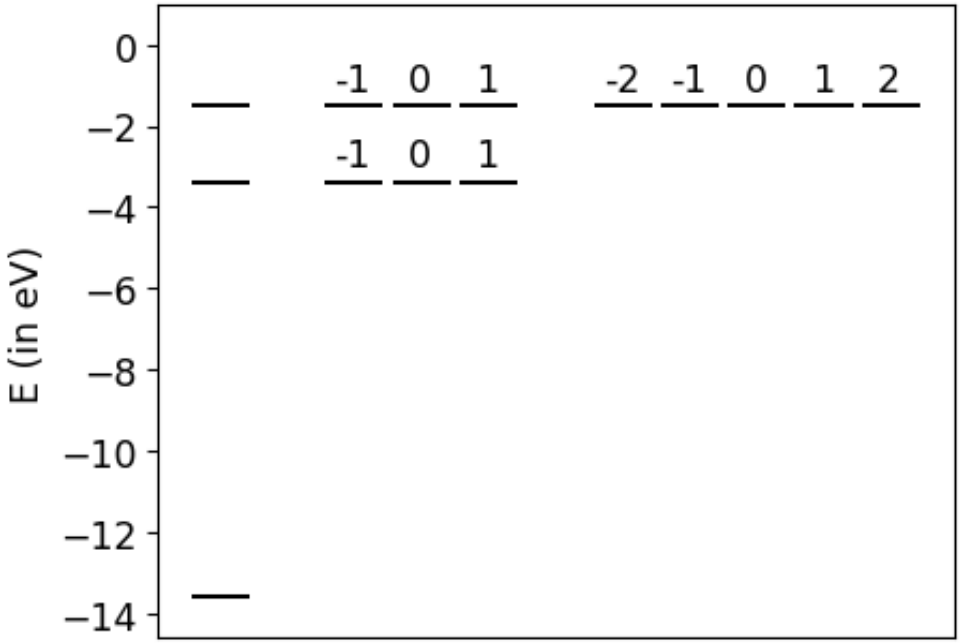
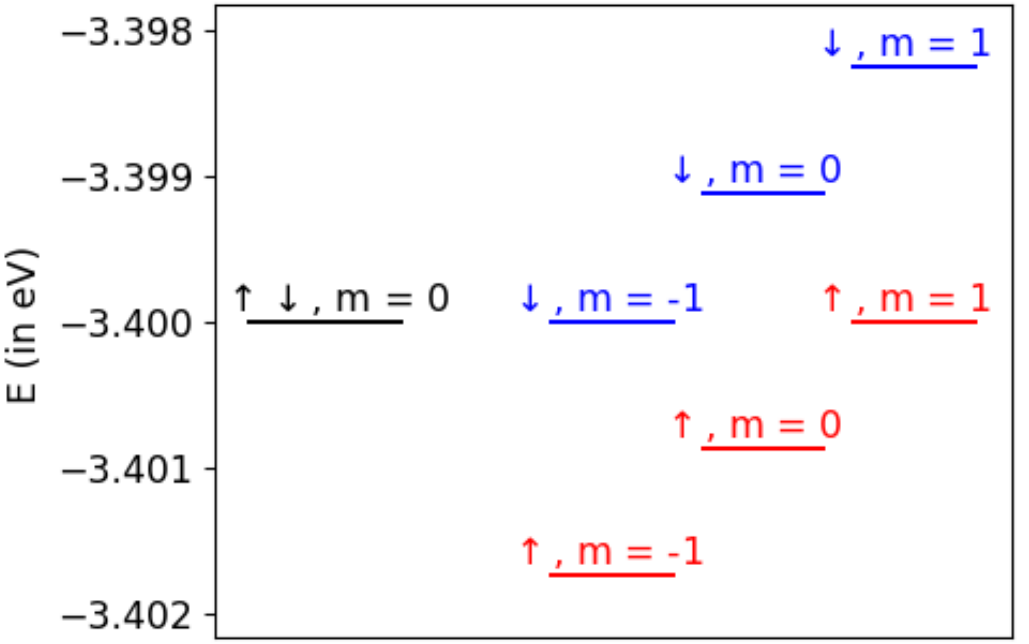
PHOT 301: Quantum Photonics

LECTURE 08

Michaël Barbier, Summer (2024-2025)

Lecture: The Hydrogen Atom, Spin, and Magnetic Fields


E (in eV)
0
−2
−4
−6
−8
−10
−12
−14
-1 0 1
-1 0 1
-2 -1 0 1 2


E (in eV)
−3.398
−3.399
−3.400
−3.401
−3.402
↓ , m = 1
↓ , m = 0
↑ ↓ , m = 0
↓ , m = -1
↑ , m = 1
↑ , m = 0
↑ , m = -1

TOWARDS SPHERICAL SYMMETRIC SYSTEMS

DIATOMIC MOLECULE: HAMILTONIAN

- Two atoms with rigid bond (approximation, ignore stretching)
- Center of mass:

$$\vec{R} = \frac{m_1 \overrightarrow{r_1} + m_2 \vec{r}_2}{m_1 + m_2}, \qquad \vec{r} = \vec{r}_2 - \vec{r}_1, \qquad M = m_1 + m_2, \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

- Hamiltonian contains linear momentum: center of mass moving
- and *internal* angular momentum with inertia $I = \mu r^2$

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{L}^2}{2I}$$

DIATOMIC MOLECULE: EIGENENERGIES

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{L}^2}{2I}$$

- Center of mass $\vec{R}$, and orientation $\vec{r}$ are **independent**
- Separation of variables: $\psi(\vec{R}, \vec{r}) = e^{i\vec{K}\cdot\vec{R}}\, Y(\theta, \phi)$
- Eigenenergies:

$$E_{\vec{K},l} = \frac{\hbar K^2}{2m} + \frac{\hbar^2 l(l+1)}{2I}.$$

- (2l + 1) Degeneracy in magnetic quantum number $m \equiv m_s$

ANGULAR MOMENTUM

ANGULAR MOMENTUM: COMMUTATORS

- Definition of angular momentum $\hat{L} = \hat{r} \times \hat{p}$
- position/momentum commutator relations in 3D: $[\hat{p}_i, r_j] = -i\hbar\delta_{ij}$

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \qquad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x, \qquad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y,$$

- Traditionally written using the Levi-Civita symbol ϵ_{ijk}:
  - $\epsilon_{ijk} = -1$ for odd permutations $(1,2,3) = 132, 213, 321$
  - $\epsilon_{ijk} = 1$ for even permutations $(1,2,3) = 123, 312, 231$
  - $\epsilon_{ijk} = 0$ for any same indices appearing $(1,2,3) = 223, 311, 333$, etc.

$$[\hat{L}_i, \hat{L}_j] = i\hbar \sum_k \epsilon_{ijk} \hat{L}_k$$

ANGULAR MOMENTUM: EIGENVALUES

- $\hat{\mathbf{L}} = (\hat{L_x}, \hat{L_y}, \hat{L_z})$ is a vector with a **magnitude** $\|\hat{L}\|$ and **direction**,
- $\hat{L_x}, \hat{L_y}, \hat{L_z}$ don't commute: no common eigenstate basis,
- Magnitude (squared) of the momentum is $\hat{\mathbf{L}}^2$
- Magnitude does commute with each vector component

  $\longrightarrow$ Use eigenstates basis ($|a, b\rangle$) of $\hat{\mathbf{L}}^2$ and one component $\hat{L_z}$.

$$\hat{\mathbf{L}}^2|a,b\rangle = a|a,b\rangle \qquad \hat{L_z}|a,b\rangle = b|a,b\rangle$$

ALGEBRAIC SOLUTION: LADDER OPERATORS

$$\hat{\mathbf{L}}^2 |a,\, b\rangle = a\,|a,\, b\rangle \qquad \hat{L}_z |a,\, b\rangle = b\,|a,\, b\rangle$$

- Define ladder operators $\hat{L_\pm} = \hat{L}_x \pm i\hat{L}_y$
- Is $\hat{L_\pm}|a,\, b\rangle$ an eigenstate?
- Yes, since $[\hat{\mathbf{L}}^2, \hat{L}_i] = 0$:

$$\hat{\mathbf{L}}^2 \left(\hat{L}_\pm |a,\, b\rangle\right) = \hat{L}_\pm \hat{\mathbf{L}}^2 |a,\, b\rangle = a \left(\hat{L}_\pm |a,\, b\rangle\right)$$

- So $\hat{L}_\pm |a,\, b\rangle$ is eigenstate of $\hat{\mathbf{L}}^2$ (or the zero state) with eigenvalue a.
- What about $\hat{L}_z$?

ALGEBRAIC SOLUTION: LADDER OPERATORS

- The ladder operators $\hat{L}_\pm$ do not commute with $\hat{L}_z$:

$$[\hat{L}_z, \hat{L}_\pm] = \pm\hbar\hat{L}_\pm$$

- We use this relation to extract the impact on the eigenstates

$$\hat{L}_z\hat{L}_\pm |a,\, b\rangle = \hat{L}_\pm\hat{L}_z |a,\, b\rangle + [\hat{L}_z\hat{L}_\pm] |a,\, b\rangle = (b \pm \hbar)\hat{L}_\pm |a,\, b\rangle$$

- So $\hat{L}_\pm |a,\, b\rangle$ is eigenstate of $\hat{L}_z$ (or the zero state) with eigenvalue $b \pm \hbar$:

$$\hat{L}_\pm |a,\, b\rangle = C_\pm(a,b)|a,\, b \pm \hbar\rangle$$

With $C_\pm(a,b)$ a normalization factor (*still unknown*)

EIGENVALUE RANGES

- Procedure is similar to the one for finding the zeroth eigenstate of the harmonic oscillator. An upper/lower bound leads to *discrete ladder*
- We use $\langle a, b|a, b\rangle = 1$ and express that the norm

$$\|\hat{L}_\pm|a, b\rangle\|^2 = \langle a, b|\hat{L}_\pm^\dagger \hat{L}_\pm|a, b\rangle \geq 0$$

We can rewrite $\hat{L}_\pm^\dagger \hat{L}_\pm = \hat{L}_\mp \hat{L}_\pm$ as:

$$\hat{L}_\mp \hat{L}_\pm = (\hat{L}_x \mp i\hat{L}_y)(\hat{L}_x \pm i\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 \pm i[\hat{L}_x, \hat{L}_y] = \hat{\mathbf{L}}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z$$

This lead to a relation between the eigenvalues

$$\langle a, b|\hat{L}_\pm^\dagger \hat{L}_\pm|a, b\rangle = \langle a, b|\hat{\mathbf{L}}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z|a, b\rangle = (a - b^2 \mp \hbar b)\langle a, b|a, b\rangle \geq 0$$

We will use $a \geq 0$ and $b \in \mathfrak{R}$ to find b and a values

EIGENVALUE RANGE: M

- $a \geq 0$ and $b \in \Re$
- Smallest eigenvalue $a = 0$ gives limits on b:

$$\langle a, b_{\max} | \hat{L}_+^\dagger \hat{L}_+ | a, b_{\max} \rangle = a - b_{\max}^2 - \hbar b_{\max} = 0$$
$$\langle a, b_{\min} | \hat{L}_-^\dagger \hat{L}_- | a, b_{\min} \rangle = a - b_{\min}^2 + \hbar b_{\min} = 0$$

This both determines a:

$$a = b_{\max}^2 + \hbar b_{\max}$$
$$a = b_{\min}^2 - \hbar b_{\min}$$

- Resulting in $b_{\min} = -b_{\max}$
- For any a: starting from $|a, b_{\min}\rangle$ and move up the ladder with $\hat{L}_+$ until $|a, b_{\max}\rangle$:

$$b_{\min}, \quad b_{\min} + \hbar, \quad b_{\min} + 2\hbar, \quad \ldots, \quad b_{\min} + n\hbar = b_{\max}$$

Lecture: The Hydrogen Atom, Spin, and Magnetic Fields

EIGENVALUE RANGE: L AND M

- Since also $b_{\max} = -b_{\min}$, the eigenvalue range $-(n-1)\hbar/2, \ldots, (n-1)\hbar/2$ or $-n\hbar/2, \ldots, n\hbar/2$
- Eigenvalues of $\hat{L}_z$ are $b = m\hbar$ with $m_{\max} = -m_{\min} = l$
- Eigenvalues a of $\hat{\mathbf{L}}^2$ are given by

$$a = m_{\max}\hbar(m_{\max}\hbar + \hbar) = l(l+1)\hbar^2$$

- In summary:

$$\boxed{\hat{\mathbf{L}}^2|l,m\rangle = l(l+1)\hbar^2|l,m\rangle} \qquad \boxed{\hat{L}_z|l,m\rangle = m\hbar|l,m\rangle}$$

- l and m either even integer or odd half-integers with integer steps

NORMALIZATION

$$\boxed{\hat{\mathbf{L}}^2|l,m\rangle = l(l+1)\hbar^2|l,m\rangle, \qquad \hat{L}_z|l,m\rangle = m\hbar|l,m\rangle}$$

Using the previous definition of the ladder operator

$$1 = \langle l,m|\hat{L}_\pm^\dagger \hat{L}_\pm|l,m\rangle = \langle l,m|\hat{\mathbf{L}}^2 - \hat{L}_z^2 \pm \hbar\hat{L}_z|l,m\rangle$$

Taking the square root of the norm results in:

$$\boxed{\begin{aligned}\hat{L}_+|l,m\rangle &= \sqrt{l(l+1)-m(m+1)}\hbar|l,m+1\rangle \\ \hat{L}_-|l,m\rangle &= \sqrt{l(l+1)-m(m-1)}\hbar|l,m-1\rangle\end{aligned}}$$

CORRESPONDING EIGENFUNCTIONS

- Constructing the eigenstate functions: Spherical harmonics $Y_{lm}(\theta, \phi) = \langle \theta, \phi | l, m \rangle$

Expressing the operators: $\hat{\mathbf{L}}^2$, $\hat{L}_z$, and $\hat{L}_\pm$ with $\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}} = -i\hbar \mathbf{r} \times \nabla$

The gradient ∇ in spherical coordinates:

$$\nabla = \vec{e}_r \frac{\partial}{\partial r} + \vec{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \vec{e}_\phi \frac{1}{r \sin\theta} \frac{\partial}{\partial \phi}$$

$$\Longrightarrow \boxed{\begin{aligned} \hat{L}_z &= -i\hbar \frac{\partial}{\partial \phi}, \quad \hat{L}_\pm = \hbar e^{\pm i\phi} \left[\pm \frac{\partial}{\partial \theta} + i \cot\theta \frac{\partial}{\partial \phi} \right] \\ \hat{\mathbf{L}}^2 &= -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial \sin\theta \frac{\partial}{\partial \theta}}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \end{aligned}}$$

Lecture: The Hydrogen Atom, Spin, and Magnetic Fields

THE ϕ- COMPONENT

$$\boxed{\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}, \quad \hat{L}_\pm = \hbar e^{\pm i\phi}\left[\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right]}$$

- Apply $\hat{L}_z$ to proposed solution $Y_{lm}(\theta,\phi)$

$$\hat{L}_z Y_{lm}(\theta,\phi) = -i\hbar\frac{\partial}{\partial\phi}Y_{lm}(\theta,\phi) = m\hbar Y_{lm}(\theta,\phi)$$

Separation of the variables:

$$Y_{lm}(\theta,\phi) = F(\theta)\, e^{im\phi}, \quad \text{with} -l \leq m \leq l$$

- If l is an integer, the requirement $e^{im\phi} = e^{im(\phi+2\pi)}$ is satisfied

THE θ- COMPONENT

$$\boxed{\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}, \quad \hat{L}_\pm = \hbar e^{\pm i\phi}\left[\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right]}$$

- Apply $\hat{L}_\pm$ to proposed solution $F(\theta)$
- Use the fact that $m_{\max}$ is l: $\hat{L}_+|l,l\rangle = 0$:

$$0 = \langle\theta,\phi|\hat{L}_+|l,l\rangle = \hbar e^{i\phi}\left[\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right]e^{il\phi}F(\theta)$$
$$= \hbar e^{i(l+1)\phi}\left[\frac{\partial}{\partial\theta} - l\cot\theta\right]F(\theta)$$

$$\Rightarrow \frac{\partial}{\partial\theta}F(\theta) = l\cot\theta F(\theta) \quad \Rightarrow \quad F(\theta) = C\sin^l(\theta)$$

SPHERICAL HARMONICS

The lower states with $m < l$ are generated by applying $\hat{L}_-$

$$Y_{lm}(\theta,\phi) = C\hat{L}_-^{(l-m)}\left[\sin^l\theta e^{il\phi}\right] = C\left[\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right]\left[\sin^l\theta e^{il\phi}\right]$$

The solutions are the spherical harmonics:

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

with the **associated Legendre polynomials**

$$P_l^m(x) = \frac{(1-x^2)^m/2}{2^l l!}\frac{d^{m+l}}{dx^{m+l}}(x^2-1)^l$$

SUMMARY ANGULAR MOMENTUM

Common basis of eigenstates of angular momentum:

$$\boxed{\hat{\mathbf{L}}^2|l,m\rangle = l(l+1)\hbar^2|l,m\rangle} \qquad \boxed{\hat{L}_z|l,m\rangle = m\hbar|l,m\rangle}$$

- l and $m = -l, \ldots, -1, 0, 1, \ldots, l$ integers to get single-valued $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi) = \Theta(\theta)e^{im\phi}$
- The solutions are the spherical harmonics $Y(\theta,\phi)$:

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

with the **associated Legendre polynomials**

$$P_l^m(x) = \frac{(1-x^2)^m/2}{2^l l!}\frac{d^{m+l}}{dx^{m+l}}(x^2-1)^l$$

SUMMARY ANGULAR MOMENTUM

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

$$P_l^m(x) = \frac{(1-x^2)^m/2}{2^l l!}\,\frac{d^{m+l}}{dx^{m+l}}(x^2-1)^l$$

Lower order $P_l^m(z)$ polynomials:

l	$m=-2$	$m=-1$	$m=0$	$m=1$	$m=2$
0			1		
1		$-\frac{1}{2}(1-x^2)^{1/2}$	x	$(1-x^2)^{1/2}$	
2	$\frac{1}{8}(1-x^2)$	$-\frac{1}{2}x(1-x^2)^{1/2}$	$\frac{1}{2}(3x^2-1)$	$3x(1-x^2)^{1/2}$	$3(1-x^2)$

LOWER ORDER EIGENFUNCTIONS

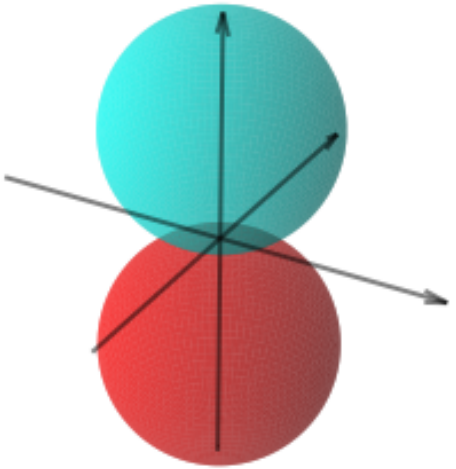
$$Y_{lm}(\theta,\phi) = (-1)^{m+|m|}\left[\frac{2l+1}{4\pi}\,\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)e^{im\phi}$$

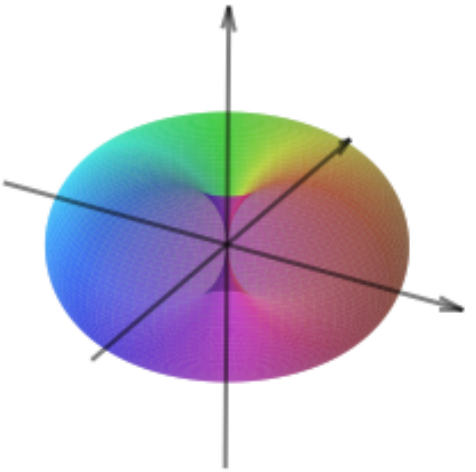
Angular momentum eigenfunction in spherical and carthesian coordinates

$Y_{l,m}$	$Y_{l,m}(\theta,\phi)$	$Y_{l,m}(x,y,z)$
$Y_{0,0}$	$\dfrac{1}{\sqrt{4\pi}}$	$\dfrac{1}{\sqrt{4\pi}}$
$Y_{1,-1}$	$\sqrt{\dfrac{3}{8\pi}}\,\sin\theta\, e^{-i\phi}$	$\sqrt{\dfrac{3}{8\pi}}\,\dfrac{x-iy}{r}$
$Y_{1,0}$	$\dfrac{1}{\sqrt{4\pi}}\cos\theta$	$\dfrac{1}{\sqrt{4\pi}}\,\dfrac{z}{r}$
$Y_{1,1}$	$\sqrt{\dfrac{3}{8\pi}}\,\sin\theta\, e^{i\phi}$	$-\sqrt{\dfrac{3}{8\pi}}\,\dfrac{x+iy}{r}$

Lecture: The Hydrogen Atom, Spin, and Magnetic Fields

VISUAL REPRESENTATION





- The $l = 1$ and $m = \pm 1$ eigenstates have a torus (donut) shape
- Specific basis connected to z-axis via $\hat{L}_z$,
- Other choices $\hat{L}_x$ or $\hat{L}_y$ possible, correspond to other bases
- The magnetic quantum numbers m_l are eigenvalues of $\hat{L}_z$

SPHERICAL HARMONICS: REAL BASIS

- Rotating the basis using spherical symmetry
- Superposition of eigenstates ($\hat{L}_z$), start from the solutions:

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

Use the identities $\cos(m\phi) = \frac{e^{im\phi}+e^{-im\phi}}{2}$ and $\sin(m\phi) = \frac{e^{im\phi}-e^{-im\phi}}{2i}$:

$$\begin{cases} Y_x(\theta,\phi) = \Re\{Y_{lm}\} = (-1)^{m+|m|}\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)\ \cos(m\phi) \\ Y_y(\theta,\phi) = \Im\{Y_{lm}\} = (-1)^{m+|m|}\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)\ \sin(m\phi) \end{cases}$$

SPHERICAL HARMONICS: REAL BASIS

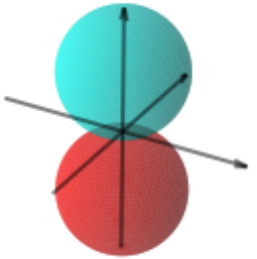
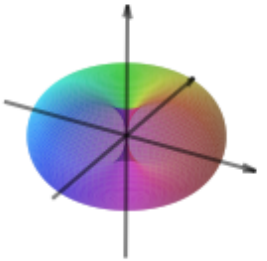
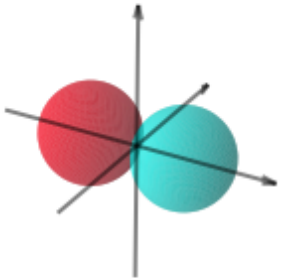
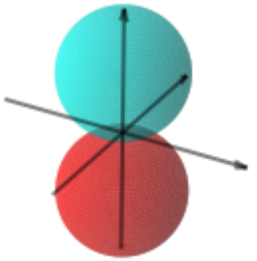
- Rotating the basis using spherical symmetry
- Superposition of eigenstates ($\hat{L}_z$), start from the solutions
- For $l = 1$ the carthesian formula shows this very clear:

$Y_{l,m}$	$Y_{l,m}(\theta, \phi)$	$Y_{l,m}(x, y, z)$
$Y_{0,0}$	$\frac{1}{\sqrt{4\pi}}$	$\frac{1}{\sqrt{4\pi}}$
$Y_{1,-1}$	$\sqrt{\frac{3}{8\pi}}\,\sin\theta\, e^{-i\phi}$	$\sqrt{\frac{3}{8\pi}}\,\frac{x - iy}{r}$
$Y_{1,0}$	$\frac{1}{\sqrt{4\pi}}\cos\theta$	$\frac{1}{\sqrt{4\pi}}\,\frac{z}{r}$
$Y_{1,1}$	$\sqrt{\frac{3}{8\pi}}\,\sin\theta\, e^{i\phi}$	$-\sqrt{\frac{3}{8\pi}}\,\frac{x + iy}{r}$

Lecture: The Hydrogen Atom, Spin, and Magnetic Fields

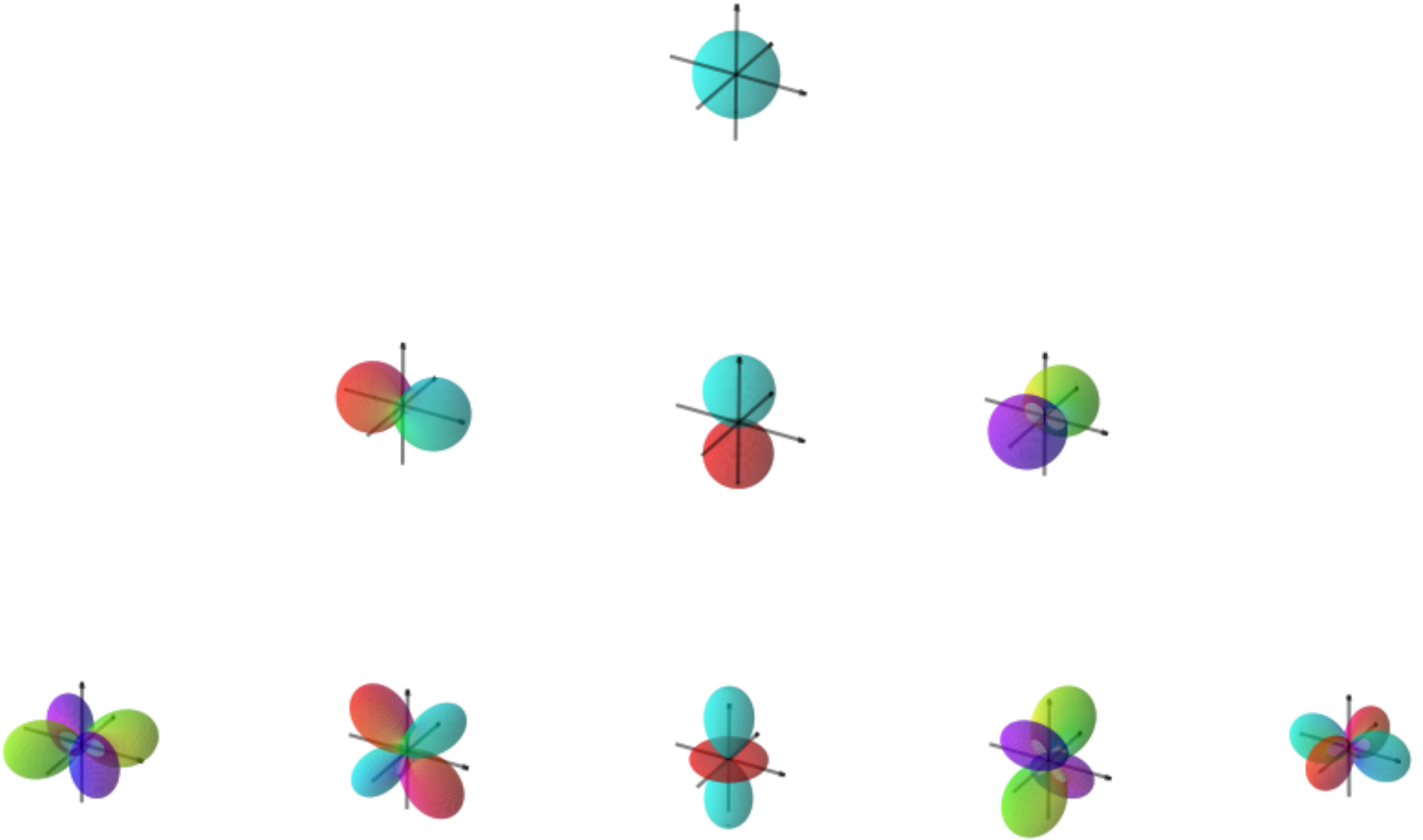
DIFFERENT BASIS FOR Y

- Different eigenstate basis: **Symmetric dumbells** vs. **donuts in xy-plane**
- Superposition of a Y_x and a Y_y (p-orbitals) gives a torus(donut) and vice versa.

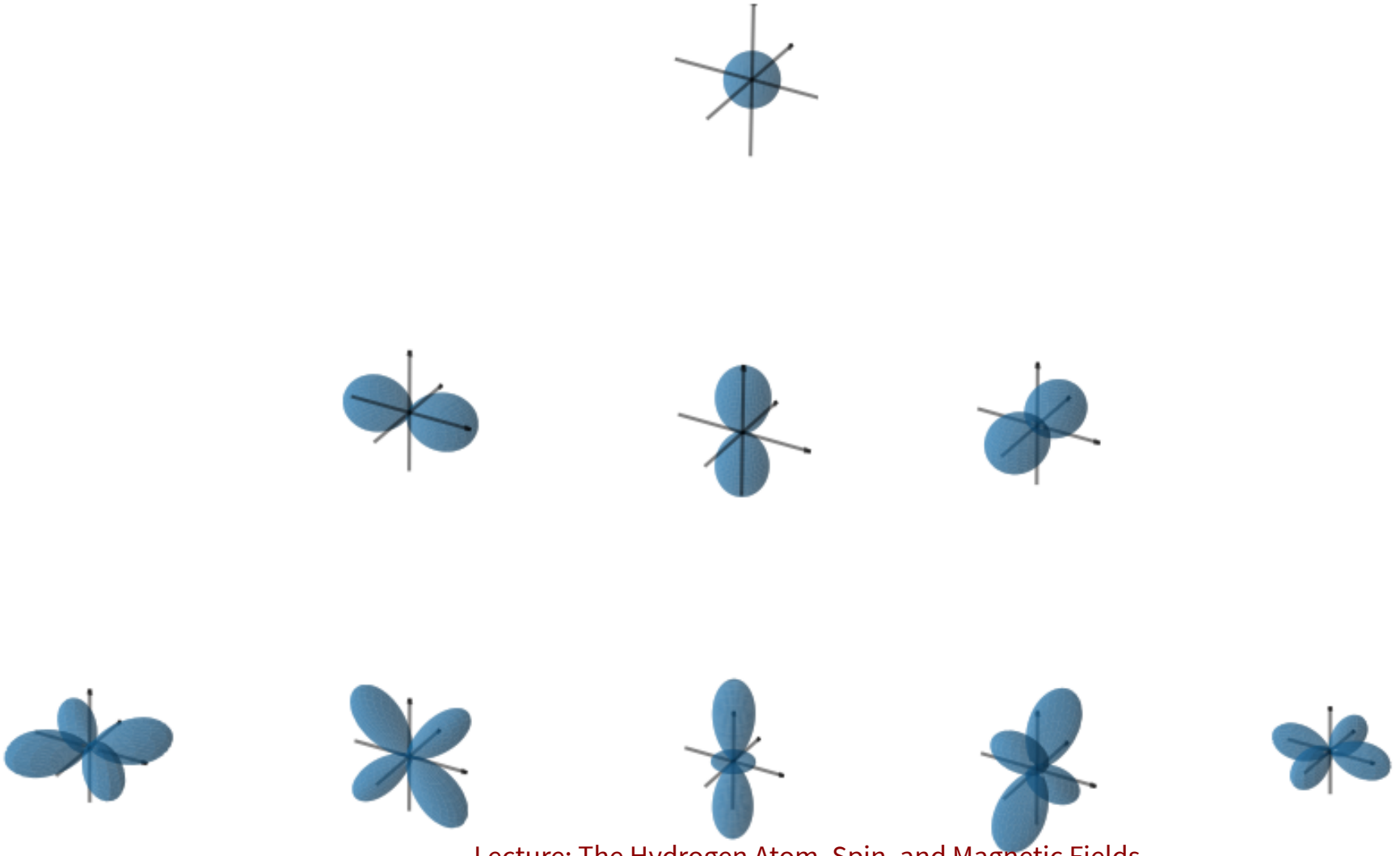

SPHERICAL HARMONICS WAVE FUNCTION

- Appropriate real-valued orthonormal basis, superposition of orbitals



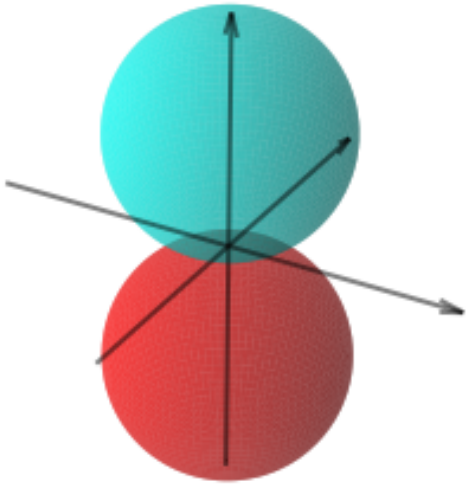
SPHERICAL HARMONICS PROBABILITY

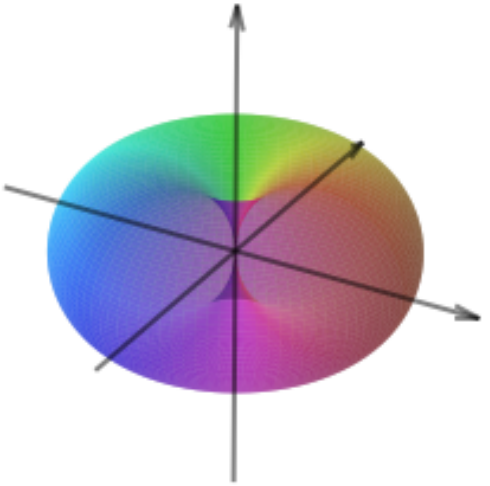
- Appropriate real-valued orthonormal basis, superposition of orbitals



SUPERPOSITION

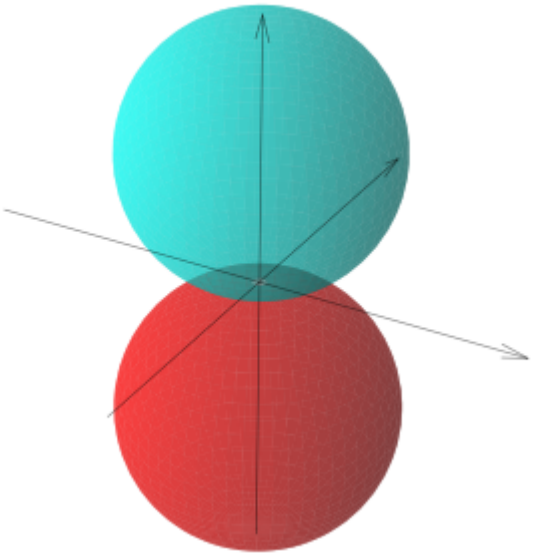
- Electrons can be in a superposition of orbital states.
- We used a specific basis, other bases are possible
- The electron magnetic quantum number m_l is an eigenvalue of the *donut* basis of eigenstates

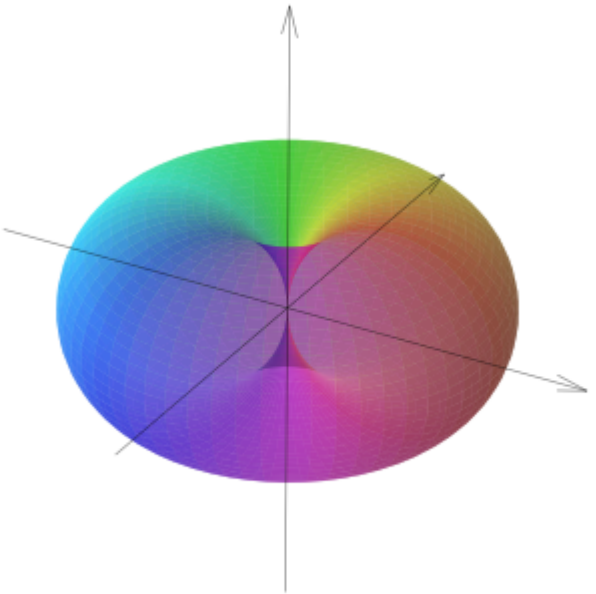




EVOLUTION IN TIME

- Phase factor $e^{im\phi + iE_{nl}t/\hbar}$ over time
  - Y_{10} (p_0-orbital): Phase changes in time, phase difference of π
  - Y_{11} (p_1-orbital): Phase rotates





HAMILTONIANS OF 3D SYSTEMS

DIATOMIC MOLECULE: HAMILTONIAN

- Two atoms with rigid bond (approximation, ignore stretching)
- Center of mass:

$$\vec{R} = \frac{m_1 \overrightarrow{r_1} + m_2 \vec{r}_2}{m_1 + m_2}, \qquad \vec{r} = \vec{r}_2 - \vec{r}_1, \qquad M = m_1 + m_2, \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

- Hamiltonian contains linear momentum: center of mass moving
- and *internal* angular momentum with inertia $I = \mu r^2$

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{L}^2}{2I}$$

DIATOMIC MOLECULE: EIGENENERGIES

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{L}^2}{2I}$$

- Center of mass $\vec{R}$, and orientation $\vec{r}$ are **independent**
- Separation of variables: $\psi(\vec{R}, \vec{r}) = e^{i\vec{K}\cdot\vec{R}}\, Y(\theta, \phi)$
- Eigenenergies:

$$E_{\vec{K},l} = \frac{\hbar K^2}{2m} + \frac{\hbar^2 l(l+1)}{2I}.$$

- (2l + 1) Degeneracy in magnetic quantum number $m \equiv m_s$

CENTRAL POTENTIAL: HAMILTONIAN

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(r)$$

- Central potential $\longrightarrow$ go to spherical coordinates
- We need $\hat{p}^2 = -\hbar^2\nabla^2$ in spherical coordinates with:

$$\nabla = \vec{e}_r \frac{\partial}{\partial r} + \vec{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \vec{e}_\phi \frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}$$

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

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\hat{L}^2}{r^2\hbar^2}$$

CENTRAL POTENTIAL: HAMILTONIAN

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(r)$$

- Central potential $\longrightarrow$ go to spherical coordinates
- We need $\hat{p}^2 = -\hbar^2\nabla^2$ in spherical coordinates with:

$$\boxed{\hat{H} = \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2} + V(r)\right]\psi(\vec{r}) = E\psi(\vec{r})}$$

CENTRAL POTENTIAL: SOLUTIONS

$$\boxed{\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{\hat{L}^2}{2mr^2}+V(r)\right]\psi(\vec{r})=E\psi(\vec{r})}$$

Separation of variables $\psi(\vec{r})=R(r)Y(\theta,\phi)$

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{\hat{L}^2}{2mr^2}+V(r)\right]R(r)Y(\theta,\phi)=ER(r)Y(\theta,\phi)$$

$$\Longrightarrow\quad\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{l(l+1)\hbar^2}{2mr^2}+V(r)\right]R(r)=ER(r)$$

Simplifying by substituting $R(r)=\chi(r)/r$ and defining a new effective potential $V_e(r)$:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+V_e(r)\right]\chi(r)=E\chi(r)\quad\text{with}\quad V_e(r)=\frac{l(l+1)\hbar^2}{2mr^2}+V(r)$$

Lecture: The Hydrogen Atom, Spin, and Magnetic Fields

BOUNDARY CONDITIONS

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+V_e(r)\right]\chi(r)=E\chi(r) \quad \text{with} \quad V_e(r)=\frac{l(l+1)\hbar^2}{2mr^2}+V(r)$$

- To find $\psi(\vec{r})=\chi(r)/rY(\theta,\phi)$ we need to find $\chi(r)$
- Because $R(r)=\chi(r)/r$ we require $\chi(0)=0$
- Normalization

$$\int_\Omega |\psi(\vec{r})|^2 d\vec{r}=\int_0^\infty |R(r)|^2 r^2 dr=\int_0^\infty |\chi(r)|^2 dr=1$$

A valid bound state requires $\chi(r)$ to decrease *fast enough*: $\lim_{r\longrightarrow\infty}\chi(r)\leq\frac{1}{\sqrt{r}}$

For a solution we need to know the potential $V(r)$

HYDROGEN ATOM

THE HYDROGEN ATOM: HAMILTONIAN

- Hamiltonian for two particles, electron and proton
- Electron and proton interact via Coulomb potential

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 + V(|\vec{r}_e - \vec{r}_p|), \quad \text{with} \quad V(r) = -\frac{e^2}{4\pi\varepsilon_0|\vec{r}_e - \vec{r}_p|}.$$

- Schrodinger equation with $\psi(\vec{r}_e, \vec{r}_p)$ having 6 degrees of freedom:

$$\left[-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 + V(|\vec{r}_e - \vec{r}_p|)\right]\psi(\vec{r}_e, \vec{r}_p) = \psi(\vec{r}_e, \vec{r}_p).$$

- Go over to relative coordinates and center of mass

HYDROGEN ATOM: RELATIVE COORDINATES

- Two particles, electron and proton, use center of mass $\vec{R}$ and relative coordinates:

$$\vec{R} = \frac{m_e \overrightarrow{r_e} + m_p \vec{r}_p}{m_e + m_p}, \qquad \vec{r} = \vec{r}_e - \vec{r}_p, \qquad M = m_e + m_p, \qquad \mu = \frac{m_e m_p}{m_e + m_p}$$

- The Schrodinger equation becomes:

$$\left[-\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 + V(r) \right] \psi(\vec{R}, \vec{r}) = E \psi(\vec{R}, \vec{r})$$

- Separation of variable $-\frac{\hbar^2}{2M} \nabla_R^2$ leads to a factor $e^{i\vec{K}\cdot\vec{R}}$ with $E_R = \frac{K^2 \hbar^2}{2M}$

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \psi(\vec{R}, \vec{r}) = E \psi(\vec{R}, \vec{r})$$

HYDROGEN ATOM: TISE

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right]\psi(\vec{R},\vec{r}) = E\psi(\vec{R},\vec{r})$$

Similar: Separation of variables $\psi(\vec{r}) = R(r)Y(\theta,\phi)$ and using $Y_{lm}(\theta,\phi)$ as solutions for the angular part:

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2\mu r^2} + V(r)\right] R(r)Y(\theta,\phi) = ER(r)Y(\theta,\phi)$$

$$\Longrightarrow \quad \left[-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)\right] R(r) = ER(r)$$

Simplifying by substituting $R(r) = \chi(r)/r$ and defining a new effective potential $V_e(r)$:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V_e(r)\right]\chi(r) = E\chi(r) \quad \text{with} \quad V_e(r) = \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)$$

SOLUTION RADIAL EQUATION

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V_e(r)\right]\chi(r) = E\chi(r) \quad \text{with} \quad V_e(r) = \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)$$

Define energy $E = -\frac{\mathrm{Ry}}{n^2}$ with $n \in \mathbb{R}$ and radial coordinate $s = \frac{2\,r}{n\,a_0}$, where:

- **Bohr radius**: *radius of Hydrogen atom*: $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{e^2\mu} = 0.529\,\mathring{\mathrm{A}}$
- **Rydberg energy**: $\mathrm{Ry} = \frac{\hbar^2}{2\mu a_0^2} = \frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2 = 13.6\ \mathrm{eV}$

This simplifies the radial equation:

$$\Longrightarrow \quad \frac{d^2\chi(s)}{ds^2} - \left[\frac{l(l+1)}{s^2} - \frac{n}{s} + \frac{1}{4}\right]\chi(s) = 0$$

SOLUTION RADIAL EQUATION CTU'D

$$\Longrightarrow \quad \frac{d^2\chi(s)}{ds^2} - \left[\frac{l(l+1)}{s^2} - \frac{n}{s} + \frac{1}{4}\right]\chi(s) = 0$$

- Propose a solution $\chi(s) \propto \exp(-s/2)$ to remove the $\frac{1}{4}$ (and decaying)
- To remove the $\frac{l(l+1)}{s^2}$ term we further require $\chi(s) \propto s^{l+1}$
- We obtain proposed solution of the form (with $f(s)$ *unknown*):

$$\chi(s) = f(s)s^{l+1}\exp(-s/2)$$

- Substitution leads to a differential equation for $f(s)$:

$$s\,\frac{d^2f(s)}{ds^2} - [s - 2\,(l+1)]\frac{df(s)}{ds} + [n - (l+1)]\,f(s) = 0$$

SOLUTION RADIAL EQUATION CTU'D

$$s\frac{d^2f(s)}{ds^2} - [s - 2(l+1)]\frac{df(s)}{ds} + [n - (l+1)]f(s) = 0$$

- Solve by expanding $f(s)$ as a power series $f(s) = \sum_{j=0}^{\infty} a_j s^j$
- Solution demands that the power series is finite:
  - n must be an integer, and
  - $n > l + 1$
- $f(s)$ is then given by the **associated Laguerre polynomials**:

$$L_{n-l-1}^{2l+1} = \sum_{q=0}^{n-l-1} (-1)^q \frac{(n+l)!}{(n-l-1-q)!\,(2l+1+q)!}\, s^q$$

SOLUTIONS

Total solutions together with the associated Laguerre polynomials

$$\chi(s) = s^{l+1} L_{n-l-1}^{2l+1}(s) e^{-s/2}, \qquad s = \frac{2r}{na_0}$$

Normalization factor for $R(r) = \chi(s)/r$:

$$1 = \int_0^\infty R^2(r)\, r^2\, dr = \int_0^\infty s^{2l} \left(L_{n-l-1}^{2l+1}(s)\right) e^{-s}\, s^2\, ds = \frac{2\,n\,(n+l)!}{(n-l-1)!}$$

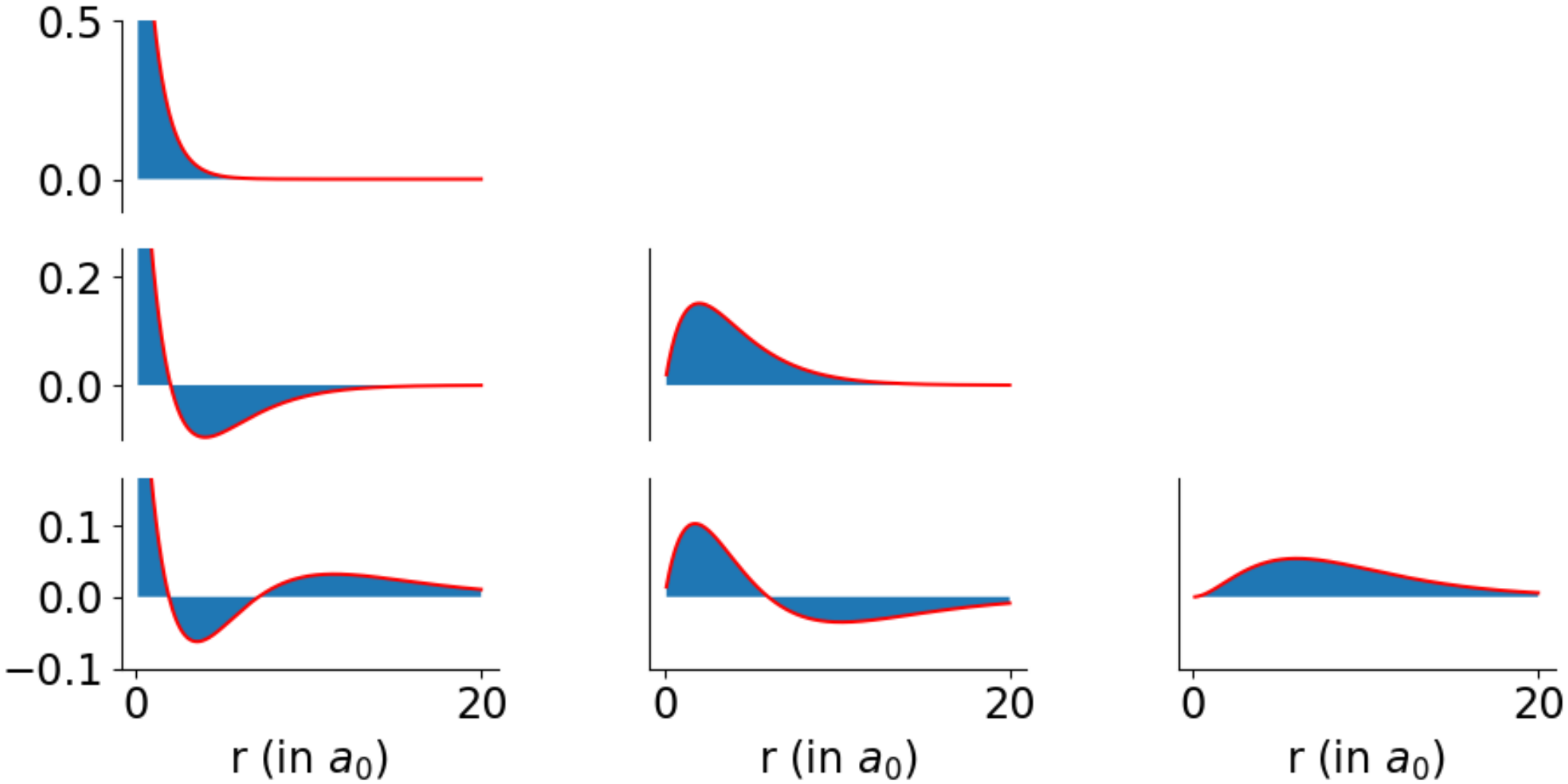
The normalized radial solutions:

$$\boxed{R_{nl}(s) = \left[\frac{(n-l-1)!}{2\,n\,(n+l)!}\left(\frac{2}{n\,a_0}\right)^3\right]^{1/2} s^l\, L_{n-l-1}^{2l+1}(s)\, e^{-s/2}}$$

And the eigenenergies are given by $E_n = -\frac{\mathrm{Ry}}{n^2} = -\frac{13.6}{n^2}$ eV

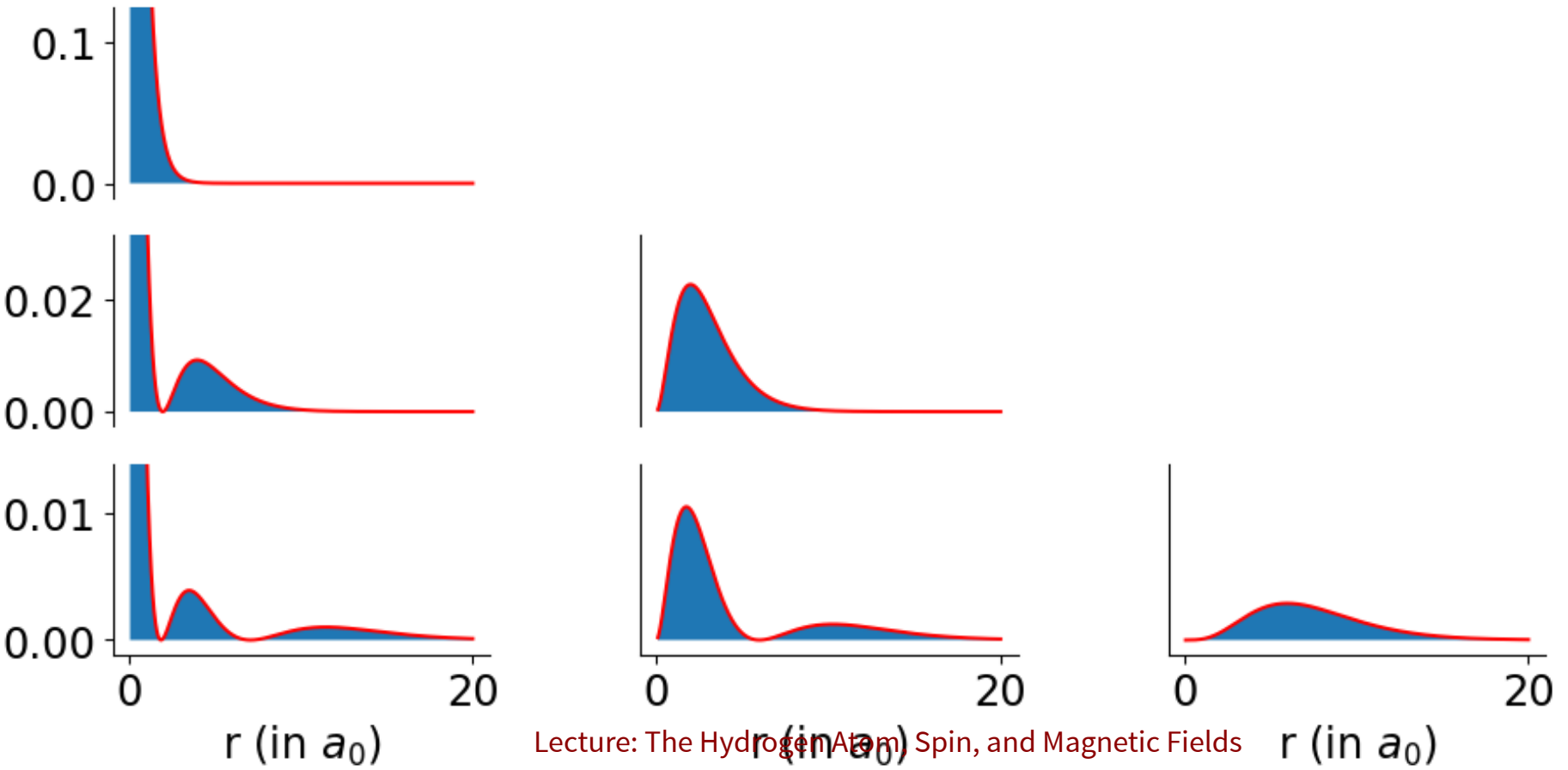
RADIAL PART: WAVE FUNCTION

- Radial wave function $R(r)$ has $n - l - 1$ zeros



RADIAL PART: PROBABILITY

- Electron localization:
  - **S-orbitals** large probability in zero
  - **P-orbital** zero probability in zero



ORBITALS: RADIAL + ANGULAR PARTS

The wave function $\psi(\vec{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)$

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

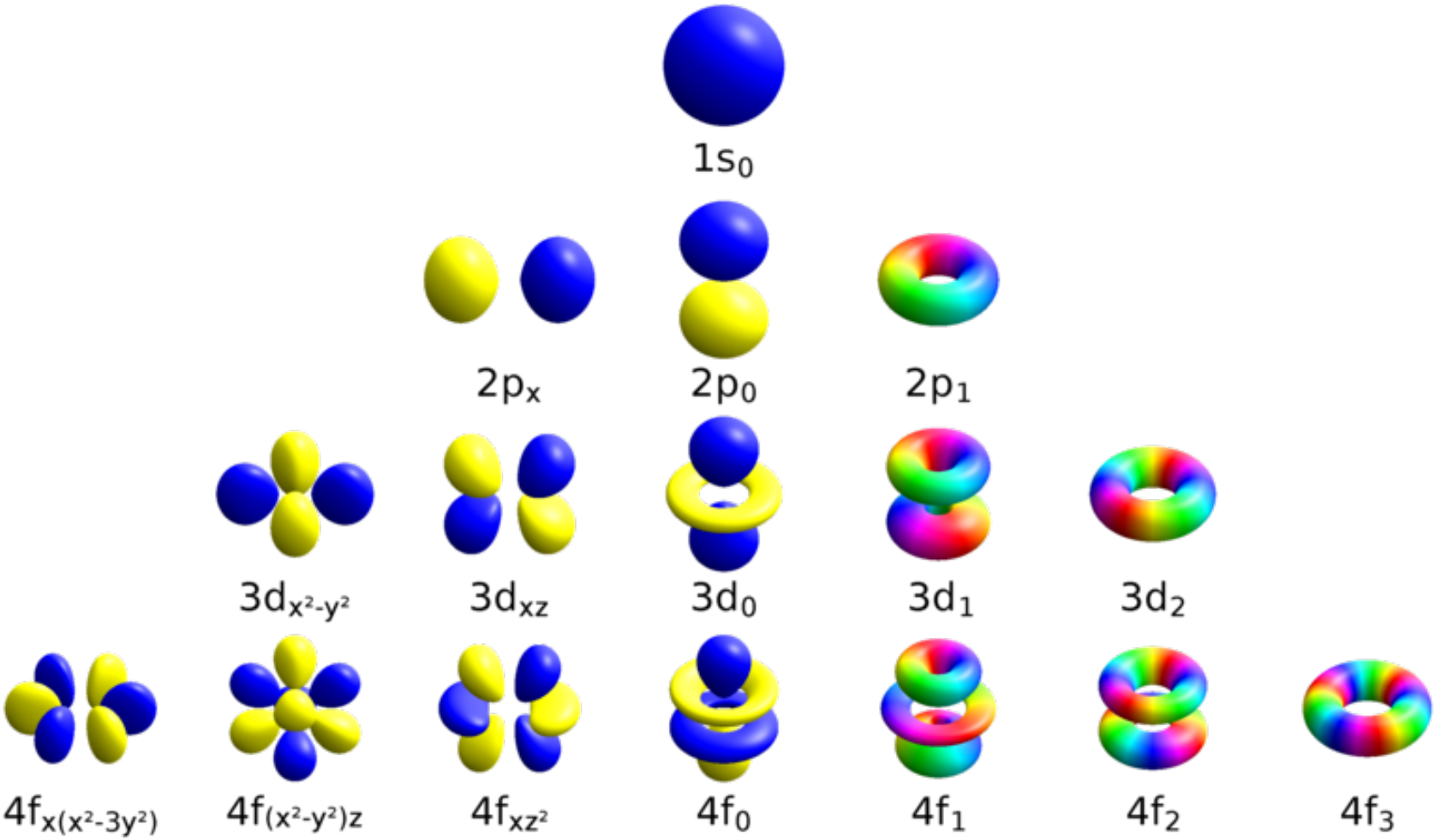
$$R_{nl}(s) = \left[\frac{(n-l-1)!}{2\,n\,(n+l)!}\left(\frac{2}{n\,a_0}\right)^3\right]^{1/2} s^l\, L_{n-l-1}^{2l+1}(s)\, e^{-s/2}$$

with $s = \frac{2\,r}{n\,a_0}$, **associated Legendre** and **associated Laguerre** polynomials

$$P_l^m(z) = \frac{(1-z^2)^m/2}{2^l l!}\frac{d^{m+l}}{dz^{m+l}}(z^2-1)^l, \qquad L_k^\alpha(z) = \sum_{j=0}^{k}(-1)^j\binom{k+\alpha}{k-j}\frac{x^j}{j!}$$

COMPARISON OF S-P-D-F ORBITALS

- Overview of all orbitals:



Adapted from Wikipedia

ORBITALS OF THE HYDROGEN ATOM

- **Orbital** eigenstates are $|n, l, m_l, m_s\rangle$
- Electron eigenstates in the Hydrogen atom are structured in:
  - **Shells**: Different **principal** quantum number n
  - **Sub-shells**: Different **azimuthal** quantum number l
    - Named **s, p, d, f orbitals**
    - Historical names: Sharp, Principal, Diffuse, and Fundamental coming from appearance of atomic spectral lines
  - Specific **orbitals**: **magnetic** quantum number m (also called m_l)
  - **Spin** of the electron: **spin** quantum number m_s *(we will see spin afterwards)*

ENERGY DIAGRAM OF S-P-D-F ORBITALS

- Hydrogen has only 1 electron: energy depends on n only (shell): $E_n = \frac{\mathrm{Ry}}{n^2}$
- Other atoms: Multiple electrons and different sub-shells have different energies
  - electron-electron interactions
  - different sub-shell result in different electron distances (interaction-energies)