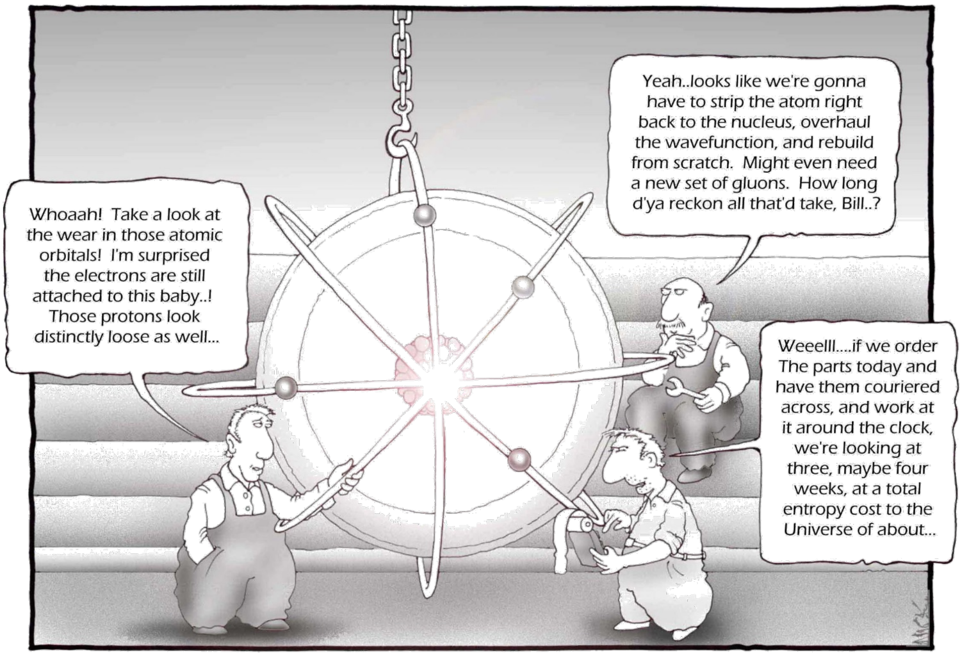
MSE 423 Fall 2025 – Week 5

ORBITALS



Last week: the mechanics of quantum mechanics

- Fifth postulate – collapse (remember the others; ket/wfct, operators, measurements, expt values/probabilities)
- Uncertainties and Heisenberg indetermination principle; natural linewidths
- Good quantum numbers
- Variational principle
- Differential equations in a basis – a linear algebra problem of matrix diagonalization
- Spherical coordinates and angular momentum

Commutation Relation

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

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

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z \neq 0$$

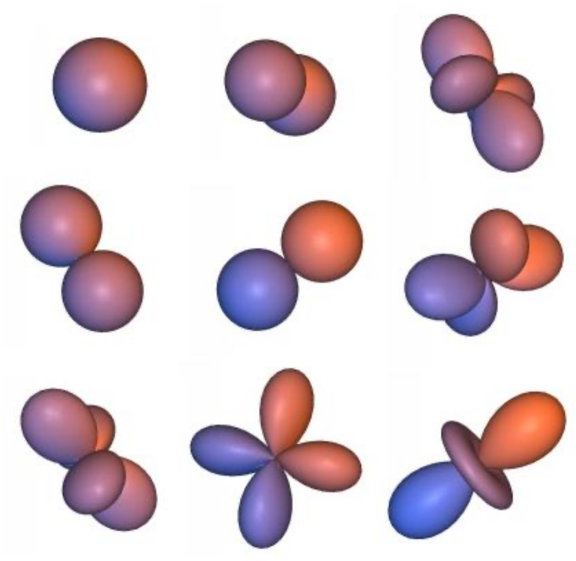
Angular Momentum in Spherical Coordinates

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

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

Simultaneous eigenfunctions of L^2, L_z

Spherical Harmonics in Real Form



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

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

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

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

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

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

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

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

Same as a beating drum…

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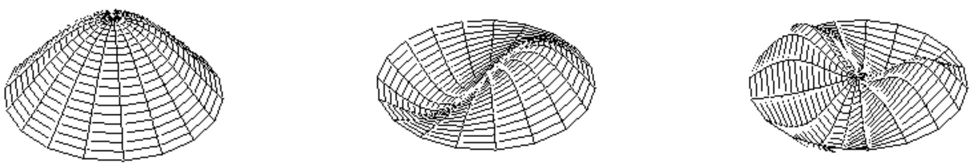
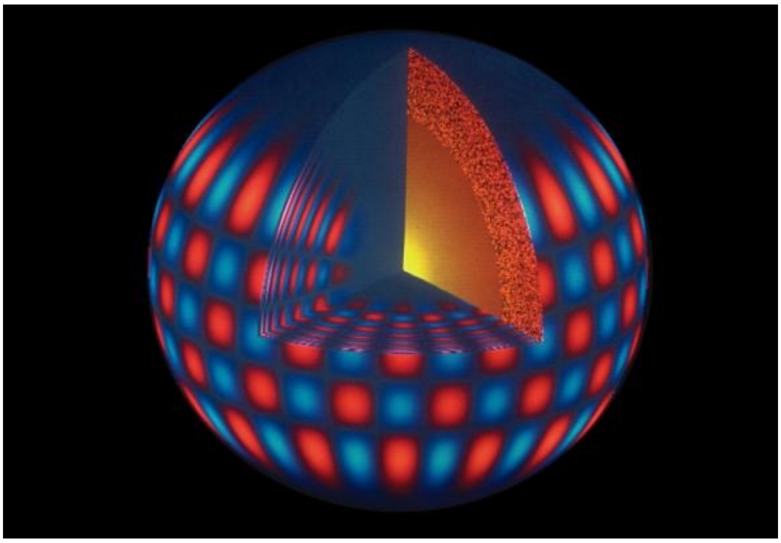


…for the career helioseismologist



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

Angular Momentum, then…

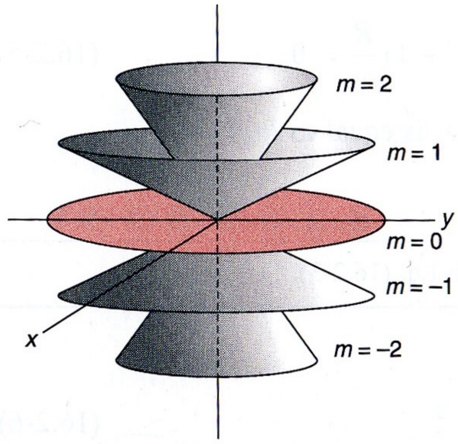


Figure 16.4. Cones of Possible Angular Momentum Directions for $l = 2$. These cones are similar to the cones of precession of a gyroscope, and represent possible directions for the angular momentum vector. The z component is arbitrarily chosen as the one component that can have a definite value.

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

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

An electron in a central potential (I)

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

∇^2 needs to be in spherical coordinates

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

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

An electron in a central potential (II)

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

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

An electron in a central potential (III)

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

An electron in a central potential (IV)

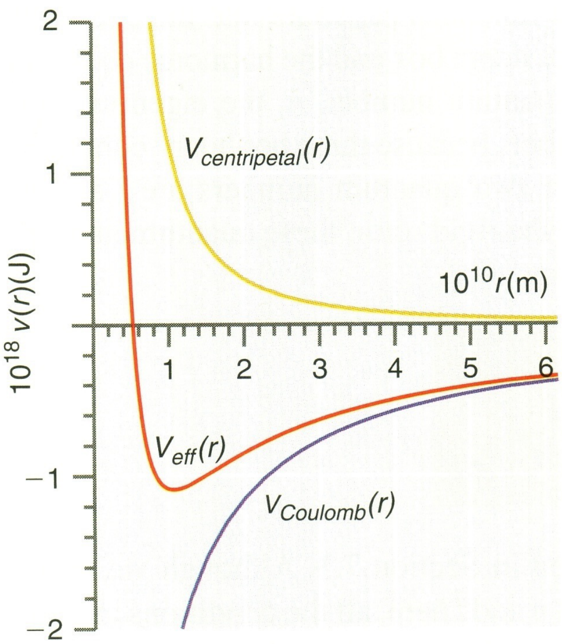
$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)+\frac{l(l+1)\hbar^2}{2\mu r^2}+V(r)\right]R_{nlm}(r)=E_{nlm}\,R_{nlm}(r)$$

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

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

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

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



Summary

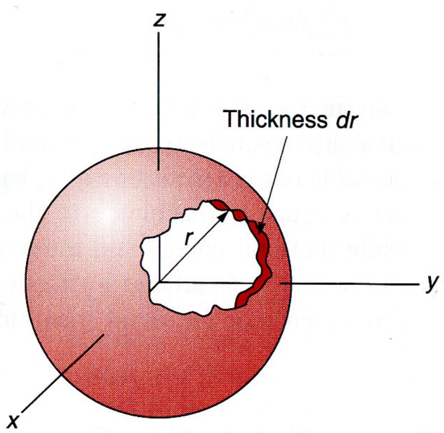
$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hat{L}^2}{2\mu r^2} + \hat{V}(r)$$

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

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

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

The Radial Wavefunctions for Coulomb V(r)



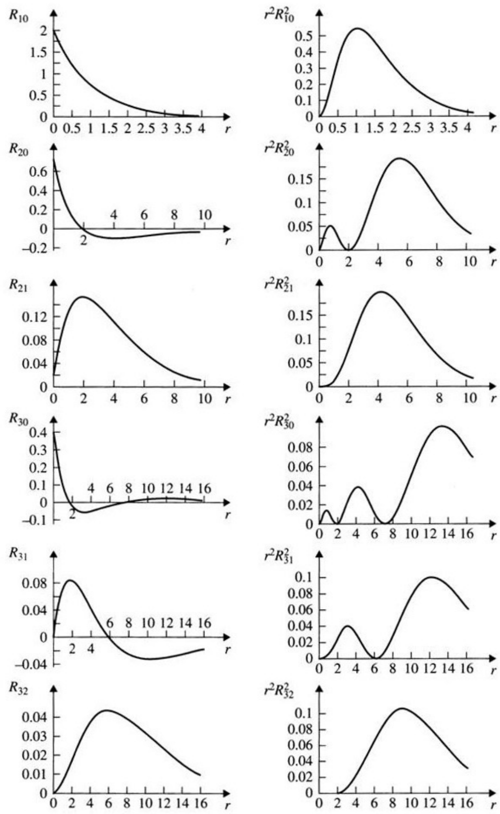
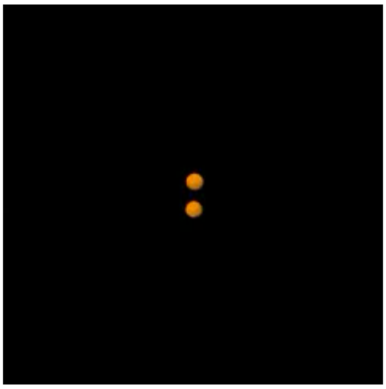
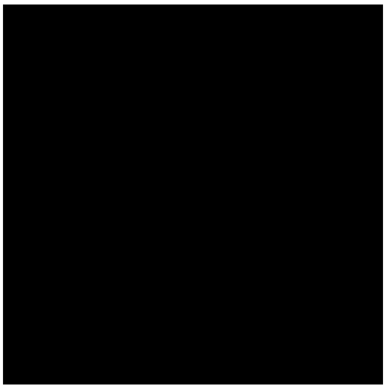
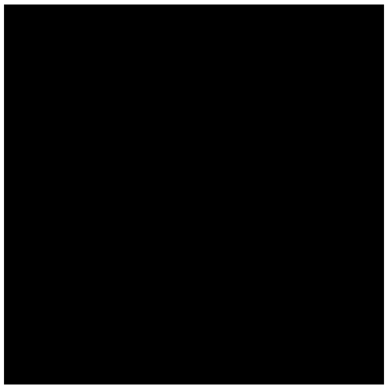


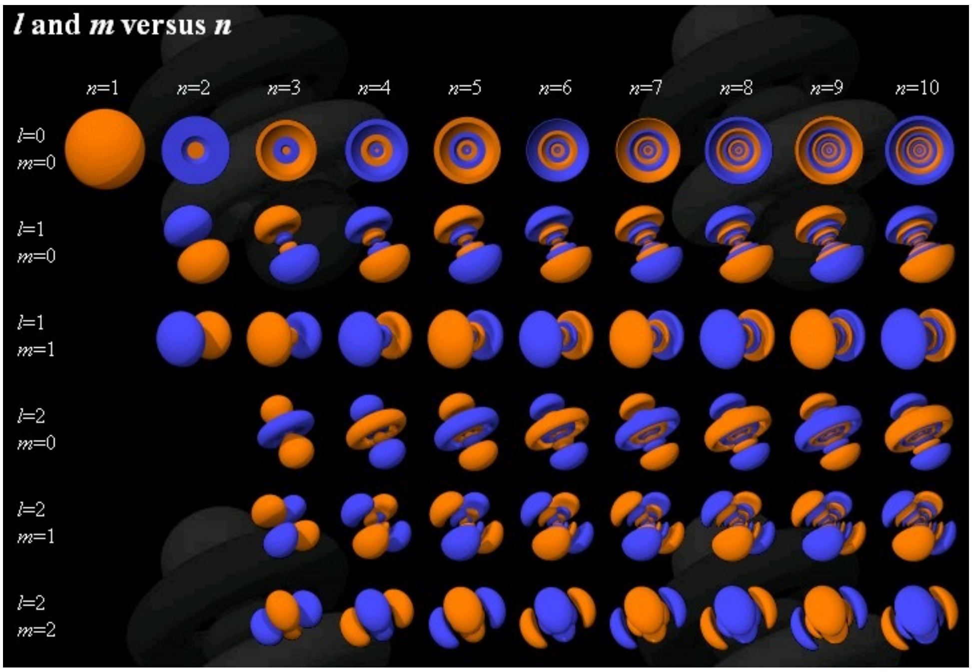
Figure 7.9 Radial functions $R_{nl}(r)$ and radial distribution functions $r^2R_{nl}^2(r)$ for atomic hydrogen. The unit of length is $a_\mu = (m/\mu)a_0$, where a_0 is the first Bohr radius (1.66).

Solutions in the central Coulomb potential

5d	4f	5g
		

The Full Alphabet Soup

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	±1	$2p_{\pm1}$	$\mp\frac{1}{8\sqrt{\pi}}(Z/a_0)^{3/2}(Zr/a_0)\exp(-Zr/2a_0)\sin\theta\exp(\pm i\phi)$
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	±1	$3p_{\pm1}$	$\mp\frac{2}{27\sqrt{\pi}}(Z/a_0)^{3/2}(1 - Zr/6a_0)(Zr/a_0)\exp(-Zr/3a_0)\sin\theta\exp(\pm i\phi)$
	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	±1	$3d_{\pm1}$	$\mp\frac{1}{81\sqrt{\pi}}(Z/a_0)^{3/2}(Z^2r^2/a_0^2)\exp(-Zr/3a_0)\sin\theta\cos\theta\exp(\pm i\phi)$
	3	2	±2	$3d_{\pm2}$	$\frac{1}{162\sqrt{\pi}}(Z/a_0)^{3/2}(Z^2r^2/a_0^2)\exp(-Zr/3a_0)\sin^2\theta\exp(\pm 2i\phi)$

Three Quantum Numbers

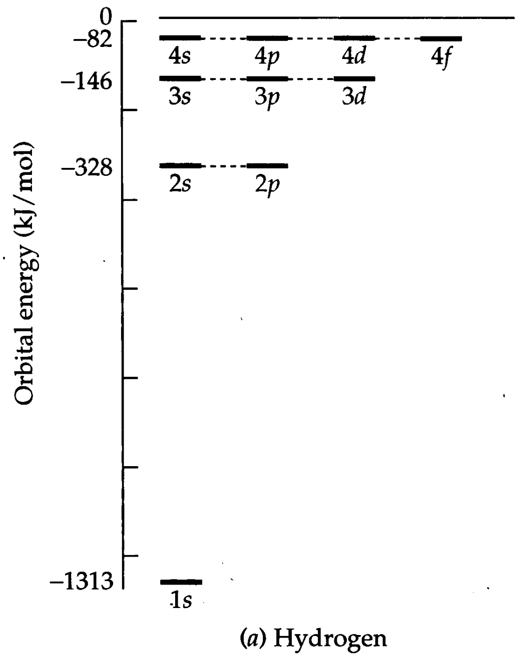
- $\hat{H} \leftrightarrow$ Principal quantum number **n** (energy, accidental degeneracy)

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

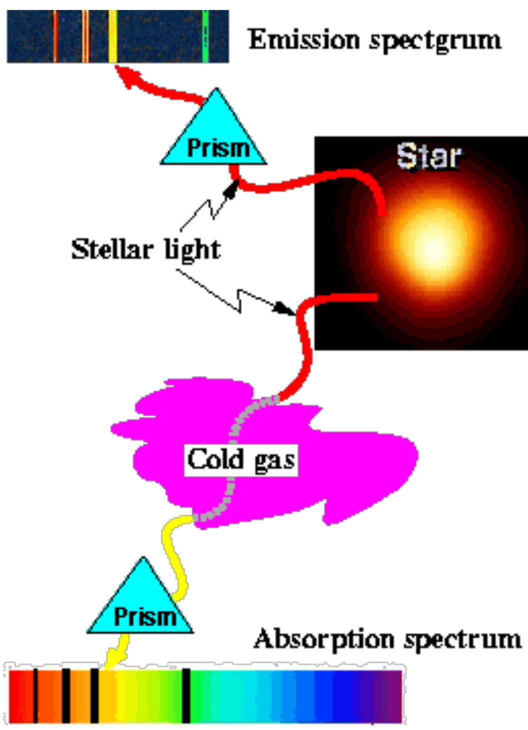
- $\hat{L}^2 \leftrightarrow$ Angular momentum quantum number ***l***
  l = 0,1,…,n-1   (a.k.a. s, p, d… orbitals)

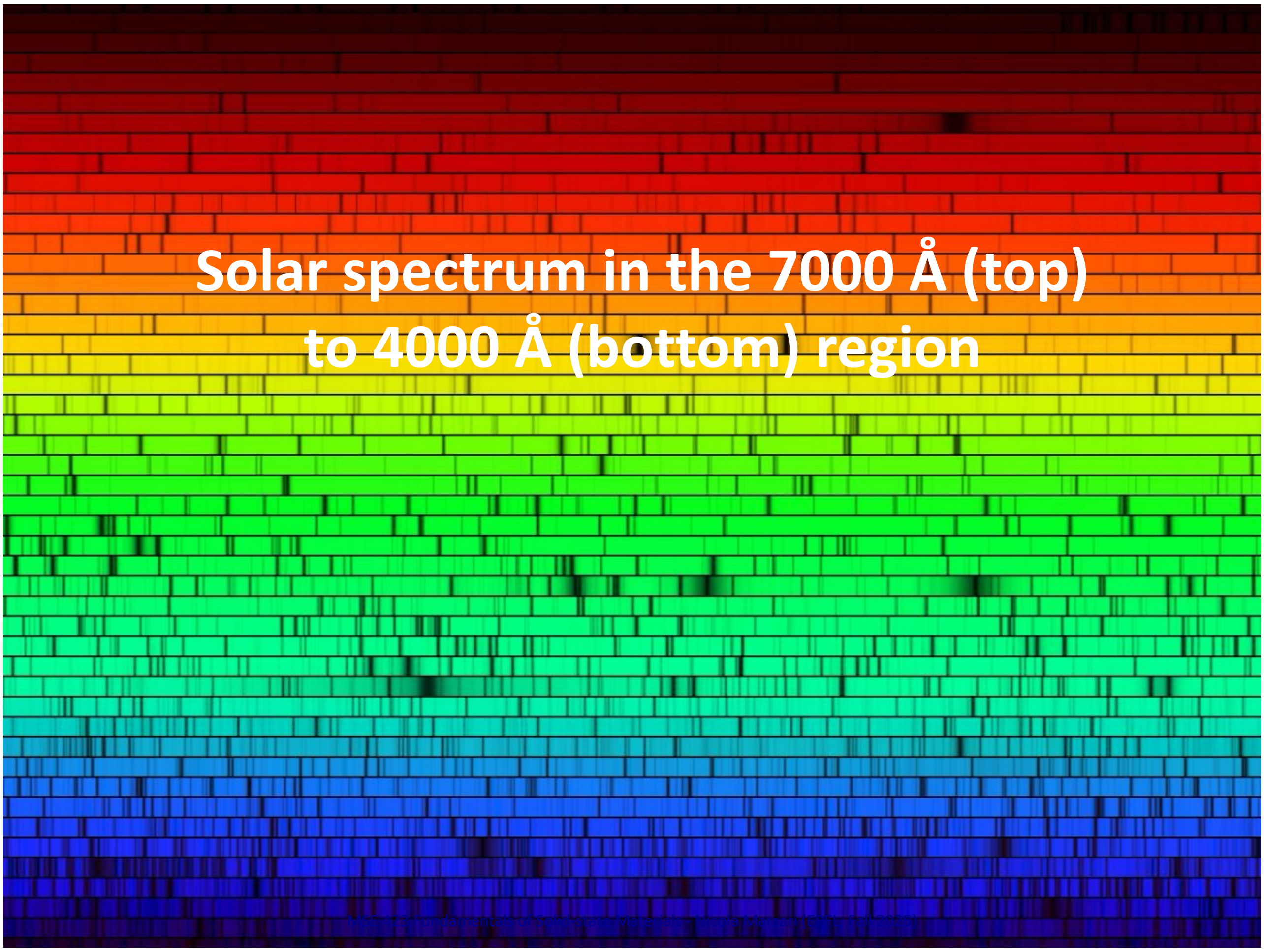
- $\hat{L}_z \leftrightarrow$ Magnetic quantum number ***m***
  m = -l,-l+1,…,l-1,l

Orbital levels in hydrogenoid atoms

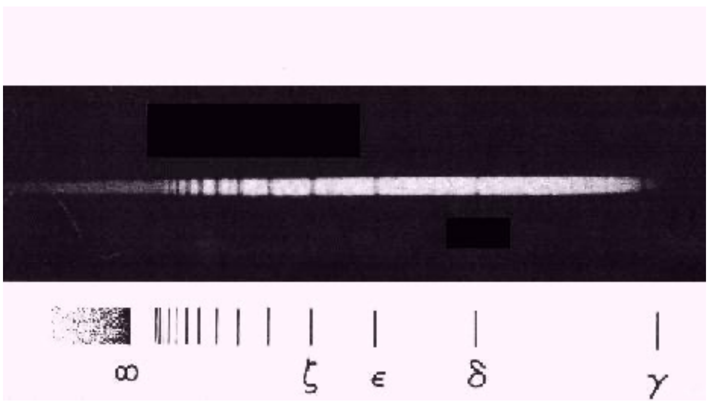


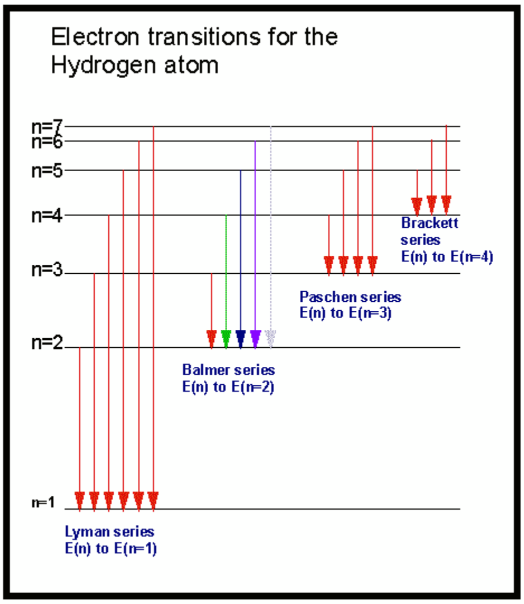
Emission and absorption lines





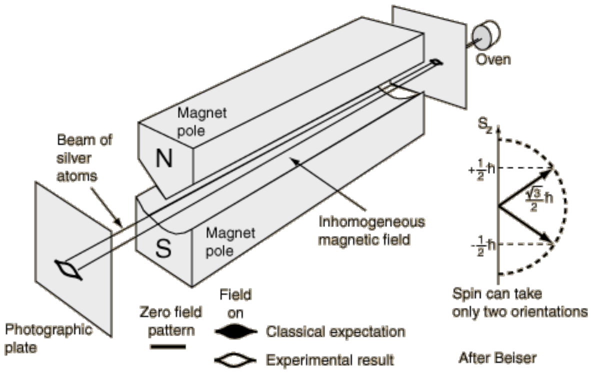
Balmer lines in a hot star

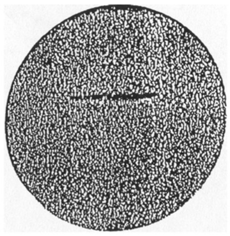




Right experiment – wrong theory (Stern-Gerlach)

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





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

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

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

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

Pauli Exclusion Principle

We can't have two electrons in the same quantum state →

Any two electrons in an atom cannot have the same 4 quantum numbers n,l,m,m_s

Atomic Units

m_e=1, e=1, a_0 (Bohr radius)=1, $\hbar = 1$

$$\varepsilon_0 = \frac{1}{4\pi}$$

Energy of 1s electron= $-\frac{1}{2}\frac{Z^2}{n^2}$

(1 atomic unit of energy=1 Hartree=2 Rydberg=27.21 eV