PHOT 301: Quantum Photonics

LECTURE 09

Michaël Barbier, Summer (2024-2025)

SUMMARY

- What can quantum mechanics describe?
  - Nanostructures - quantumdots, quantum wells, nanowire, nanotubes, low-dimensional materials, thin films, surfaces, …
  - Materials - electronic structure (periodic structures)
  - Atoms and Molecules - Hydrogen atom
- The Schrodinger equation in 3D:
  - Momentum operator: $\hat{p}_x \longrightarrow \hat{\vec{p}} = i\hbar\vec{\nabla}$
  - Potential $V(\hat{\vec{r}})$ and position operator: $\hat{\vec{r}}$
- Extra quantum numbers $|n, l, m_l, m_s\rangle$:
  - **Principal**, **Azimuthal**, **Magnetic**, **Spin** quantum numbers
- Spin leads to Pauli “Schrodinger” equation
- Multiple electrons/particles: bosons & fermions

RECAP OF HYDROGEN ATOM

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**

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

SUMMARY ANGULAR MOMENTUM

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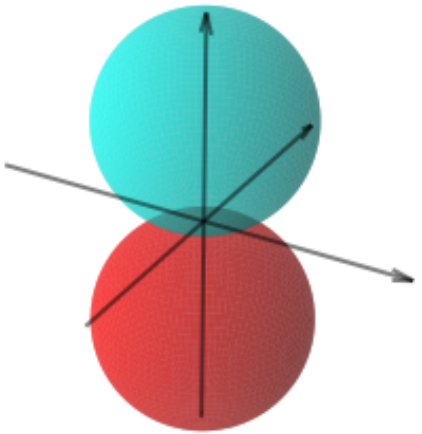
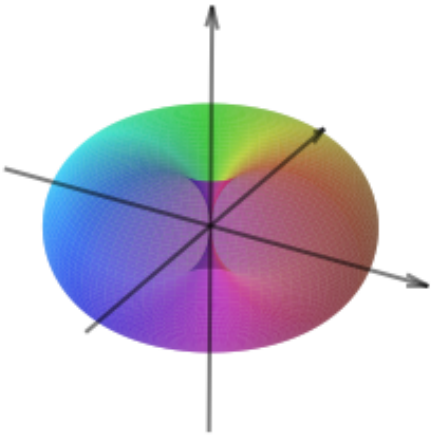
$$P_l^m(z) = \frac{(1-z^2)^m/2}{2^l l!}\frac{d^{m+l}}{dz^{m+l}}(z^2-1)^l$$

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	$\frac{1}{8}(1-x^2)$	$-\frac{1}{2}x(1-x^2)^{1/2}$	$\frac{1}{2}(3x^2-1)$	$3x(1-x^2)^{1/2}$	$3(1-x^2)$

VISUAL REPRESENTATION





- The $m = \pm 1$ 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:

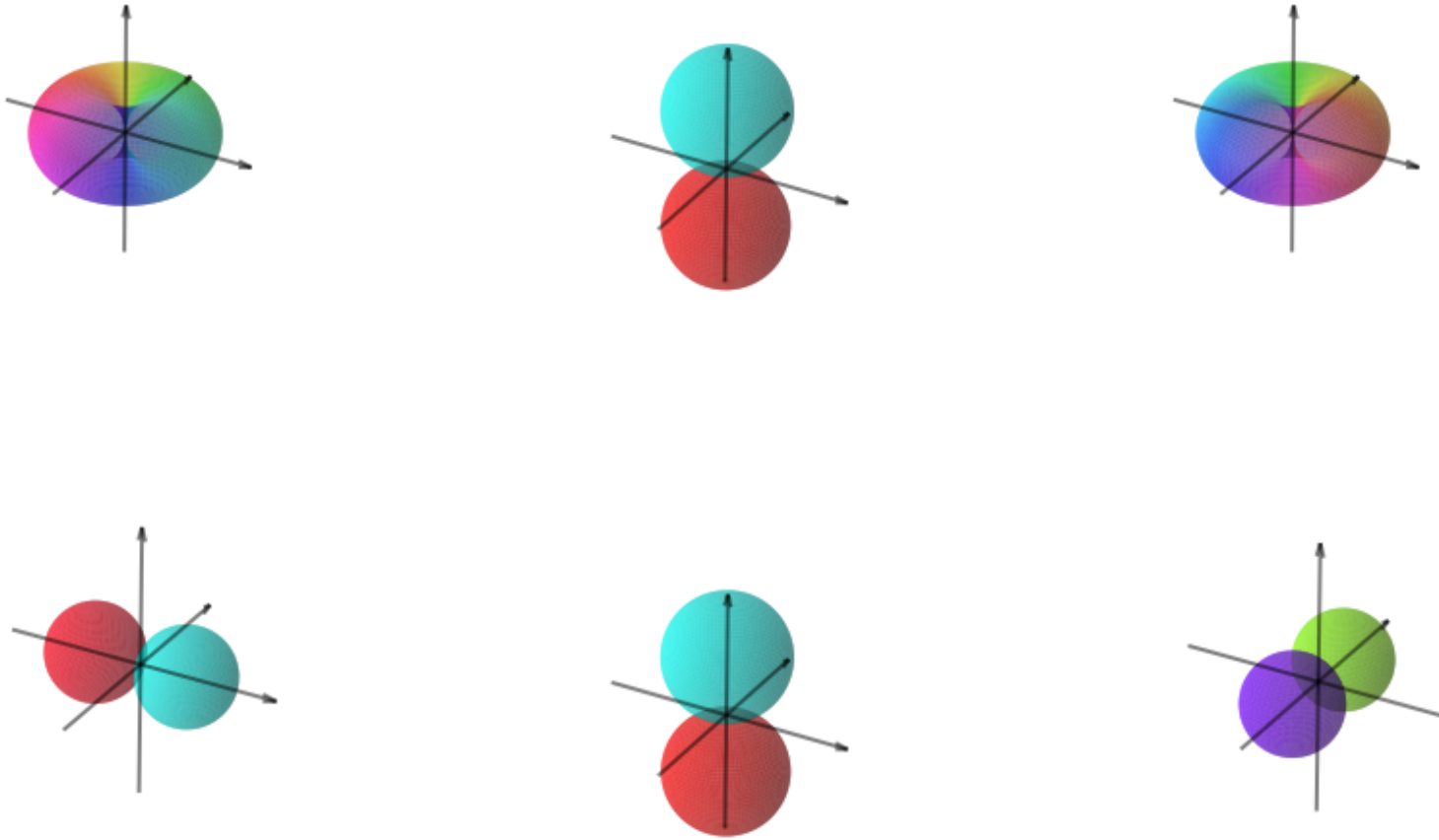
$$Y_{lm}(\theta,\phi) = (-1)^{m+|m|}\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)e^{im\phi}$$

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

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

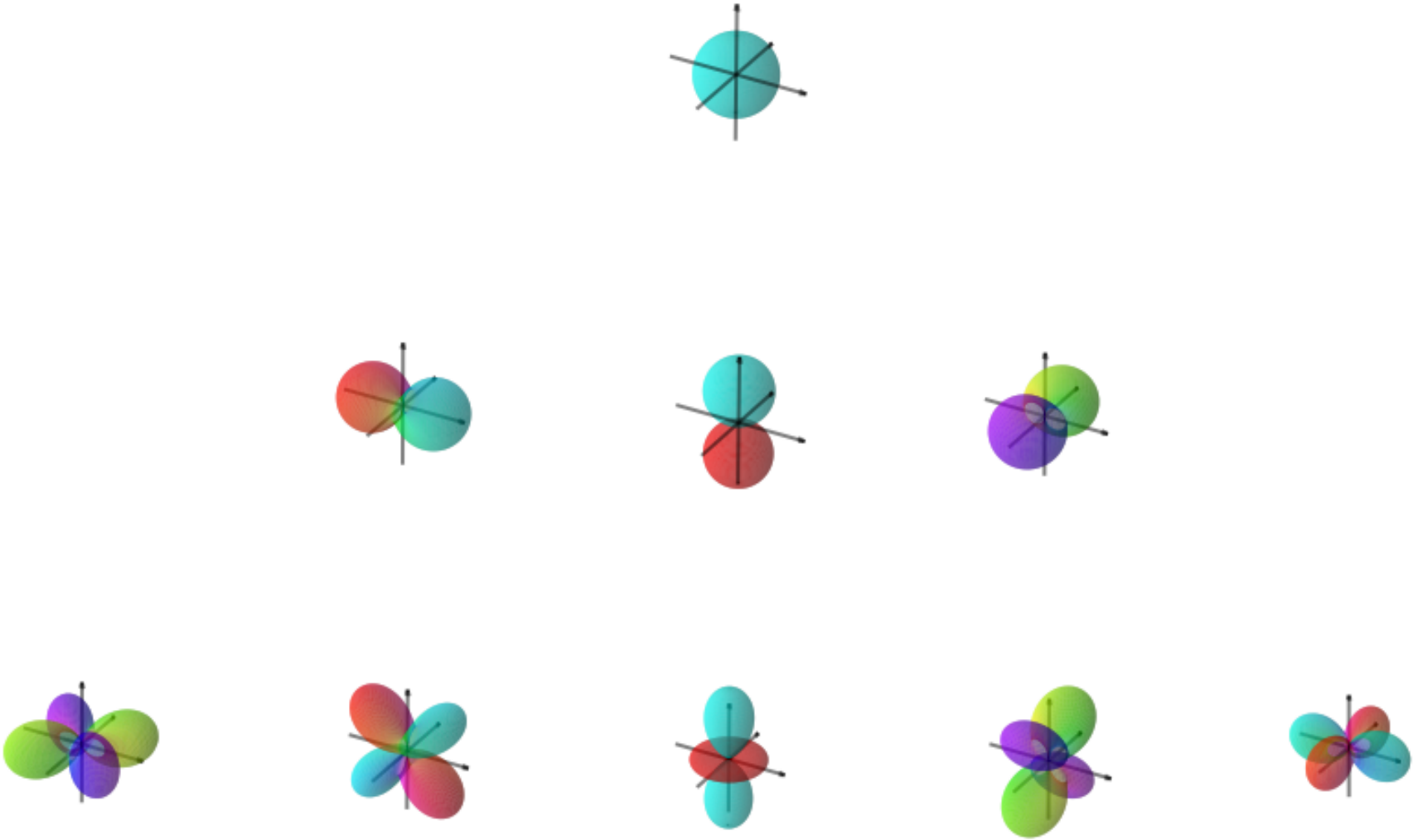
DIFFERENT BASIS P-STATES

- Different eigenstate basis: **Symmetric dumbells** vs. **donuts in xy-plane**
- Superposition of a p_x and a p_y-orbital gives a torus(donut)-orbital and vice versa.



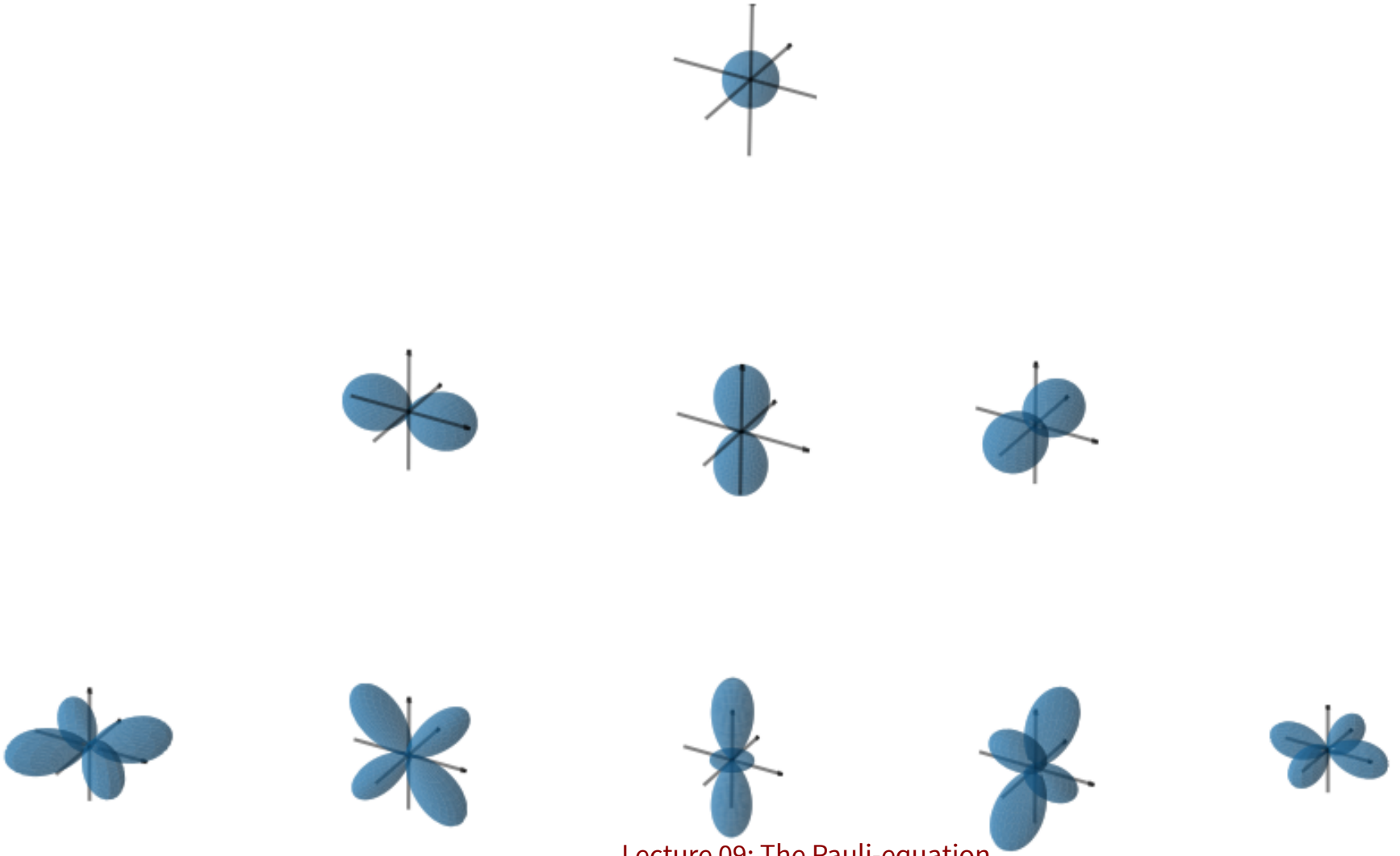
SPHERICAL HARMONICS WAVE FUNCTION

- Appropriate real-valued orthonormal basis, superposition of orbitals



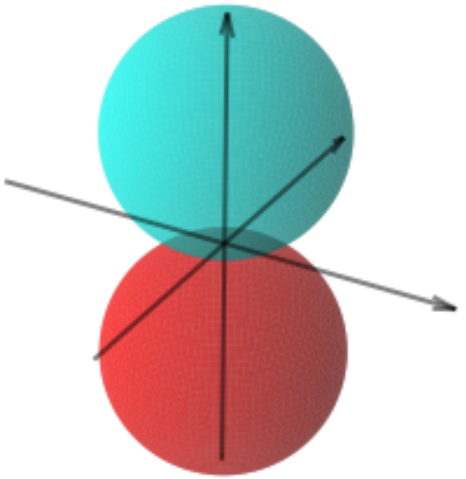
SPHERICAL HARMONICS PROBABILITY

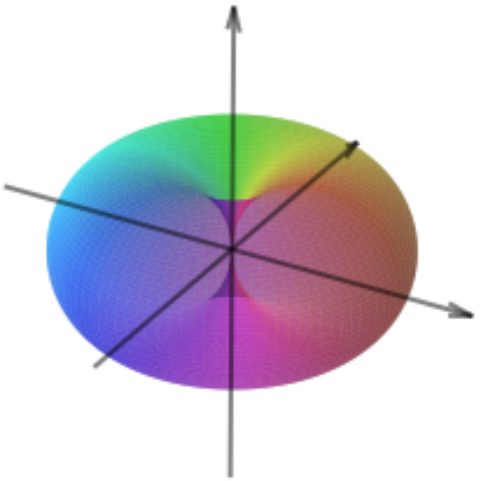
- Appropriate real-valued orthonormal basis, superposition of orbitals



SUPERPOSITION

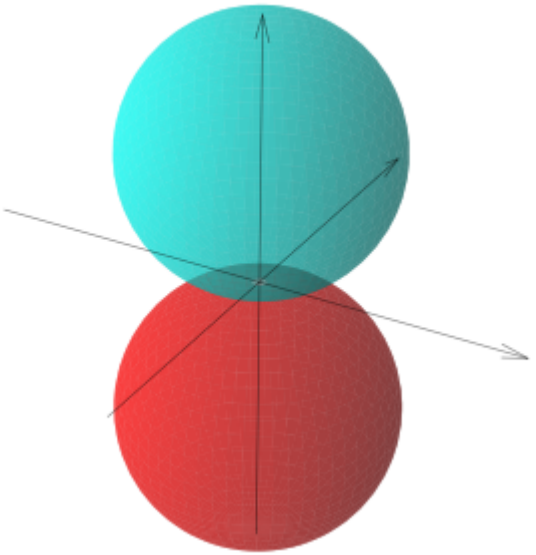
- Electrons can be in a superposition of orbital states.
- We used a specific basis, other bases are possible
- The electron magnetic quantum number m_l is an eigenvalue of the *donut* basis of eigenstates

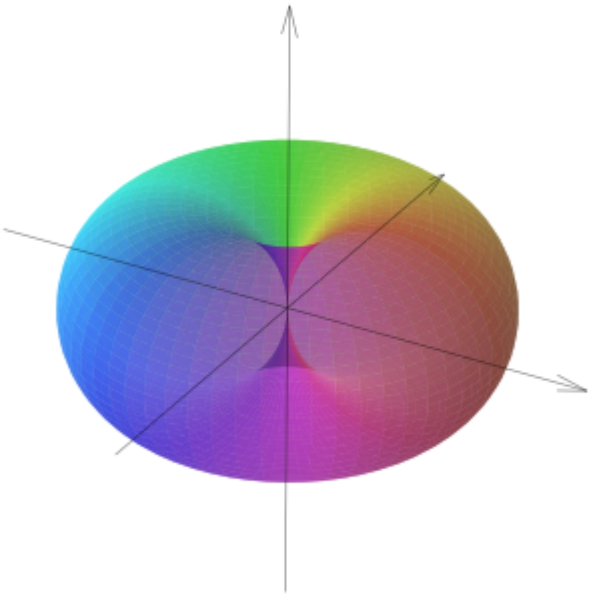




EVOLUTION IN TIME

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





RADIAL SOLUTIONS

Solutions are given by Laguerre polynomials

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

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

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:

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

Lecture 09: The Pauli-equation

RADIAL SOLUTIONS

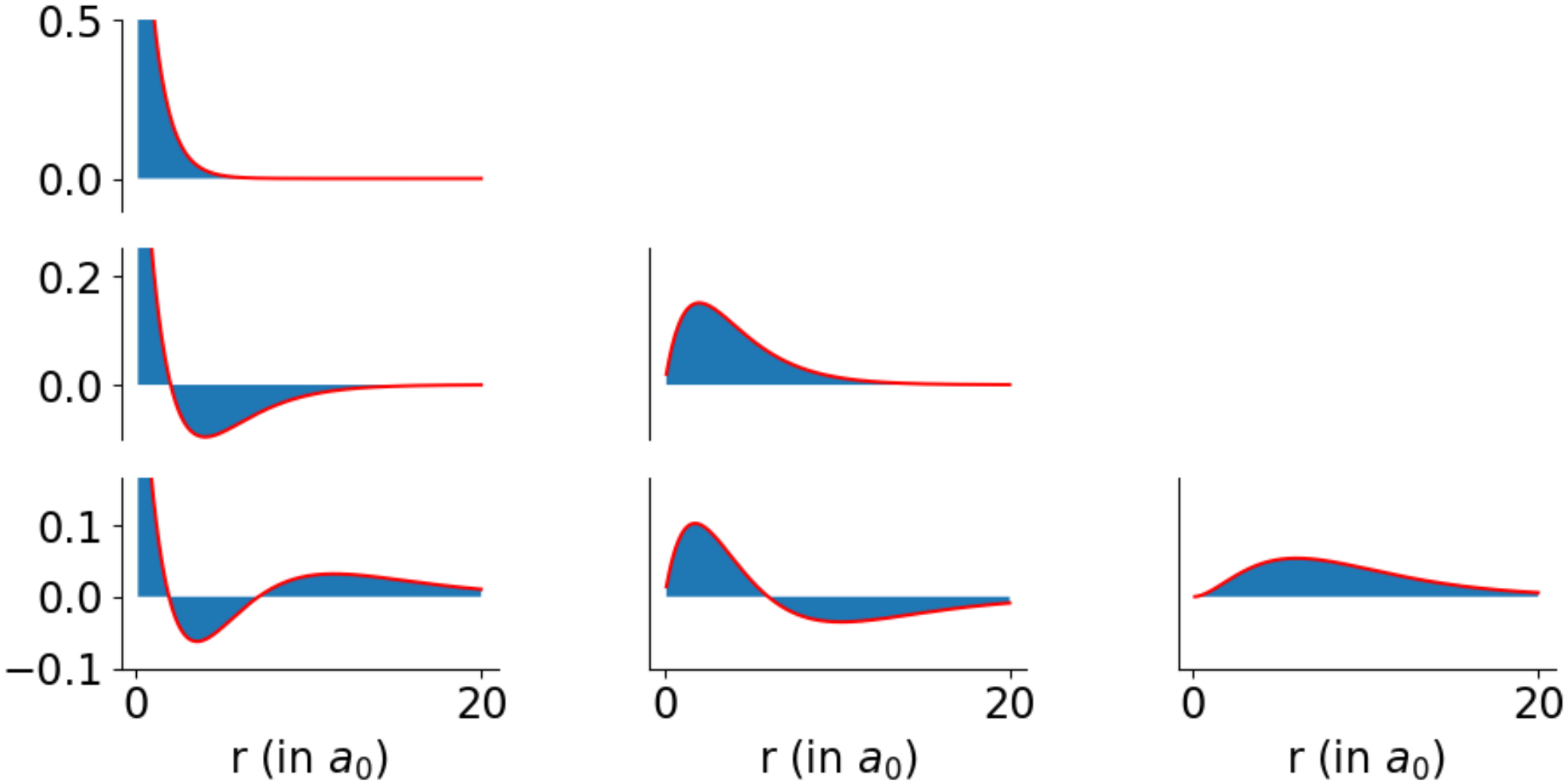
$$R_{nl}(s) = \left[\frac{(n-l-1)!}{2\,n\,(n+l)!} \left(\frac{2}{n\,a_0} \right)^3 \right]^{1/2} s^l \, L_{n-l-1}^{2l+1}(s)\, e^{-s/2}$$

$$s = \frac{2r}{n a_0}, \qquad a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{e^2 \mu} = 0.529\ \text{A}$$

$$E_n = -\frac{Ry}{n^2}, \qquad Ry = \frac{\hbar^2}{2\mu a_0^2} = \frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_0 \hbar} \right)^2 = 13.6\,\text{eV}$$

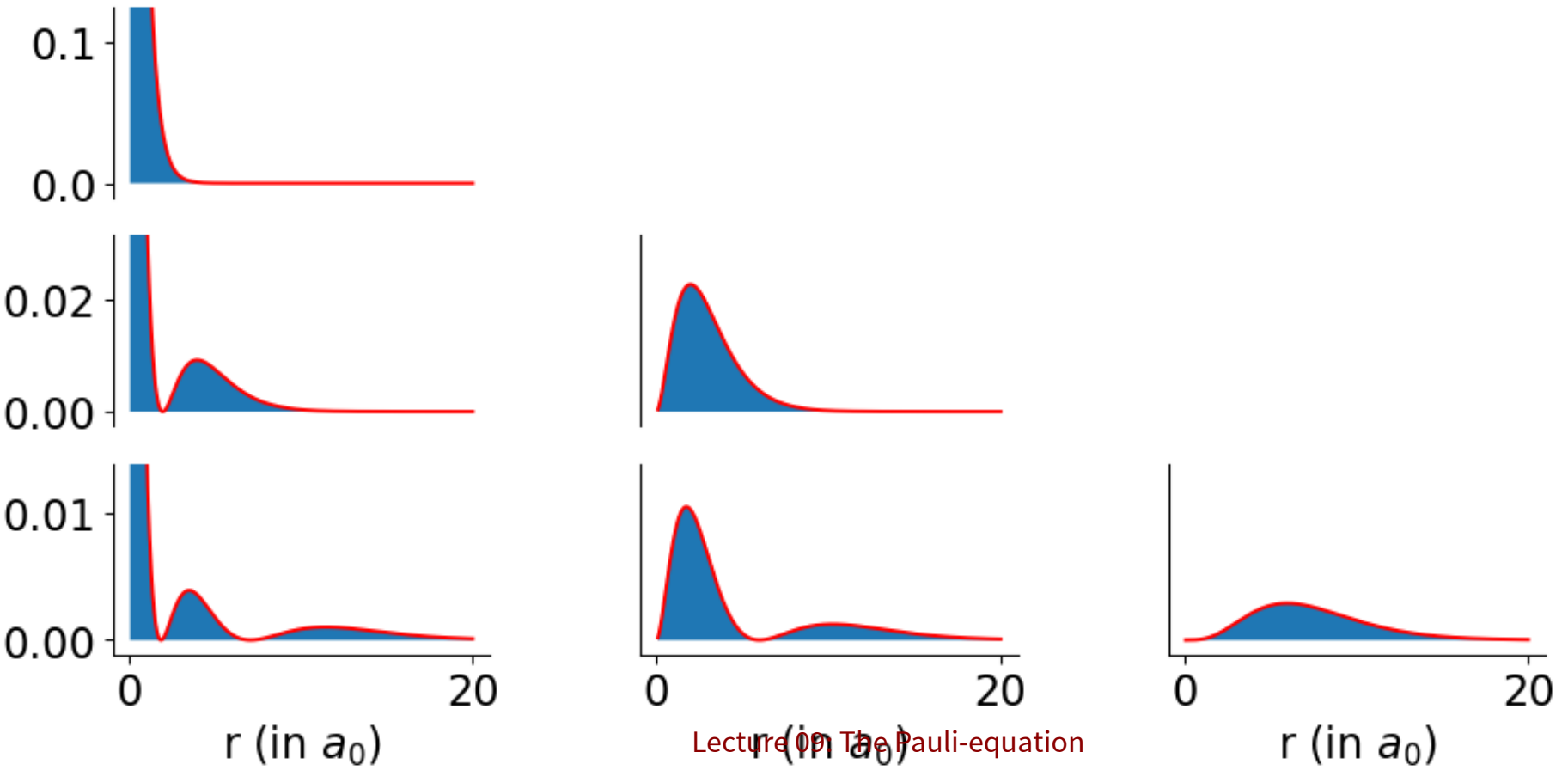
RADIAL PART: WAVE FUNCTION

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

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

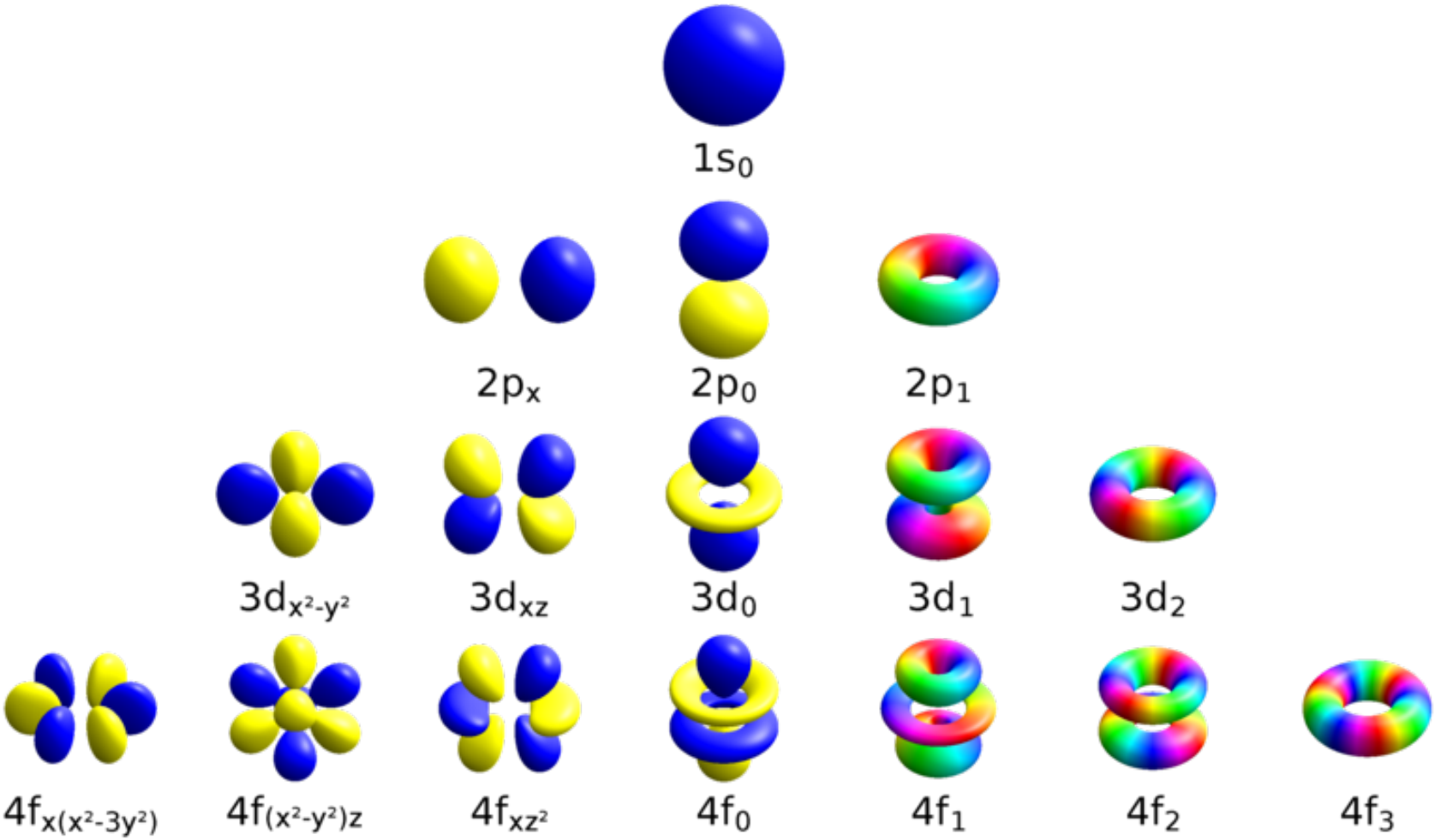
$$R_{nl}(s) = \left[\frac{(n-l-1)!}{2\,n\,(n+l)!}\left(\frac{2}{n\,a_0}\right)^3\right]^{1/2} s^l\, L_{n-l-1}^{2l+1}(s)\, e^{-s/2}$$

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:



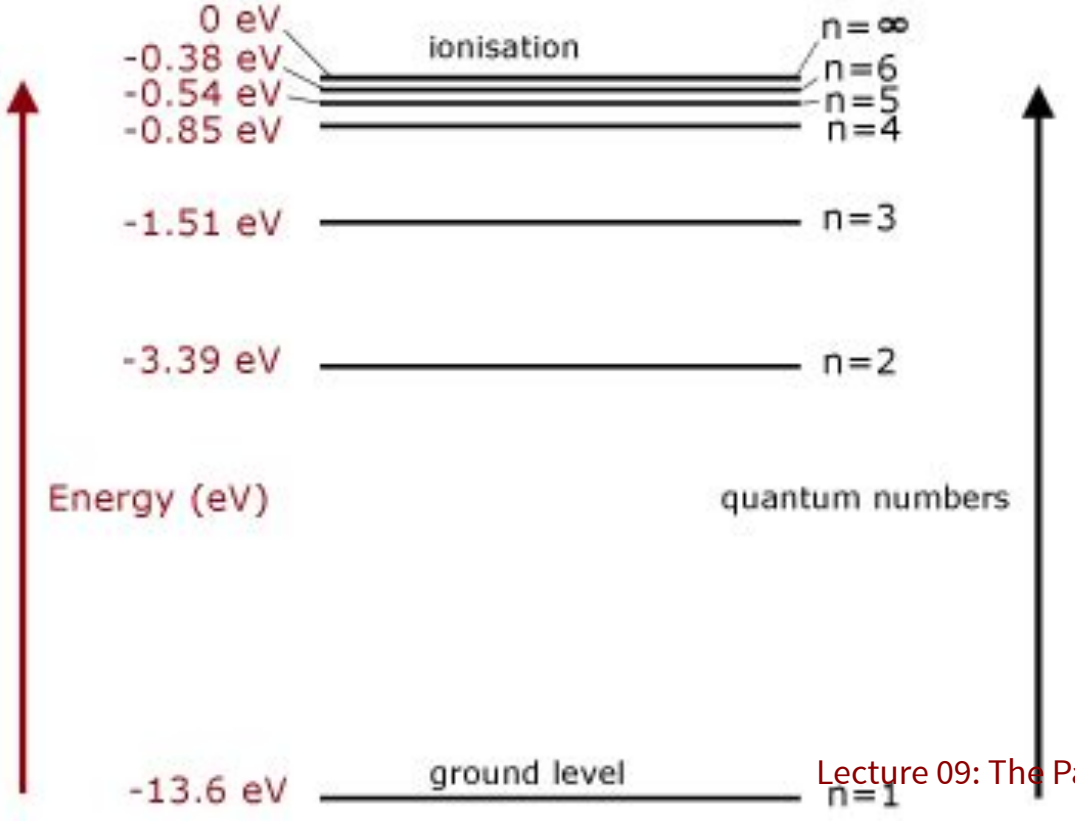
From Wikipedia

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)
- Other atoms: Multiple electrons and different sub-shells have different energies
  - electron-electron interactions
  - different sub-shell result in different electron distances (interaction-energies)



THE PAULI EQUATION

MAGNETIC FIELD: SPIN INTERACTION

- Extension Schrodinger equation
- Includes the spin magnetic moment: $\overrightarrow{\mu_e} = g\mu_B\vec{\sigma}$
- Energy of spin magnetic moment in magnetic field $\vec{B}$

$$E_s = \overrightarrow{\mu_e} \cdot \vec{B} = g\mu_B\vec{\sigma} \cdot \vec{B}$$

Quantum Mechanics: Corresponding Hamiltonian (convert to operators)

$$\hat{H}_s = \frac{g\mu_B}{2}\hat{\vec{\sigma}} \cdot \vec{B} = \frac{g\mu_B}{2}\left[B_x \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + B_y \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + B_z \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right]$$

Factor 1/2 comes from $\hat{\vec{\sigma}}$ definition

MAGNETIC FIELD: MOVING CHARGES

Classically: Lorentz force:

$$\vec{F} = q\vec{E} + q(\vec{v} \times \vec{B})$$

- Write the electric and magnetic fields ($\vec{E}$ and $\vec{B}$) as potentials:

$$\text{Electric field:} \qquad \vec{E} = -e\nabla V - \frac{\partial \vec{A}}{\partial t}$$

$$\text{Magnetic field:} \qquad \vec{B} = \nabla \times \vec{A}$$

- These potentials are derived from Maxwell's equations
- The particle's momentum $\vec{p} \longrightarrow \vec{p} - e\vec{A}$

Quantum Mechanics: use corresponding momentum operator $\hat{\vec{p}} \longrightarrow \hat{\vec{p}} - e\vec{A}$

Lecture 09: The Pauli-equation

PAULI EQUATION

Add both spin $\frac{g\mu_B}{2}\hat{\vec{\sigma}} \cdot \vec{B}$ and vector potential $\hat{\vec{p}} - e\vec{A}$.

$$\left[\frac{1}{2m_0}(\hat{\vec{p}} - e\vec{A})^2 1 + V1 + \frac{g\mu_B}{2}\hat{\vec{\sigma}} \cdot \vec{B}\right] \Psi(\vec{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t)$$

where $\Psi(\vec{r}, t) = \begin{pmatrix} \Psi_\uparrow(\vec{r}, t) \\ \Psi_\downarrow(\vec{r}, t) \end{pmatrix}$ is a spinor

The part $(\hat{\vec{p}} - e\vec{A})^2$ can be written as (*operator precedence*):

$$(\hat{\vec{p}} - e\vec{A}) \cdot (\hat{\vec{p}} - e\vec{A}) = \hat{p}^2 - e\vec{A} \cdot \hat{\vec{p}} + i\hbar e\nabla \cdot \vec{A} + e^2 A^2$$

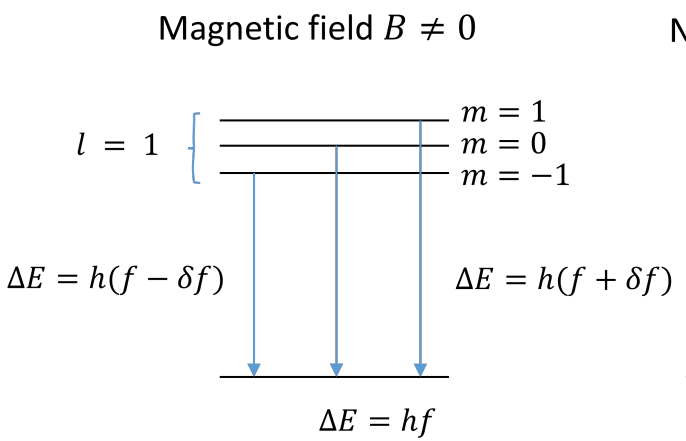
- Last term $e^2 A^2 \approx 0$ for most magnetic fields

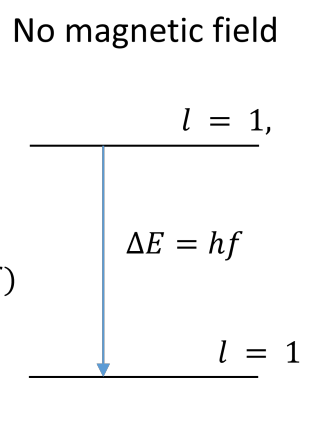
Lecture 09: The Pauli-equation

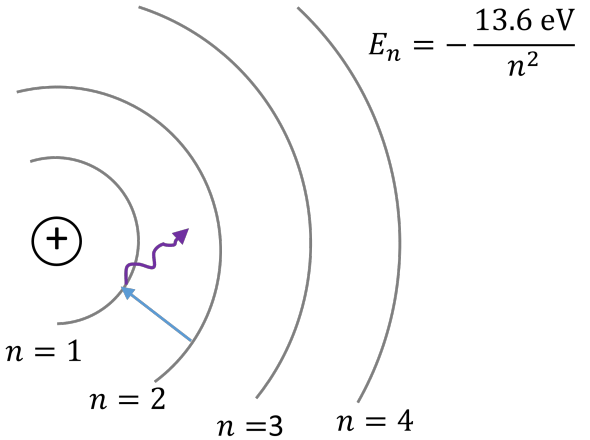
EXAMPLE: THE ZEEMAN EFFECT

ZEEMAN EFFECT

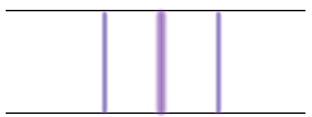
- The Zeeman effect: splitting of spectral lines under magnetic field
- Energy level splitting of atomic orbital levels
- Level-splitting depends on spin and magnetic quantum number
- Additional selection rules for observed emission/spectral lines



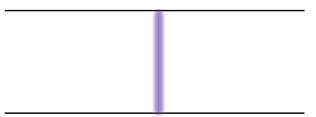




Emission of light by electron falling back from excited level



Spectral line



$$\Delta E_{2\to1} = 13.6\ \text{eV} - 3.4\ \text{eV} \approx 10.2\ \text{eV}$$

$$\Longrightarrow \quad \lambda = 122\ nm$$

ZEEMAN EFFECT FOR HYDROGEN

- Hydrogen as a model system (only 1 electron)
- Assume magnetic field $\vec{B} = (0, 0, B_z)$ along the z-direction (spherical symmetry)
- Start from the Pauli-equation

$$\left[\frac{1}{2m_0} (\hat{\vec{p}} - e\vec{A})^2 1 + V1 + \frac{g\mu_B}{2} \hat{\vec{\sigma}} \cdot \vec{B} \right] \Psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t)$$

where a we choose vector potential $\vec{A} = \frac{1}{2} B (-y, x, 0)$

$$(\hat{\vec{p}} - e\vec{A})^2 = \hat{p}^2 - e\vec{A} \cdot \hat{\vec{p}} + i\hbar e \nabla \cdot \vec{A}$$

where we approximated $e^2 A^2 \approx 0$

DERIVATION ZEEMAN EFFECT

$$
\begin{aligned}
(\hat{\vec{p}} - e\vec{A})^2 &= \hat{p}^2 + i\hbar e\vec{A}\cdot\nabla + i\hbar e\nabla\cdot\vec{A} \\
&= \hat{p}^2 + \frac{i\hbar eB}{2}(-y, x, 0)\cdot(\hat{p}_x, \hat{p}_y, \hat{p}_z) + \frac{i\hbar eB}{2}(\hat{p}_x, \hat{p}_y, \hat{p}_z)\cdot(-y, x, 0) \\
&= \hat{p}^2 + \frac{\hbar^2 eB}{2}(-y\partial_x + x\partial_y) + \frac{\hbar^2 eB}{2}\,0 \\
&= \hat{p}^2 + \frac{\hbar eB}{2}\hat{L}_z
\end{aligned}
$$

where the z-component of angular momentum: $\hat{L}_z = -i\hbar(x\partial_x - y\partial_x)$

Filling this in the Pauli equation:

$$
\left[\left(\frac{\hat{\vec{p}}^2}{2m_0} + V\right) + \frac{\hbar eB}{4m_0}\hat{L}_z + \frac{g\mu_B}{2}\hat{\vec{\sigma}}\cdot\vec{B}\right]\Psi(\vec{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t)
$$

DERIVATION ZEEMAN EFFECT CTU'D

Approximating $g/2 \approx 1$ and using the Bohr magneton $\mu_B = \frac{e\hbar}{m_0}$

$$\left[\left(\frac{\hat{\vec{p}}^2}{2m_0} + V\right) + \frac{\mu_B B}{2\hbar}\left(\hat{L}_z + B\hat{\sigma}_z\right)\right]\Psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)$$

The first term is just the Hydrogen Hamiltonian $\hat{H}_0$

$$\left[\hat{H}_0 + \frac{\mu_B B}{2\hbar}\left(\hat{L}_z + \hat{\sigma}_z\right)\right]\Psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)$$

For stationary solutions we assume $\Psi(\vec{r},t) = \psi(\vec{r})\, e^{-iEt/\hbar}$

$$\left[\hat{H}_0 + \frac{\mu_B B}{2\hbar}\left(\hat{L}_z + \hat{\sigma}_z\right)\right]\psi(\vec{r}) = E\psi(\vec{r})$$

Lecture 09: The Pauli-equation

DERIVATION ZEEMAN EFFECT CTU'D

Remember that $\psi(\vec{r}) = \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix}$ and we have a matrix equation:

$$\left[\hat{H}_0\, 1 + \frac{\mu_B\, B}{2\hbar}\left(\hat{L}_z\, 1 + \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right)\right] \begin{pmatrix} \psi_\uparrow(\vec{r}) \\ \psi_\downarrow(\vec{r}) \end{pmatrix} (\vec{r}) = E \begin{pmatrix} \psi_\uparrow(\vec{r}) \\ \psi_\downarrow(\vec{r}) \end{pmatrix}$$

This corresponds to two **uncoupled** equations for spin-up and spin-down:

$$\left[\hat{H}_0 + \frac{\mu_B\, B}{\hbar}\left(\hat{L}_z + \hbar\right)\right] \psi_\uparrow(\vec{r}) = E\, \psi_\uparrow(\vec{r})$$

$$\left[\hat{H}_0 + \frac{\mu_B\, B}{\hbar}\left(\hat{L}_z - \hbar\right)\right] \psi_\downarrow(\vec{r}) = E\, \psi_\downarrow(\vec{r})$$

Fill in solutions of the Hydrogen atom (eigenstates of $\hat{H}_0$):

$$|n, l, m, \uparrow\rangle = \psi_\uparrow, \qquad |n, l, m, \downarrow\rangle = \psi_\downarrow$$

Lecture 09: The Pauli-equation

EIGENENERGIES AND EIGENSTATES

$$\hat{H}_0\psi_\uparrow(\vec{r}) + \frac{\mu_B\, B}{\hbar}\left(\hat{L}_z + \hbar\right)\psi_\uparrow(\vec{r}) = E\,\psi_\uparrow(\vec{r})$$
$$\hat{H}_0\psi_\downarrow(\vec{r}) + \frac{\mu_B\, B}{\hbar}\left(\hat{L}_z - \hbar\right)\psi_\downarrow(\vec{r}) = E\,\psi_\downarrow(\vec{r})$$

The solutions are eigenstates of the Hydrogen atom, and $\hat{L}_z$

[Math Processing Error]

Fill in solutions of the Hydrogen atom (eigenstates of $\hat{H}_0$):

$$E_{nl}\psi_\uparrow(\vec{r}) + \mu_B\, B(m+1)\psi_\uparrow(\vec{r}) = E\,\psi_\uparrow(\vec{r})$$
$$E_{nl}\psi_\uparrow(\vec{r}) + \mu_B\, B(m-1)\psi_\uparrow(\vec{r}) = E\,\psi_\uparrow(\vec{r})$$

EIGENENERGIES AND EIGENSTATES

Fill in solutions of the Hydrogen atom (eigenstates of $\hat{H}_0$):

$$E_{nl}\psi_\uparrow(\vec{r}) + \mu_B\, B(m+1)\psi_\uparrow(\vec{r}) = E\,\psi_\uparrow(\vec{r})$$
$$E_{nl}\psi_\uparrow(\vec{r}) + \mu_B\, B(m-1)\psi_\uparrow(\vec{r}) = E\,\psi_\uparrow(\vec{r})$$

The eigenenergies $E = E_{nlm\uparrow}$ depend now also on the magnetic quantum number m and the spin $\uparrow$ ($\downarrow$):

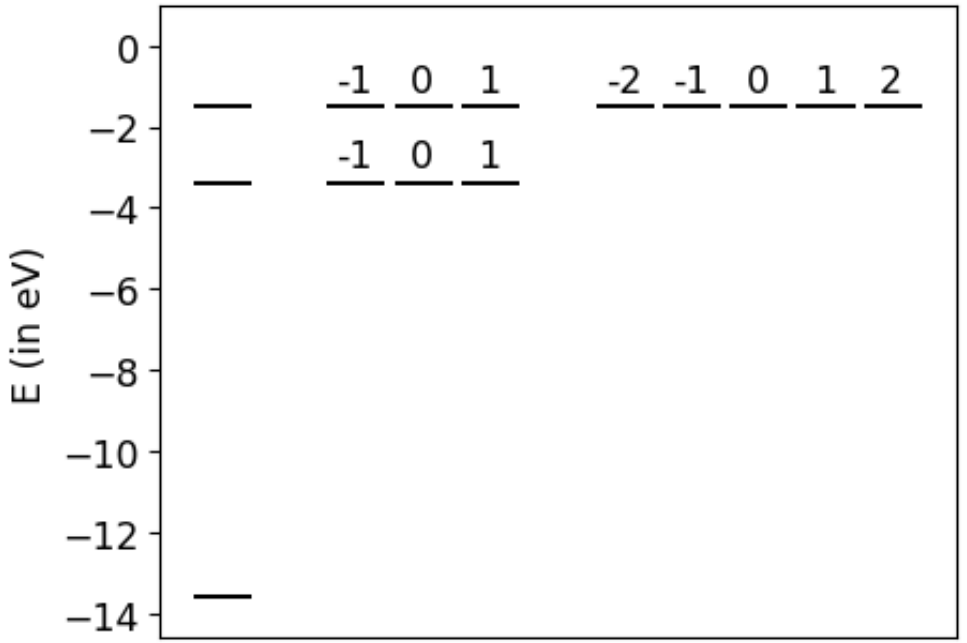
$$\boxed{\begin{aligned} E_{nlm\uparrow} &= E_{nl} + \mu_B\, B(m+1) \quad \text{with} \quad \psi_\uparrow \\ E_{nlm\downarrow} &= E_{nl} + \mu_B\, B(m-1) \quad \text{with} \quad \psi_\downarrow \end{aligned}}$$

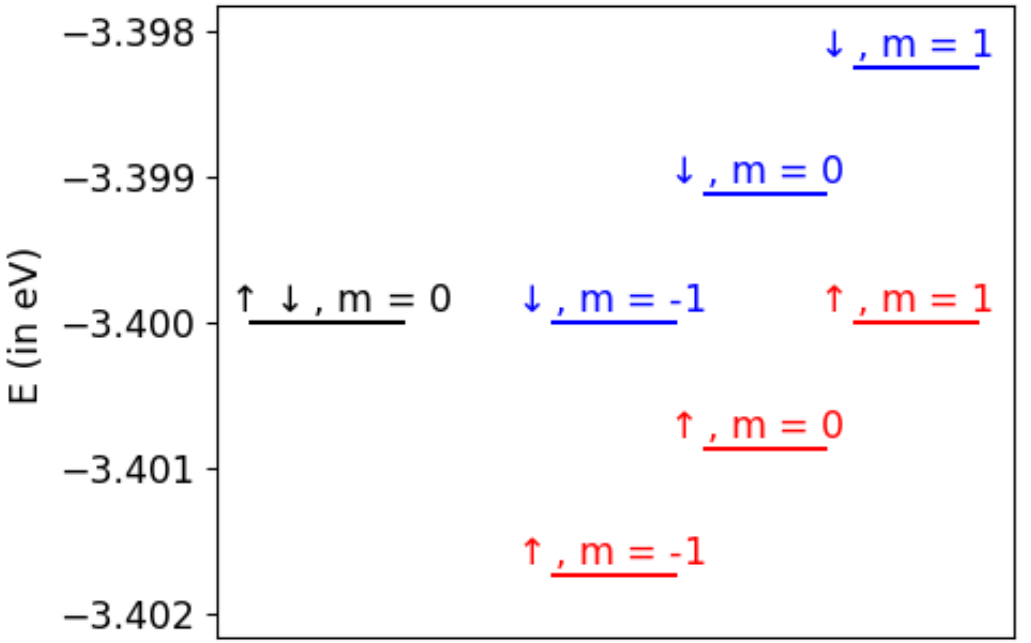
- The splitting of energy levels depends on magnetic field strength B
- Selection rules determine between which energy levels emission is allowed

ENERGY-LEVEL SPLITTING

$$\boxed{\begin{aligned} E_{nlm\uparrow} &= E_{nl} + \mu_B\, B(m+1) \qquad \text{with} \quad \psi_\uparrow \\ E_{nlm\downarrow} &= E_{nl} + \mu_B\, B(m-1) \qquad \text{with} \quad \psi_\downarrow \end{aligned}}$$

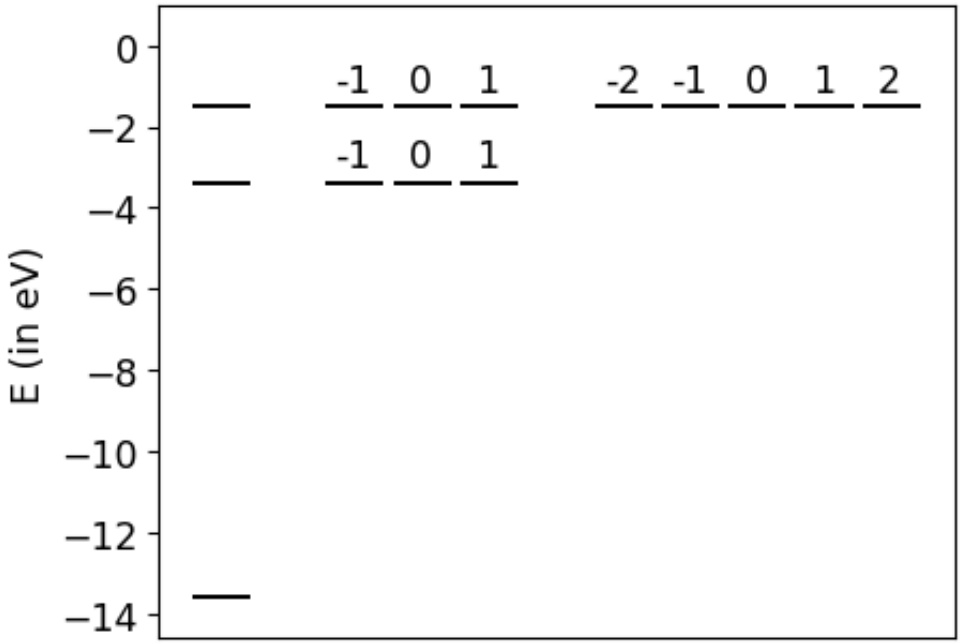
- The splitting of energy levels depends on magnetic field strength B
- Magnetic field for p-orbital level splitting (right plot) $B = 15\,\mathrm{T}$

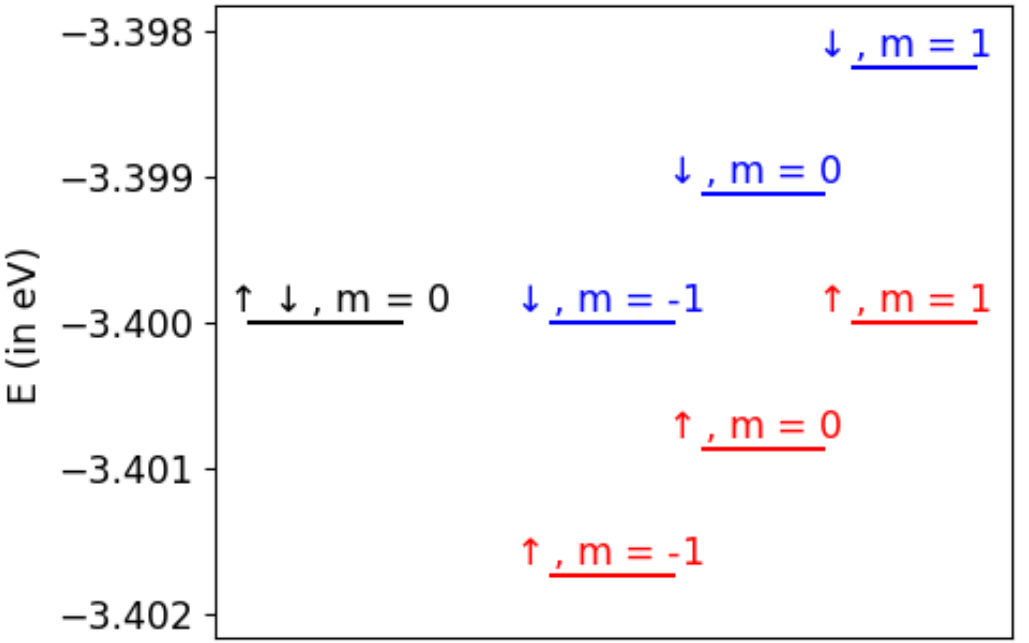




ENERGY-LEVEL SPLITTING

- Bohr magneton $\mu_B \approx 5.8 \times 10^{-5}$ eV/T $\longrightarrow$ splitting small for *normal* magnetic field strengths B. Record laboratory magnetic fields are *e.g.*:
  - Stable magnetic field of 45.5 T
  - Peak, *i.e.* only a few μs, magnetic fields as a pulsed magnetic field: 1200 T
- Selection rules determine between which energy levels emission is allowed





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- The wavelength or frequency differences in spectral lines is given by:

$$\frac{2\pi}{\Delta\lambda} = \Delta f = \frac{\Delta\omega}{2\pi} = \Delta E/h$$

- The Hydrogen emission spectral line at 122 nm will split in three lines.
- Selection rules: Spin is preserved, $l \to l - \pm 1$ while different polarizations of light, therefore