{\gamma = n = \text{INTEGER} \Rightarrow E \text{ QUANTIZED!!}}$

$$E = -\frac{\mu^2 Z^2 e^4 \hbar^2}{(4\pi\varepsilon_0)^2 \hbar^4 n^2 2\mu} = -\frac{\beta^2 \hbar^2}{2\mu}$$

$$\Rightarrow \boxed{E_n = -\frac{\mu Z^2 e^4}{(4\pi\varepsilon_0)^2\, 2\hbar^2} \cdot \frac{1}{n^2} \qquad n = 1, 2, 3 \ldots} \quad \text{(III.6)}$$

ENERGY QUANTIZATION, WITH EXACT SAME VALUES AS (EXPERIMENT) BOHR LEVELS

The $F_{n\ell}(\rho)$ are (related with assoc. Laguerre polynomials):

$$\boxed{\begin{array}{l} F_{10} = 1 \\ F_{20} = 2-\rho \;;\quad F_{21} = \rho \\ F_{30} = 6-6\rho+\rho^2 \;;\quad F_{31} = 4\rho-\rho^2 \;;\quad F_{32} = \rho^2 \\ \dots \end{array}} \qquad \text{III.7}$$

And the full radial solutions $R_{n\ell} = e^{-\rho/2} F_{n\ell}$

or in the original variables: $R_{n\ell}(r) = e^{-\frac{Zr}{na_0}} \left(\frac{Zr}{a_0}\right)^{\ell} G_{n\ell}$ III.8

(cf. defin of $\beta, \rho, \delta$)

(where $G_{n\ell}$ are polynomials similar to $F_{n\ell}$)

$$\left( F(\rho) = \rho^{\ell} \underbrace{\sum a_k \rho^k}_{G_{n\ell}} \right)$$

$$\beta = \sqrt{\frac{2\mu E}{\hbar^2}} = \frac{\mu Z e^2}{4\pi\varepsilon_0 \hbar^2} \frac{1}{n} = \frac{Z}{a_0} \frac{1}{n}$$

with $a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2}$ = radius of $n=1$ $Z=1$ Bohr orbit ($=0.529$ Å)

TWO COMMON OPTIONS IN THE LITERATURE TO EXPRESS THE FINAL WAVEFUNCTIONS:

OPTION (A): $$\boxed{\Psi_{n l m_\ell}(r,\theta,\varphi) = R_{n\ell}(r)\,\Theta_{\ell m_\ell}(\theta)\,\Phi_{m_\ell}(\varphi)}$$

OPTION (B): $$\boxed{\Psi_{n l m_\ell}(r,\theta,\varphi) = R'_{n\ell}(r)\,Y_{\ell m_\ell}(\theta,\varphi)}$$

where:

$\Phi_{m_\ell}(\varphi) = e^{i m_\ell \varphi}$ (I.1)

$\Theta_{\ell m_\ell}(\theta)$ are the ASSOCIATED LEGENDRE FUNCTIONS (see: II.2 & II.7)

$Y_{\ell m_\ell}(\theta,\varphi)$ are the SPHERICAL HARMONICS, which contain the angular part ($\theta$ and $\varphi$ together) of the wave function and thus the product: $\Theta\,\Phi$

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$$\boxed{Y_{\ell m_\ell}(\theta,\varphi) = \sqrt{\frac{(2\ell+1)}{4\pi}\,\frac{(\ell-m_\ell)!}{(\ell+m_\ell)!}}\;\Theta_{\ell m_\ell}(\theta)\,\Phi_{m_\ell}(\varphi)}$$

and where: $R'_{n\ell}$ and $R_{n\ell}$ are the {RADIAL EIGENFUNCTIONS / radial part of the wave functions} and differ only by a normalization constant.

(see III.2 & III.8)

The probability density (per unit volume, since we're in 3-D) of finding the electron at $r, \theta, \varphi$ is:

$$P(r,\theta,\varphi) = \Psi^*_{n l m_l} \Psi_{n l m_l} = \begin{cases} |R_{nl}|^2 \cdot |\Theta_{l m_l}|^2 \cdot |\Phi_{m_l}|^2 & \text{(A)} \\ |R'_{nl}|^2 \cdot |Y_{l m_l}|^2 & \text{(B)} \end{cases}$$

To normalize $\Psi$ we require that the probability of finding the $e^-$ anywhere is 1 (integrate over full volume $V$):

$$\int_V P(r,\theta,\varphi)\, dV = 1$$

where the volume element in sperical coords is $\underline{dV = r^2 \sin\theta\, d\theta\, d\varphi\, dr}$

Because we're normalizing the product of (2) functions, there's some freedom in the choice of normalization constants:

DEPENDING ON WHETHER WE CHOSE (A) OR (B):

$$\text{(A)}\quad 1 = \int_0^\infty |R_{nl}|^2 r^2\, dr \underbrace{\int_0^{2\pi} |\underbrace{\Phi_{m_l}}_{1 = e^{-im_l\varphi} \cdot e^{im_l\varphi}}|^2\, d\varphi}_{= 2\pi} \underbrace{\int_0^\pi |\Theta_{l m_l}|^2 \sin\theta\, d\theta}_{= 2 \text{ for } l = m_l = 0} = \int_0^\infty \underbrace{|R_{n0}|^2 4\pi r^2}_{\boxed{\text{RADIAL PROBABILITY DENSITY FOR } l=0 \text{ CASE!}}}\, dr$$

THIS INTEGRAL DEPENDS ON $l, m_l$

$\Rightarrow$ Normalization of $R_{nl}$ ALSO!

$\Theta$ ARE NOT NORMALIZED

(e.g. $\Theta_{00} = 1 \Rightarrow \int = -\cos\pi + \cos 0 = 2$

($\Theta_{10} = \cos\theta \Rightarrow \int = \frac{2}{3}$)

By integrating over all possible angles we project the probability density from 3D to 1D, and find the probability of finding the $e^-$ between $r$ and $r+dr$: $P_r(r)\,dr$

$$P_r(r) = |R_{n0}|^2 \cdot 4\pi r^2$$

Hence $R_{n0}$ are normalized so that $\boxed{\int_0^\infty |R_{n0}|^2 4\pi r^2\, dr = 1}$

... If we chose (B) instead, the normalization condition is

$$(B) \quad 1 = \int_0^\infty |R'_{n\ell}|^2 r^2 dr \iint |Y_{\ell m_\ell}|^2 \sin\theta \, d\theta \, d\varphi$$

but the spherical harmonics are normalized so that their integral over all angles = 1 (i.e. over $4\pi$ sterad).

That's what gives the normalization constant upfront!

$$Y_{\ell m_\ell}(\theta,\varphi) = \underbrace{\sqrt{\frac{2\ell+1}{4\pi} \cdot \frac{(\ell-m_\ell)!}{(\ell+m_\ell)!}}}_{\text{NORMALIZATION CONSTANT}} \Theta_{\ell m_\ell}(\theta) \, \Phi(\varphi)$$

$$\Rightarrow \int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi} |Y_{\ell m_\ell}|^2 \underbrace{\sin\theta \, d\theta \, d\varphi}_{d\Omega \text{ 'solid angle differential'}} = 1$$

$$\left(\text{indeed, e.g. } Y_{00} = \frac{1}{\sqrt{4\pi}}\right) \quad \frac{1}{4\pi}\int d\Omega = 1$$

$$\Rightarrow \int_0^\infty \underbrace{|R'_{n\ell}|^2 r^2}_{\text{RADIAL PROBABILITY DENSITY}} dr = 1$$

$$\boxed{P_r(r) = r^2 |R'_{n\ell}|^2}$$

THUS: $r^2 |R'_{n0}|^2 = 4\pi |R_{n0}|^2 r^2 \Rightarrow R'_{n0} = \sqrt{4\pi}\, R_{n0}$

$\left(\text{in general } R'_{n\ell} = \sqrt{\frac{4\pi}{2\ell+1} \cdot \frac{(\ell+m_\ell)!}{(\ell-m_\ell)!}}\, R_{n\ell}\right)$

IN SUMMARY:

- The radial probability density MUST BE OF THE FORM

$$P_r(r) = K\, r^2 \, |R_{n\ell}|^2 \qquad \text{where } K = \text{constant}$$

- The factor $r^2$ accounts for the radial dependence of the volume element $dV$ in spherical coordinates.
- Can be also seen as converting VOLUME density into LINEAR density:

$$\frac{\text{PROBABILITY}}{\text{UNIT VOLUME}} \times \text{AREA} = \frac{\text{PROBABILITY}}{\text{UNIT LENGTH}}$$

- No matter what value of K we choose initially!

TRUE NORMALIZATION CONSTANT IS IMPOSED BY $\int_0^\infty P_r(r)\, dr = 1$

AND BY THE ACTUAL FORM OF $|R_{n\ell}|^2$ THAT WE CHOOSE.

(see PROBLEM 3 AND EXAMPLE 7.3!)

# The Radial Wavefunction Solutions

Defining the **Bohr radius**

$$a_0 = \frac{\hbar}{\alpha mc},$$

we can compute the radial wave functions Here is a list of the first several radial wave functions

$(R_{n\ell}(r).)$ NORMALIZED SO THAT $\int_0^\infty r^2 |R_{n\ell}|^2 dr = 1$

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$$

$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$R_{20} = 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(1-\frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$R_{32} = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

$$R_{31} = \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)\left(1-\frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$$

$$R_{30} = 2\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(1-\frac{2Zr}{3a_0}+\frac{2(Zr)^2}{27a_0^2}\right) e^{-Zr/3a_0}$$

For a given principle quantum number $n$ ,the largest $\ell$ radial wavefunction is given by

$$R_{n,n-1} \propto r^{n-1} e^{-Zr/na_0}$$

The radial wavefunctions should be **normalized** as below.

$$\int_0^\infty r^2 R^*_{n\ell} R_{n\ell}\, dr = 1$$

* Example: Compute the expected values of $E$ , $L^2$ , $L_z$ , and $L_y$ in the Hydrogen state

$$\frac{1}{6}(4\psi_{100} + 3\psi_{211} - i\psi_{210} + \sqrt{10}\psi_{21-1})$$ *

The pictures below depict the probability distributions in space for the Hydrogen wavefunctions.

# Table of spherical harmonics

$(-1)^m$

This is a **table of orthonormalized spherical harmonics** that employ the Condon-Shortley phase up to degree $l = 10$. Some of these formulas give the "Cartesian" version. This assumes $x$, $y$, $z$, and $r$ are related to $\theta$ and $\varphi$ through the usual spherical-to-Cartesian coordinate transformation:

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

NORMALIZED SUCH THAT: $\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi} |Y_{lm}|^2 \operatorname{sen}\theta \, d\theta \, d\varphi = 1$

## Spherical harmonics

**l = 0**[1]

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

**l = 1**[1]

$$Y_1^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x-iy)}{r}$$
$$Y_1^{0}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\cos\theta = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\frac{z}{r}$$
$$Y_1^{1}(\theta,\varphi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x+iy)}{r}$$

**l = 2**[1]

$$Y_2^{-2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{-2i\varphi}\cdot\sin^2\theta = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)^2}{r^2}$$
$$Y_2^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta\cdot\cos\theta = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)z}{r^2}$$
$$Y_2^{0}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot(3\cos^2\theta-1) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot\frac{(2z^2-x^2-y^2)}{r^2}$$
$$Y_2^{1}(\theta,\varphi) = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta\cdot\cos\theta = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)z}{r^2}$$
$$Y_2^{2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{2i\varphi}\cdot\sin^2\theta = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)^2}{r^2}$$

**l = 3**[1]

$$Y_3^{-3}(\theta,\varphi) = \frac{1}{8}\sqrt{\frac{35}{\pi}}\cdot e^{-3i\varphi}\cdot\sin^3\theta = \frac{1}{8}\sqrt{\frac{35}{\pi}}\cdot\frac{(x-iy)^3}{r^3}$$
$$Y_3^{-2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{105}{2\pi}}\cdot e^{-2i\varphi}\cdot\sin^2\theta\cdot\cos\theta = \frac{1}{4}\sqrt{\frac{105}{2\pi}}\cdot\frac{(x-iy)^2z}{r^3}$$
$$Y_3^{-1}(\theta,\varphi) = \frac{1}{8}\sqrt{\frac{21}{\pi}}\cdot e^{-i\varphi}\cdot\sin\theta\cdot(5\cos^2\theta-1) = \frac{1}{8}\sqrt{\frac{21}{\pi}}\cdot\frac{(x-iy)(4z^2-x^2-y^2)}{r^3}$$
$$Y_3^{0}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{7}{\pi}}\cdot(5\cos^3\theta-3\cos\theta) = \frac{1}{4}\sqrt{\frac{7}{\pi}}\cdot\frac{z(2z^2-3x^2-3y^2)}{r^3}$$
$$Y_3^{1}(\theta,\varphi) = -\frac{1}{8}\sqrt{\frac{21}{\pi}}\cdot e^{i\varphi}\cdot\sin\theta\cdot(5\cos^2\theta-1) = \frac{-1}{8}\sqrt{\frac{21}{\pi}}\cdot\frac{(x+iy)(4z^2-x^2-y^2)}{r^3}$$
$$Y_3^{2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{105}{2\pi}}\cdot e^{2i\varphi}\cdot\sin^2\theta\cdot\cos\theta = \frac{1}{4}\sqrt{\frac{105}{2\pi}}\cdot\frac{(x+iy)^2z}{r^3}$$
$$Y_3^{3}(\theta,\varphi) = -\frac{1}{8}\sqrt{\frac{35}{\pi}}\cdot e^{3i\varphi}\cdot\sin^3\theta = \frac{-1}{8}\sqrt{\frac{35}{\pi}}\cdot\frac{(x+iy)^3}{r^3}$$

### l = 4[1]

$$Y_4^{-4}(\theta,\varphi) = \frac{3}{16}\sqrt{\frac{35}{2\pi}} \cdot e^{-4i\varphi} \cdot \sin^4\theta = \frac{3}{16}\sqrt{\frac{35}{2\pi}} \cdot \frac{(x-iy)^4}{r^4}$$

$$Y_4^{-3}(\theta,\varphi) = \frac{3}{8}\sqrt{\frac{35}{\pi}} \cdot e^{-3i\varphi} \cdot \sin^3\theta \cdot \cos\theta = \frac{3}{8}\sqrt{\frac{35}{\pi}} \cdot \frac{(x-iy)^3 z}{r^4}$$

$$Y_4^{-2}(\theta,\varphi) = \frac{3}{8}\sqrt{\frac{5}{2\pi}} \cdot e^{-2i\varphi} \cdot \sin^2\theta \cdot (7\cos^2\theta - 1) = \frac{3}{8}\sqrt{\frac{5}{2\pi}} \cdot \frac{(x-iy)^2 \cdot (7z^2 - r^2)}{r^4}$$

$$Y_4^{-1}(\theta,\varphi) = \frac{3}{8}\sqrt{\frac{5}{\pi}} \cdot e^{-i\varphi} \cdot \sin\theta \cdot (7\cos^3\theta - 3\cos\theta) = \frac{3}{8}\sqrt{\frac{5}{\pi}} \cdot \frac{(x-iy) \cdot z \cdot (7z^2 - 3r^2)}{r^4}$$

$$Y_4^{0}(\theta,\varphi) = \frac{3}{16}\sqrt{\frac{1}{\pi}} \cdot (35\cos^4\theta - 30\cos^2\theta + 3) = \frac{3}{16}\sqrt{\frac{1}{\pi}} \cdot \frac{(35z^4 - 30z^2r^2 + 3r^4)}{r^4}$$

$$Y_4^{1}(\theta,\varphi) = \frac{-3}{8}\sqrt{\frac{5}{\pi}} \cdot e^{i\varphi} \cdot \sin\theta \cdot (7\cos^3\theta - 3\cos\theta) = \frac{-3}{8}\sqrt{\frac{5}{\pi}} \cdot \frac{(x+iy) \cdot z \cdot (7z^2 - 3r^2)}{r^4}$$

$$Y_4^{2}(\theta,\varphi) = \frac{3}{8}\sqrt{\frac{5}{2\pi}} \cdot e^{2i\varphi} \cdot \sin^2\theta \cdot (7\cos^2\theta - 1) = \frac{3}{8}\sqrt{\frac{5}{2\pi}} \cdot \frac{(x+iy)^2 \cdot (7z^2 - r^2)}{r^4}$$

$$Y_4^{3}(\theta,\varphi) = \frac{-3}{8}\sqrt{\frac{35}{\pi}} \cdot e^{3i\varphi} \cdot \sin^3\theta \cdot \cos\theta = \frac{-3}{8}\sqrt{\frac{35}{\pi}} \cdot \frac{(x+iy)^3 z}{r^4}$$

$$Y_4^{4}(\theta,\varphi) = \frac{3}{16}\sqrt{\frac{35}{2\pi}} \cdot e^{4i\varphi} \cdot \sin^4\theta = \frac{3}{16}\sqrt{\frac{35}{2\pi}} \cdot \frac{(x+iy)^4}{r^4}$$

### l = 5[1]

$$Y_5^{-5}(\theta,\varphi) = \frac{3}{32}\sqrt{\frac{77}{\pi}} \cdot e^{-5i\varphi} \cdot \sin^5\theta$$

$$Y_5^{-4}(\theta,\varphi) = \frac{3}{16}\sqrt{\frac{385}{2\pi}} \cdot e^{-4i\varphi} \cdot \sin^4\theta \cdot \cos\theta$$

$$Y_5^{-3}(\theta,\varphi) = \frac{1}{32}\sqrt{\frac{385}{\pi}} \cdot e^{-3i\varphi} \cdot \sin^3\theta \cdot (9\cos^2\theta - 1)$$

$$Y_5^{-2}(\theta,\varphi) = \frac{1}{8}\sqrt{\frac{1155}{2\pi}} \cdot e^{-2i\varphi} \cdot \sin^2\theta \cdot (3\cos^3\theta - \cos\theta)$$

$$Y_5^{-1}(\theta,\varphi) = \frac{1}{16}\sqrt{\frac{165}{2\pi}} \cdot e^{-i\varphi} \cdot \sin\theta \cdot (21\cos^4\theta - 14\cos^2\theta + 1)$$

$$Y_5^{0}(\theta,\varphi) = \frac{1}{16}\sqrt{\frac{11}{\pi}} \cdot (63\cos^5\theta - 70\cos^3\theta + 15\cos\theta)$$

$$Y_5^{1}(\theta,\varphi) = \frac{-1}{16}\sqrt{\frac{165}{2\pi}} \cdot e^{i\varphi} \cdot \sin\theta \cdot (21\cos^4\theta - 14\cos^2\theta + 1)$$

$$Y_5^{2}(\theta,\varphi) = \frac{1}{8}\sqrt{\frac{1155}{2\pi}} \cdot e^{2i\varphi} \cdot \sin^2\theta \cdot (3\cos^3\theta - \cos\theta)$$

$$Y_5^{3}(\theta,\varphi) = \frac{-1}{32}\sqrt{\frac{385}{\pi}} \cdot e^{3i\varphi} \cdot \sin^3\theta \cdot (9\cos^2\theta - 1)$$

$$Y_5^{4}(\theta,\varphi) = \frac{3}{16}\sqrt{\frac{385}{2\pi}} \cdot e^{4i\varphi} \cdot \sin^4\theta \cdot \cos\theta$$

$$Y_5^{5}(\theta,\varphi) = \frac{-3}{32}\sqrt{\frac{77}{\pi}} \cdot e^{5i\varphi} \cdot \sin^5\theta$$

### l = 6

# H-atom: Probability densities

ANGULAR or DIRECTIONAL part of the EIGENFUNCTIONS:

$$\psi(r,\theta,\varphi) = R(r)\underline{\Theta(\theta)\Phi(\varphi)}$$

Often written in terms of SPHERICAL HARMONICS:

$$\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi)$$

Note the probability density $\psi^*_{nlm_l}\psi_{nlm_l} = R^*_{nl}R_{nl}\Theta^*_{lm_l}\Theta_{lm_l}\Phi^*_{m_l}\Phi_{m_l}$

is INDEPENDENT OF AZIMUTH: $\Phi^*_{m_l}(\varphi)\Phi_{m_l}(\varphi) = e^{-im_l\varphi}e^{im_l\varphi} = 1$

(i.e., rotational symmetry around z axis)

(i.e., we only need to study dependence with polar angle, θ)

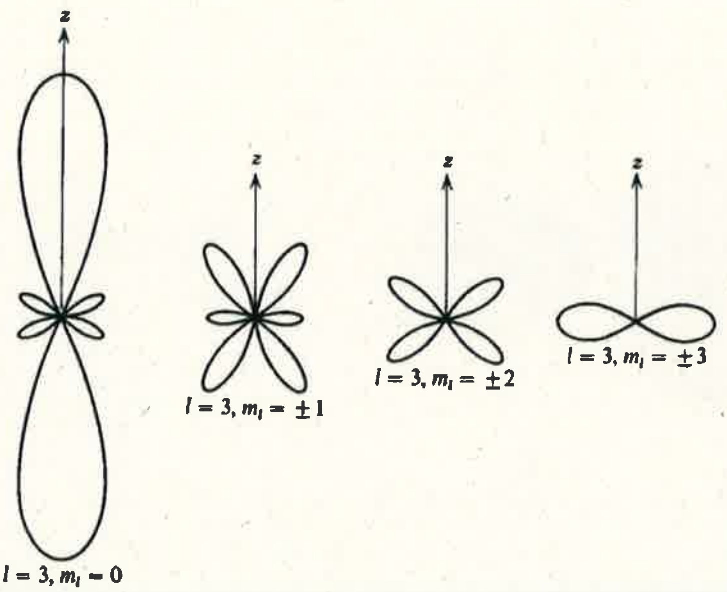


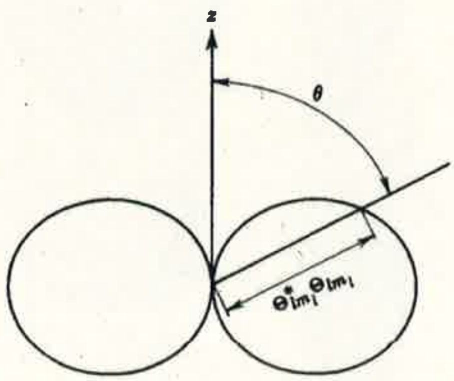


# H-atom: Probability densities

ANGULAR or DIRECTIONAL part of the EIGENFUNCTIONS

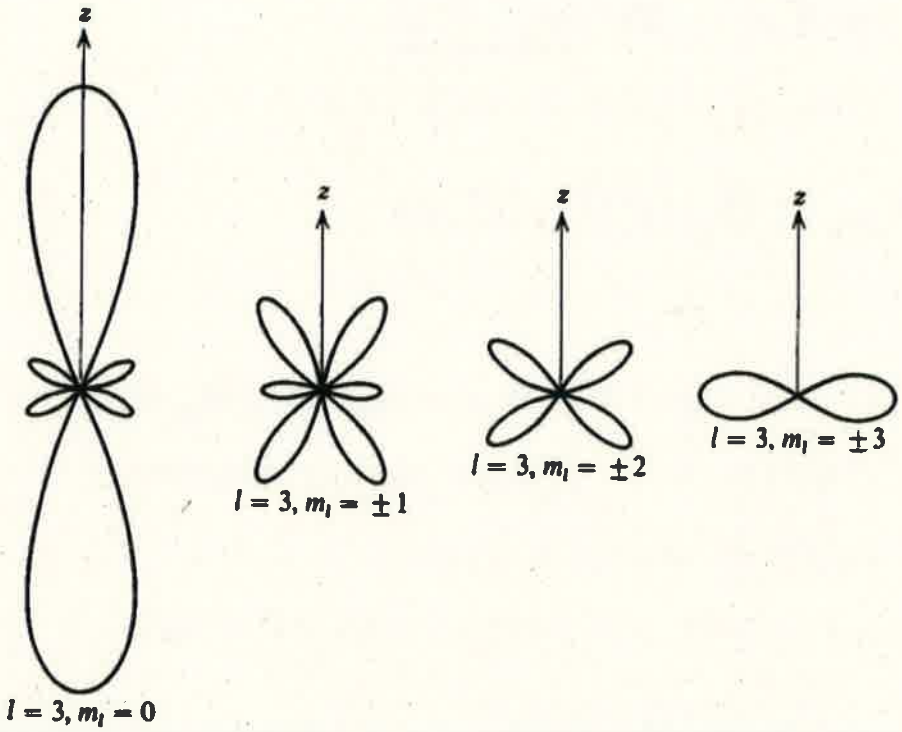
Polar diagrams: distance from origin to line proportional to probability in that direction, i.e., to $\Theta^*_{lm_l}(\theta)\Theta_{lm_l}(\theta)$ or $|Y_{lm}(\theta,\phi)|^2$.



# H-atom: Probability densities

ANGULAR or DIRECTIONAL part of the EIGENFUNCTIONS, $\ell$=3:



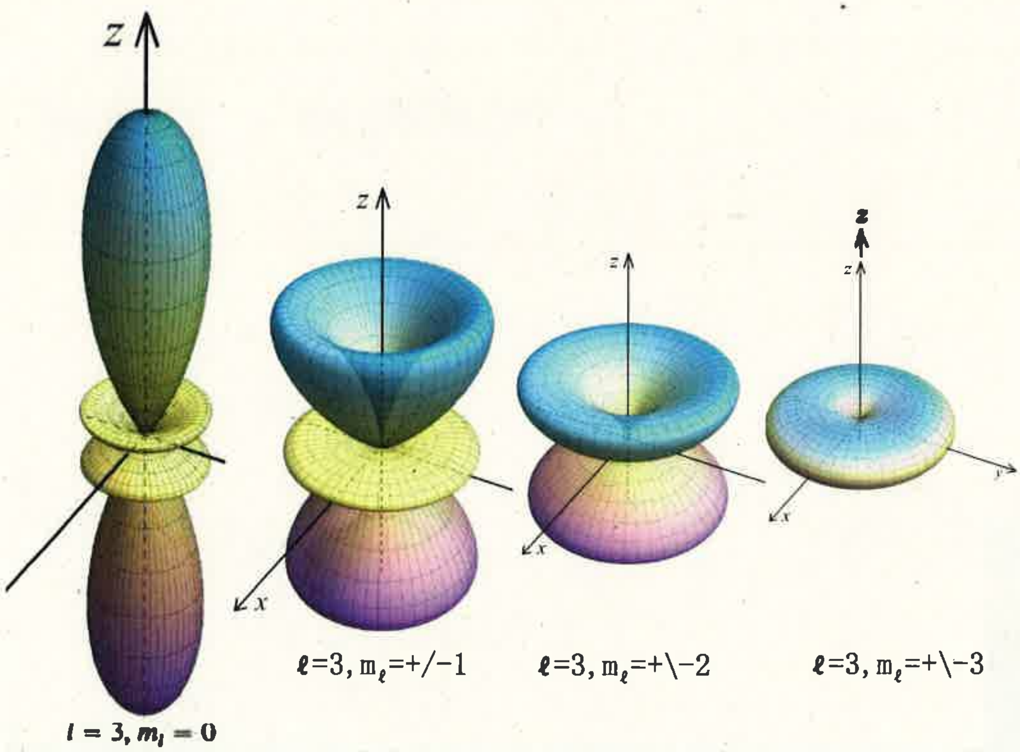

$$|Y_{lm}(\theta,\phi)|^2.$$





# H-atom: Probability densities

ANGULAR or DIRECTIONAL part of the EIGENFUNCTIONS, $\ell$=3:



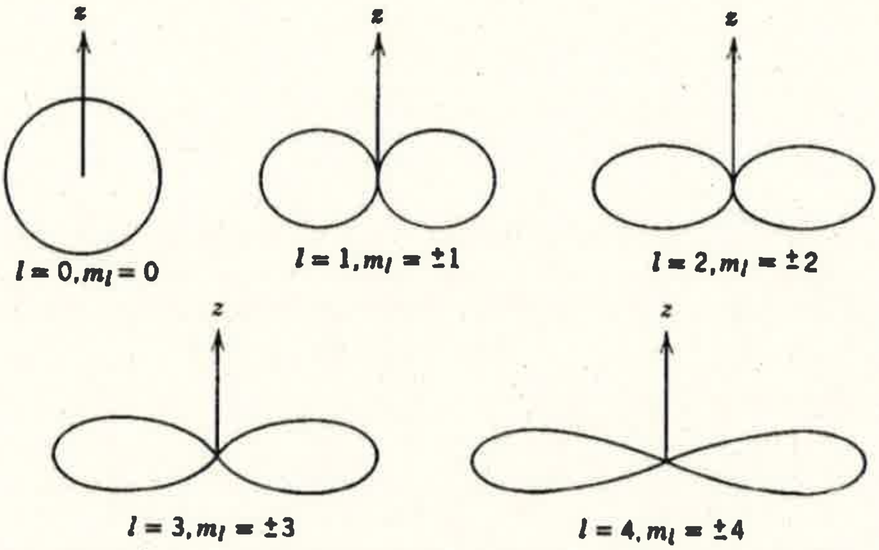

$$|Y_{lm}(\theta,\phi)|^2.$$

# H-atom: Probability densities

ANGULAR or DIRECTIONAL part of the EIGENFUNCTIONS

Note angular part depends on $\ell$ and $m_\ell$ (not n).

More polar diagrams (2D), $\ell = m_\ell$:




$|Y_{lm}(\theta,\phi)|^2$:



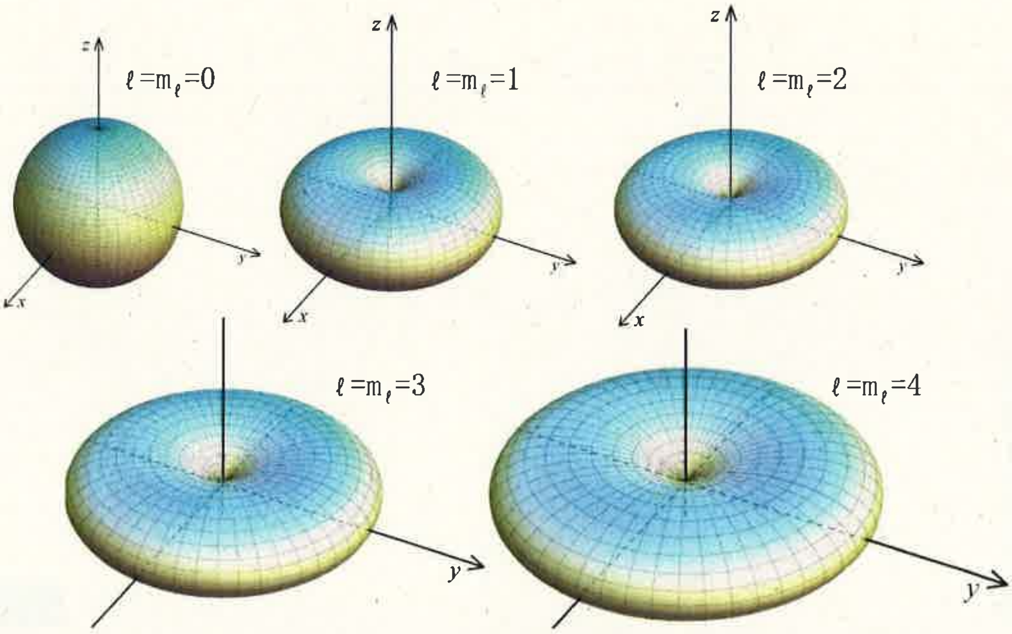


# H-atom: Probability densities

ANGULAR or DIRECTIONAL part of the EIGENFUNCTIONS

Note angular part depends on $\ell$ and $m_\ell$ (not n).

More polar diagrams (3D 'orbitals'), $\ell = m_\ell$:




$|Y_{lm}(\theta,\phi)|^2$: