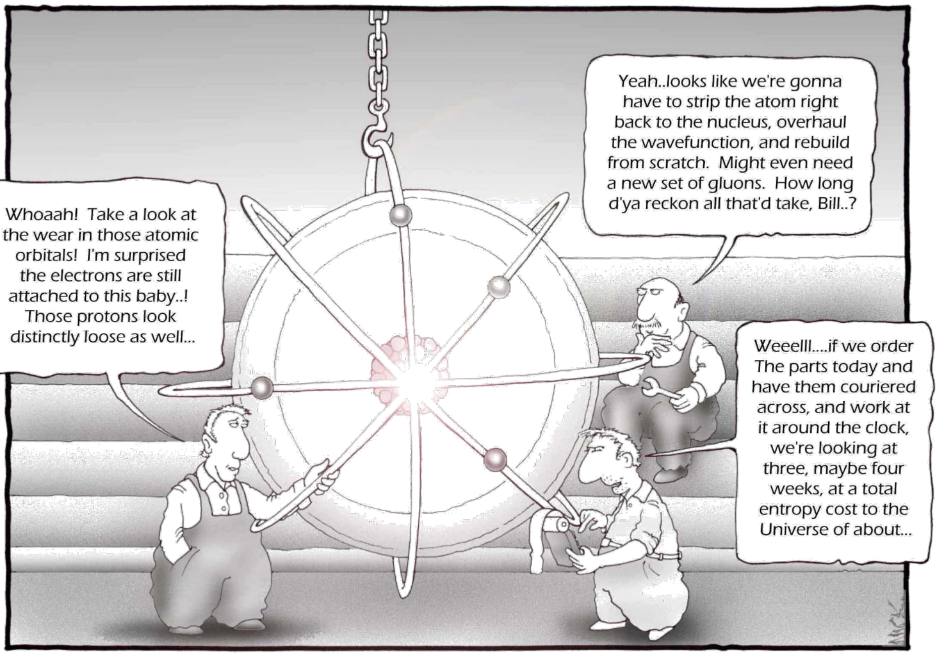
# MSE 423 Fall 2025 – Week 5

# ORBITALS






# Last week: the mechanics of quantum mechanics

$\frac{1}{\sqrt{2}}|\varphi_1\rangle + \frac{1}{\sqrt{2}}|\varphi_3\rangle \nearrow |\psi\rangle$

- Fifth postulate – collapse (remember the others; ket/wfct, operators, measurements, exp~~t~~d values/probabilities) $\| \langle \varphi_n | \psi \rangle \|^2$
- Uncertainties and Heisenberg indetermination principle; natural linewidths
- Good quantum numbers $[\hat{A}, \hat{H}] = 0$ $\quad \frac{d\langle \hat{A} \rangle}{dt} = 0$ → HOMEWORK
- (I) Variational principle ~ $\frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = E[\psi] \geq \mathcal{E}_0 \qquad E[\psi] = \mathcal{E}_0 \Leftrightarrow \psi = \varphi_0$
- (II) Differential equations in a basis – a linear algebra problem of matrix diagonalization $\hat{H}|\psi\rangle = \varepsilon|\psi\rangle$ $\quad \boxed{|\psi\rangle = \sum_{n=1,10} c_n |\varphi_n\rangle}$
- Spherical coordinates and angular momentum

$$\hat{L} = \hat{r} \times \hat{p}$$

$$L_x = y p_z - z p_y = y\left(-i\hbar \frac{\partial}{\partial z}\right) - z\left(-i\hbar \frac{\partial}{\partial y}\right)$$

$$L_y = \vdots \qquad L_z = \vdots$$

$$\begin{pmatrix} H_{11} & \cdots & H_{1,10} \\ H_{21} & \cdots & H_{2,10} \\ \vdots & \ddots & \\ & & H_{10,10} \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_{10} \end{pmatrix} = E \begin{pmatrix} c_1 \\ \vdots \\ c_{10} \end{pmatrix}$$

$$\det \| \underline{H} - E \underline{\mathbb{1}} \| = 0$$

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

# Commutation Relation

SQ. MOM. OF ANG. MOM.

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

THEY CAN BE MEASURED SIMUL.

$$\left[\hat{L}^2, \hat{L}_x\right] = \left[\hat{L}^2, \hat{L}_y\right] = \left[\hat{L}^2, \hat{L}_z\right] = 0$$

$$\underbrace{\left[\hat{L}_x, \hat{L}_y\right]}_{\text{DO NOT COMMUTE}} = i\hbar \hat{L}_z \neq 0$$



# Angular Momentum in Spherical Coordinates

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi} \quad \cancel{= -i\hbar \frac{\partial}{\partial \theta}} \quad = -i\hbar \frac{\partial}{\partial \varphi}$$

$$\hat{L}^2 = -\hbar^2 \left( \underbrace{\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right)}_{\vartheta} + \underbrace{\frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2}}_{\vartheta,\,\varphi} \right)$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

SPHERICAL HARMONICS

# Simultaneous eigenfunctions of $\hat{L}^2$, $\hat{L}_z$

$$\hat{L}_z Y_\ell^m(\vartheta,\varphi) = m\hbar \; Y_\ell^m(\vartheta,\varphi) \qquad -\ell \le m \le \ell$$

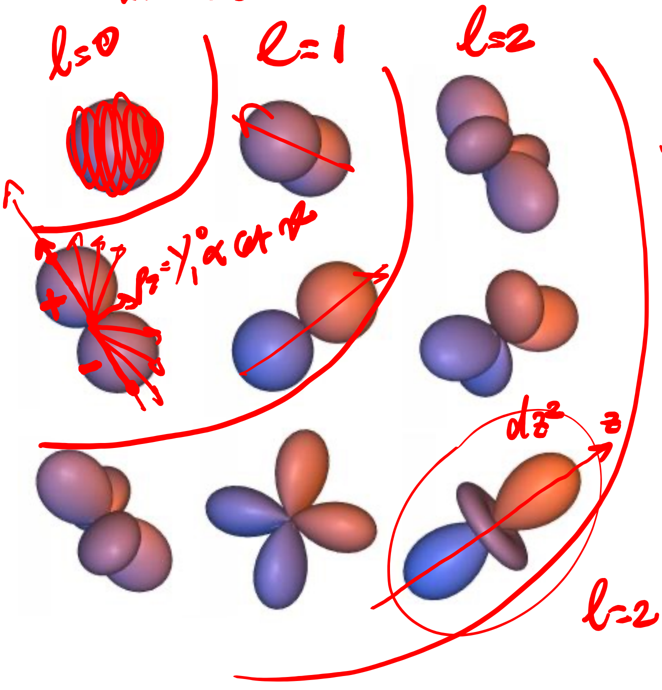
$$\hat{L}^2 Y_\ell^m(\vartheta,\varphi) = \hbar^2 \ell(\ell+1) \; Y_\ell^m(\vartheta,\varphi)$$

$\ell$ = INTEGER NUMBERS = 0, 1, 2, 3, ......

EVAL OF $L^2$ = 0, $\hbar^2 2$, $\hbar^2 6$, ....



# Spherical Harmonics in Real Form




$\ell=0 \quad Y_0^0 = \frac{1}{\sqrt{4\pi}}$

$\ell=1$

$$p_x = \frac{1}{\sqrt{2}}\left(Y_1^1 + Y_1^{-1}\right) = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi$$

$$p_y = \frac{1}{\sqrt{2}\,i}\left(Y_1^1 - Y_1^{-1}\right) = \sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi$$

$$p_z = Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$d_{z^2} = Y_2^0 = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right) \qquad (m=0,\ \ell=2)$$

$$d_{xz} = \frac{1}{\sqrt{2}}\left(Y_2^1 + Y_2^{-1}\right) = \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\cos\phi$$

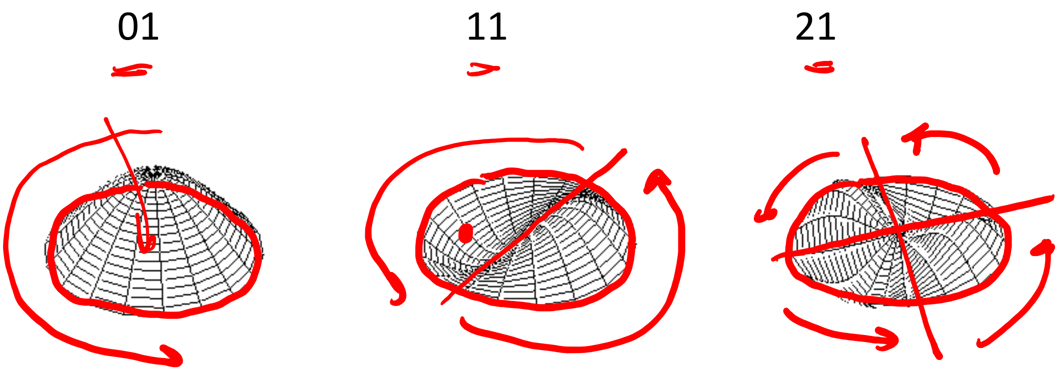
$$d_{yz} = \frac{1}{\sqrt{2}\,i}\left(Y_2^1 - Y_2^{-1}\right) = \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\sin\phi$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}\left(Y_2^2 + Y_2^{-2}\right) = \sqrt{\frac{15}{16\pi}}\sin^2\theta\cos 2\phi$$

$$d_{xy} = \frac{1}{\sqrt{2}\,i}\left(Y_2^2 - Y_2^{-2}\right) = \sqrt{\frac{15}{16\pi}}\sin^2\theta\sin 2\phi$$

$\ell=2$

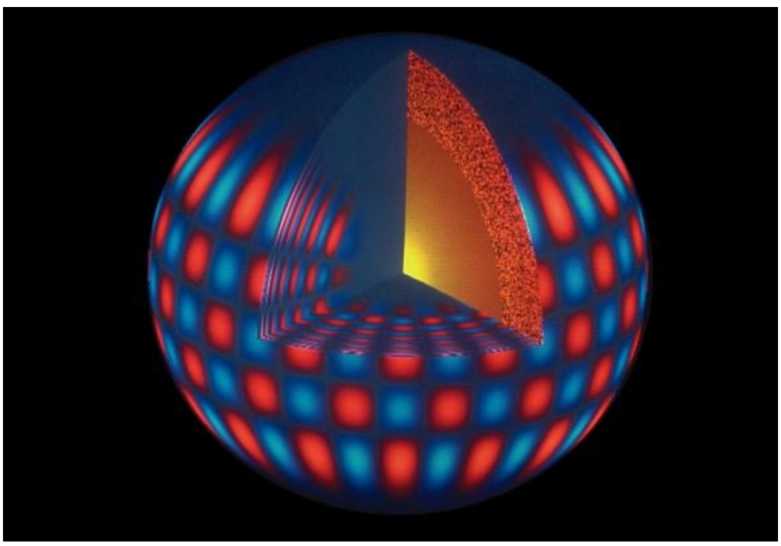
# Same as a beating drum…






SUN   SUN ~~EARTH~~QUAKE

# …for the career helioseismologist



Normal modes (i.e. sound, or seismic waves) for the Sun (basically jello in a 3d spherical box)

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

# Angular Momentum, then…

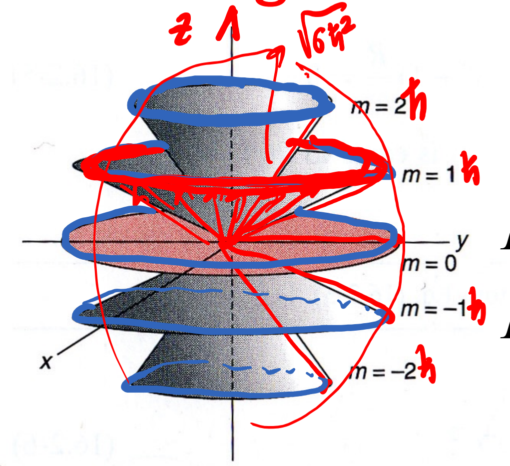



**Figure 16.4. Cones of Possible Angular Momentum Directions for $l = 2$.** These cones are similar to the cones of precession of a gyroscope, and represent possible directions for the angular momentum vector. The $z$ component is arbitrarily chosen as the one component that can have a definite value.

$\sqrt{l(l+1)\hbar^2} = \sqrt{6\hbar^2}$

$\hat{L}^2 Y_2^m = \hbar^2 6\, Y_2^m$

$$L^2 = l(l+1)\hbar^2 = 0, \quad 2\hbar^2, \quad 6\hbar^2 \ldots$$

$$L_z = 0, \quad \pm\hbar, \quad \pm 2\hbar, \quad \pm 3\hbar \ldots$$



# An electron in a central potential (I)

$Z=1$

SPH COORD: $r, \vartheta, \varphi$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$\nabla^2$ needs to be in spherical coordinates

$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \ldots (r, \vartheta, \varphi)$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\underbrace{\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right]}_{\nabla^2} + V(r)$$

$$\hat{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

$\frac{1}{\mu} = \cancel{\frac{1}{M_p}} + \frac{1}{m_e}$

$\hat{H}\psi = E\psi$

# An electron in a central potential (II)

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hat{L}^2}{2\mu r^2} + \hat{V}(r)$$

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}r^2\frac{d^2}{dr^2} + \frac{1}{r^2}2r\frac{d}{dr}\right]RY + \frac{\hat{L}^2}{2\mu r^2}RY + \hat{V}RY = ERY$$

$\hat{L}^2 RY = R\hat{L}^2 Y = ??$

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

$\boxed{\hat{H}RY = ERY}$

ANSATZ

$\psi = RY$

$$\boxed{\psi_{nlm}(\vec{r}) = R_{nlm}(r)Y_{lm}(\vartheta,\varphi)}$$



# An electron in a central potential (III)

$$\psi(x,y,z) \longrightarrow \psi(r,\vartheta,\varphi) \longrightarrow \underbrace{R(r)}\underbrace{Y(\vartheta,\varphi)}_{\Downarrow\ L^2,\ L_z}$$

$\hat{H}_l$ RADIAL DIFF. EQUATION

$$\boxed{\left[-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)\right]R_{nl}(r) = E_{nl}R_{nl}(r)}$$

# An electron in a central potential (IV)

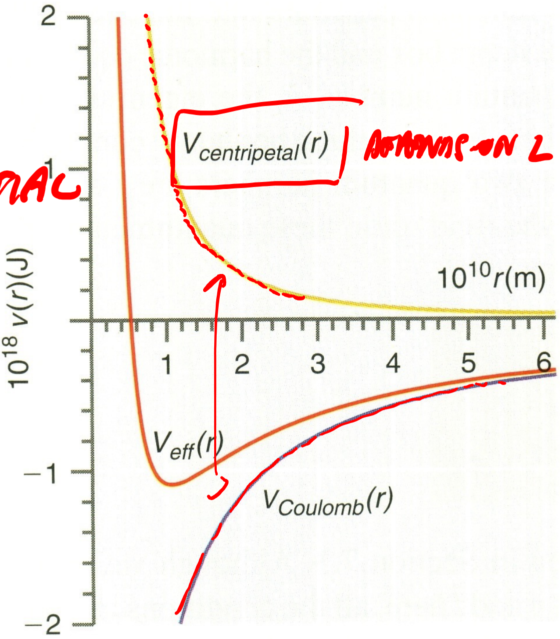
$$\left[\underbrace{-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)+\frac{l(l+1)\hbar^2}{2\mu r^2}+V(r)}_{\text{He}}\right]R_{nl}(r)=E_{nl}\,R_{nl}(r)$$

$$\underbrace{u_{nl}(r)=r\,R_{nl}(r)}$$

$$\boxed{\left[\underbrace{-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}}+\underbrace{V_{eff}(r)}\right]u_{nl}(r)=E_{nl}\,u_{nl}(r)}$$

# What is the $V_{eff}(r)$ potential ?

$$V_{eff}(r)=\underbrace{\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}}_{\text{COMES FROM THE LAPLACIAN}}-\underbrace{\frac{Ze^2}{4\pi\varepsilon_0 r}}_{\text{TRUE POTENTIAL}}$$



$-\frac{\hbar^2}{2\mu}\nabla^2$ IN SPHERICAL COORDINATES

# Summary

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hat{L}^2}{2\mu r^2} + \hat{V}(r)$$

IN SPHERICAL COORDINATES

$$\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\vartheta,\varphi) \qquad \boxed{u_{nl}(r) = r\,R_{nl}(r)}$$

$+\frac{1}{r}l(l+1) \quad -\frac{1}{r}$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V_{eff}(r)\right]u_{nl}(r) = E_{nl}\,u_{nl}(r)$$

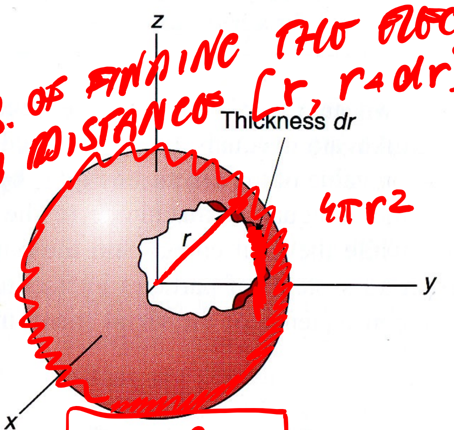
$$V_{eff}(r) = \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$



# The Radial Wavefunctions for Coulomb V(r)

$\|\psi\|^2$

PROB. OF FINDING THE ELECT. AT A DISTANCE $[r, r+dr]$




$\boxed{n-l-1}$ # NODES

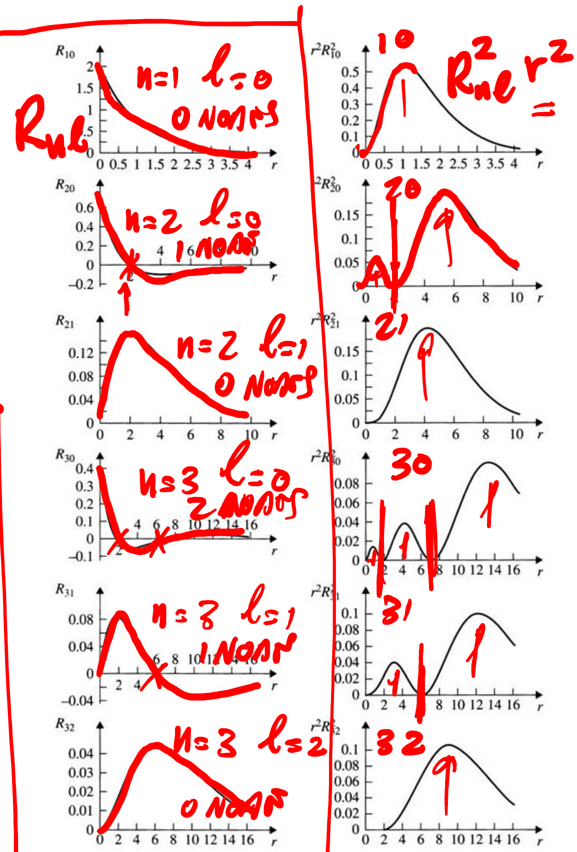
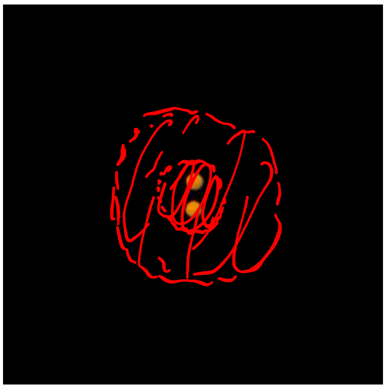


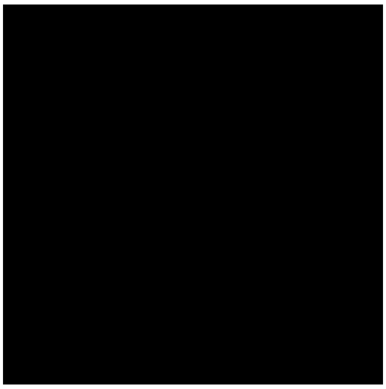

*Figure 7.9* Radial functions $R_{nl}(r)$ and radial distribution functions $r^2R_{nl}^2(r)$ for atomic hydrogen. The unit of length is $a_\mu = (m/\mu)a_0$, where $a_0$ is the first Bohr radius (1.66).

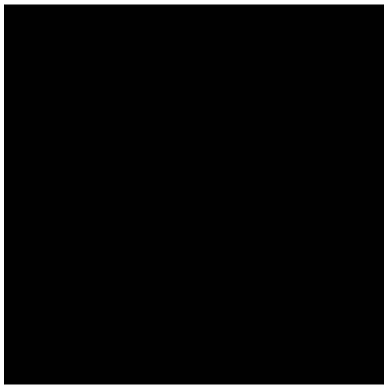
# Solutions in the central Coulomb potential

$n=5 \quad \ell=2 \quad n-\ell-1$ $\qquad$ $n=4 \quad \ell=3$ $\qquad$ $n=5 \quad \ell=4$

$d_{z^2}=Y_2^0$ 5d $Y_2^{m=0}$ $\qquad$ 4f 0 NODES $\qquad$ 5g 0 NODES





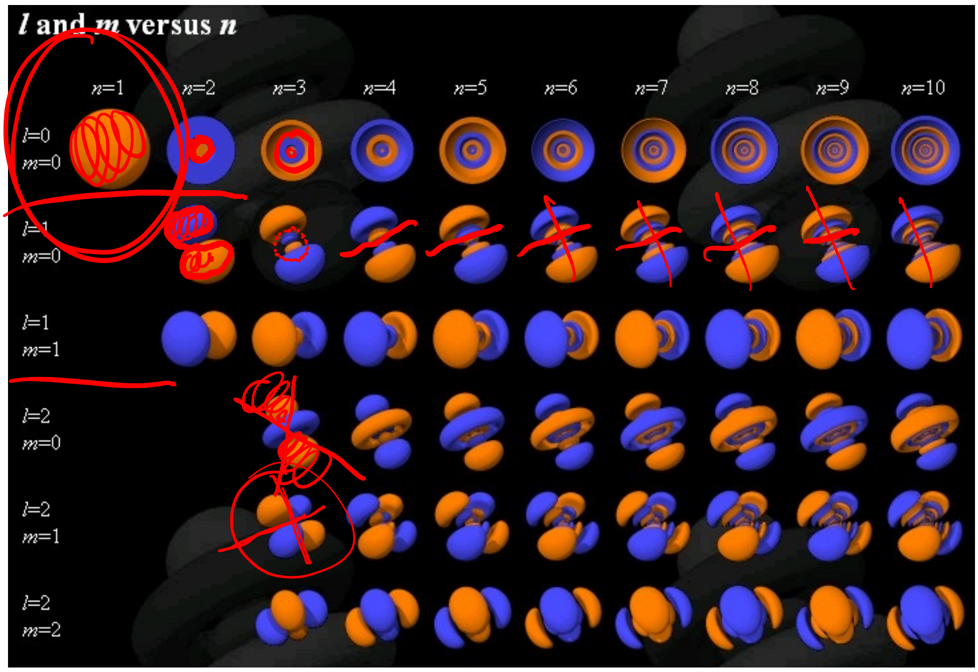




# The Full Alphabet Soup

$n-\ell-1$

http://www.orbitals.com/orb/orbtable.htm



# The Grand Table

**Table 3.1** The complete normalised hydrogenic wave functions corresponding to the first three shells, for an 'infinitely heavy' nucleus. The quantity $a_0 = 4\pi\varepsilon_0\hbar^2/me^2$ is the first Bohr radius. In order to take into account the reduced mass effect one should replace $a_0$ by $a_\mu = a_0(m/\mu)$

| Shell | Quantum numbers $n$ | $l$ | $m$ | Spectroscopic notation | Wave function $\psi_{nlm}(r,\theta,\phi)$ |
|---|---|---|---|---|---|
| K | 1 | 0 | 0 | 1s | $\frac{1}{\sqrt{\pi}}(Z/a_0)^{3/2}\exp(-Zr/a_0)$ |
| L | 2 | 0 | 0 | 2s | $\frac{1}{2\sqrt{2\pi}}(Z/a_0)^{3/2}(1-Zr/2a_0)\exp(-Zr/2a_0)$ |
| | 2 | 1 | 0 | $2p_0$ | $\frac{1}{4\sqrt{2\pi}}(Z/a_0)^{3/2}(Zr/a_0)\exp(-Zr/2a_0)\cos\theta$ |
| | 2 | 1 | $\pm1$ | $2p_{\pm1}$ | $\mp\frac{1}{8\sqrt{\pi}}(Z/a_0)^{3/2}(Zr/a_0)\exp(-Zr/2a_0)\sin\theta\exp(\pm i\phi)$ |
| M | 3 | 0 | 0 | 3s | $\frac{1}{3\sqrt{3\pi}}(Z/a_0)^{3/2}(1-2Zr/3a_0+2Z^2r^2/27a_0^2)\exp(-Zr/3a_0)$ |
| | 3 | 1 | 0 | $3p_0$ | $\frac{2\sqrt{2}}{27\sqrt{\pi}}(Z/a_0)^{3/2}(1-Zr/6a_0)(Zr/a_0)\exp(-Zr/3a_0)\cos\theta$ |
| | 3 | 1 | $\pm1$ | $3p_{\pm1}$ | $\mp\frac{2}{27\sqrt{\pi}}(Z/a_0)^{3/2}(1-Zr/6a_0)(Zr/a_0)\exp(-Zr/3a_0)\sin\theta\exp(\pm i\phi)$ |
| | 3 | 2 | 0 | $3d_0$ | $\frac{1}{81\sqrt{6\pi}}(Z/a_0)^{3/2}(Z^2r^2/a_0^2)\exp(-Zr/3a_0)(3\cos^2\theta-1)$ |
| | 3 | 2 | $\pm1$ | $3d_{\pm1}$ | $\mp\frac{1}{81\sqrt{\pi}}(Z/a_0)^{3/2}(Z^2r^2/a_0^2)\exp(-Zr/3a_0)\sin\theta\cos\theta\exp(\pm i\phi)$ |
| | 3 | 2 | $\pm2$ | $3d_{\pm2}$ | $\frac{1}{162\sqrt{\pi}}(Z/a_0)^{3/2}(Z^2r^2/a_0^2)\exp(-Zr/3a_0)\sin^2\theta\exp(\pm 2i\phi)$ |

$\hat{L}$ $\hat{L}^2$ $[\hat{L}^2, \hat{L}_z] = 0$

# Three Quantum Numbers

- $\hat{H} \leftrightarrow$ Principal quantum number **n** (energy, accidental degeneracy)

$$E_n = -\frac{e^2}{8\pi\varepsilon_0}\frac{Z^2}{a_0 n^2} = -(13.6058\ \text{eV})\frac{Z^2}{n^2} = -(1\ \text{Ry})\frac{Z^2}{n^2}$$

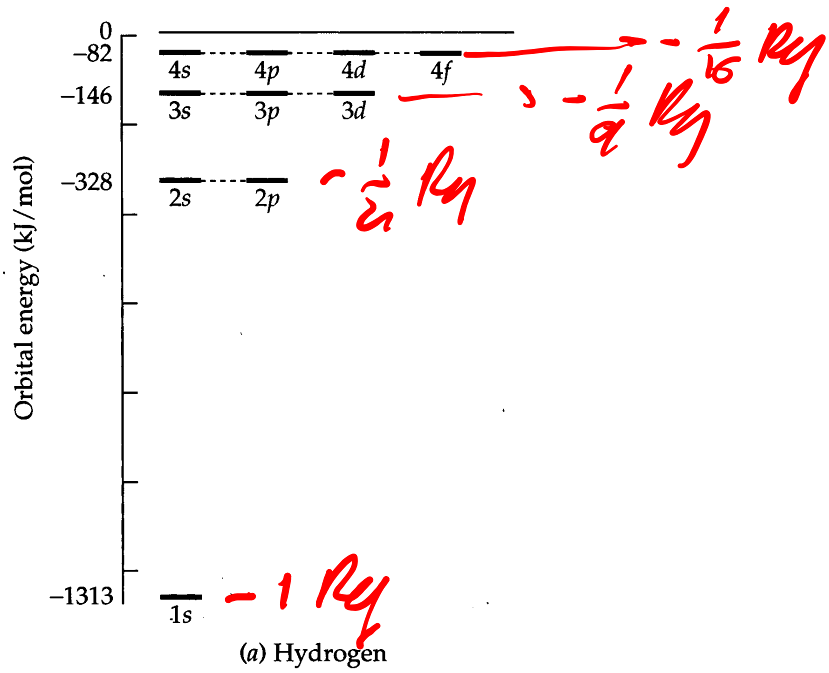
- $\hat{L}^2 \leftrightarrow$ Angular momentum quantum number ***l***

***l* = 0,1,…,n-1 (a.k.a. s, p, d… orbitals)**

- $\hat{L}_z \leftrightarrow$ Magnetic quantum number ***m***

***m* = -l,-l+1,…,l-1,l**

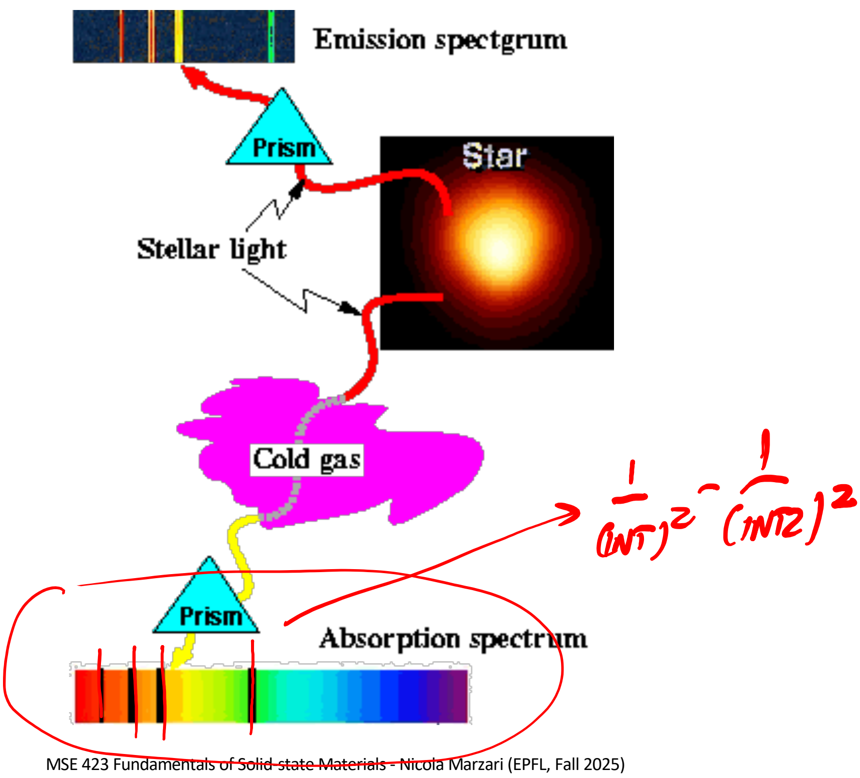
# Orbital levels in hydrogenoid atoms

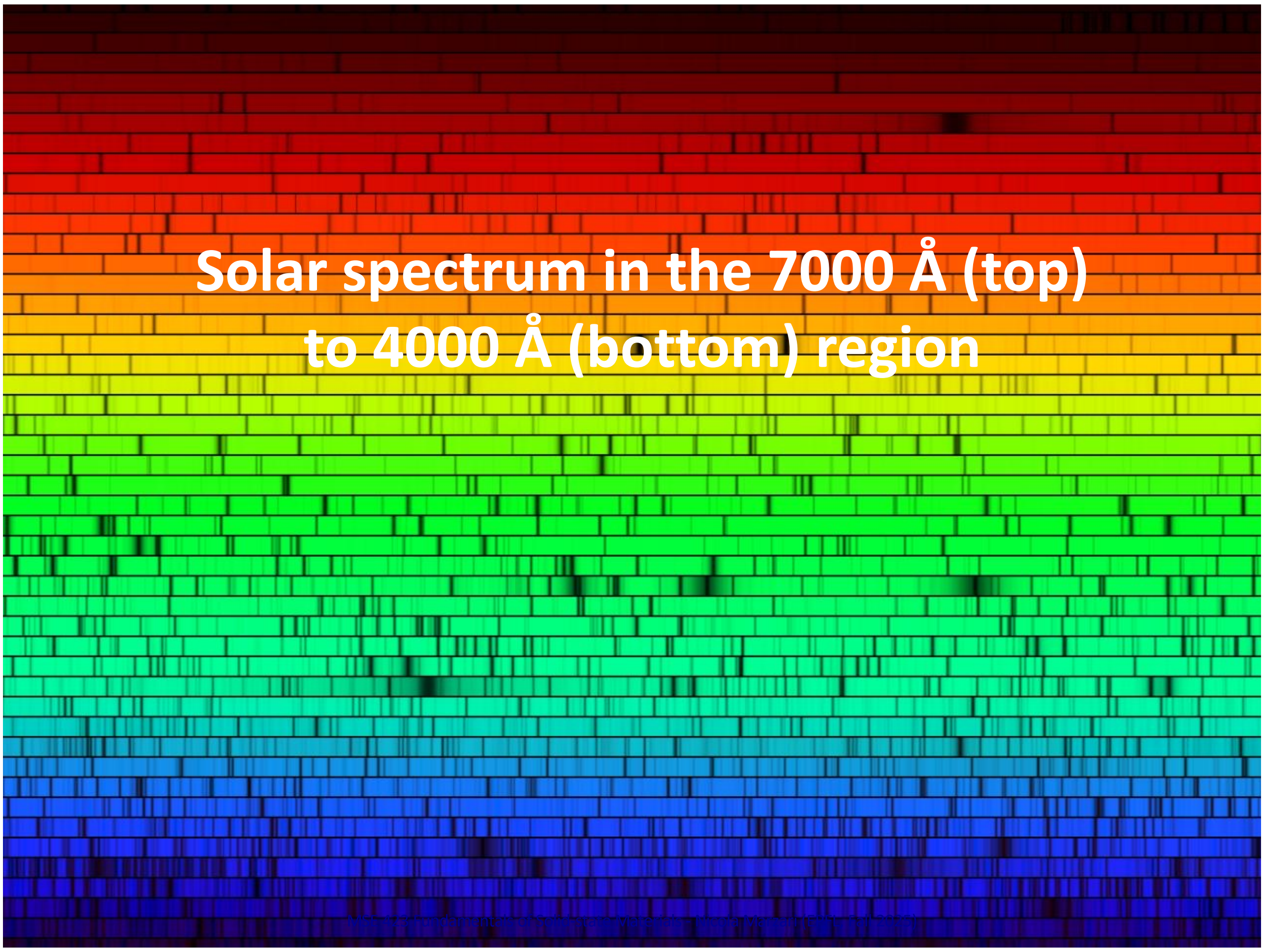



(a) Hydrogen

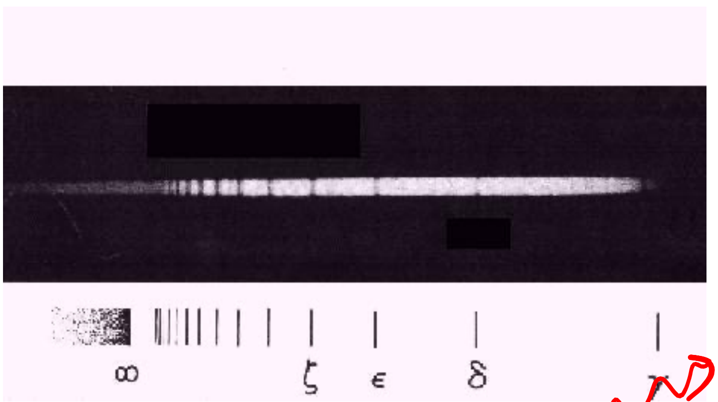


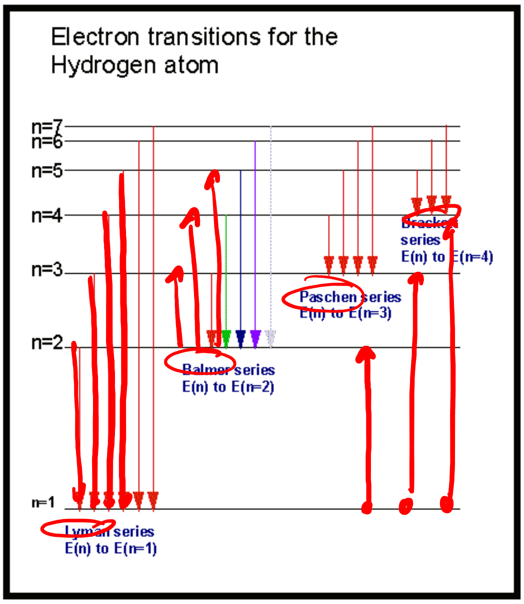
# Emission and absorption lines





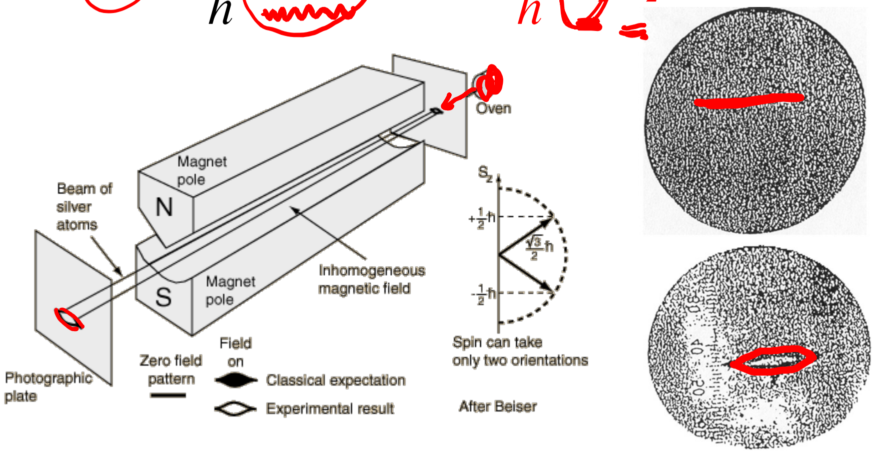

# Balmer lines in a hot star



# Right experiment – wrong theory (Stern-Gerlach)

$$\cancel{\hat{H} \to \hat{H} + \frac{\mu_B}{\hbar}\hat{L}\cdot\vec{B} = \hat{H} + \frac{\mu_B}{\hbar}\hat{L} B_z}$$




$$\hat{H} \to \hat{H} + \frac{\mu_B}{\hbar}(\hat{L} + 2\hat{S})\cdot\vec{B} = \hat{H} + \frac{\mu_B}{\hbar}(\hat{L}_z + 2\hat{S}_z)B_z$$

Goudsmit and Uhlenbeck



# Spin

- Dirac derived the relativistic extension of Schrödinger's equation; for a free particle he found two independent solutions for a given energy
- There is an operator (spin S) that commutes with the Hamiltonian and that can only have two eigenvalues
- In a magnetic field, the spin combines with the angular momentum, and they couple via

$$\boxed{\hat{H} \to \hat{H} + \frac{\mu_B}{\hbar}(\hat{L} + 2\hat{S})\cdot\vec{B}}$$

# Spin Eigenvalues/Eigenfunctions

- Norm (s integer → bosons, half-integer → fermions)

$$\hat{S}^2 \Psi_{spin} = \hbar^2 s(s+1) \Psi_{spin}$$

- Z-axis projection (electron is a fermion with s=1/2)

$$\hat{S}_z \Psi_{spin} = \pm \frac{\hbar}{2} \Psi_{spin}$$

- Spin-orbital: product of the “space” wavefunction and the “spin” wavefunction