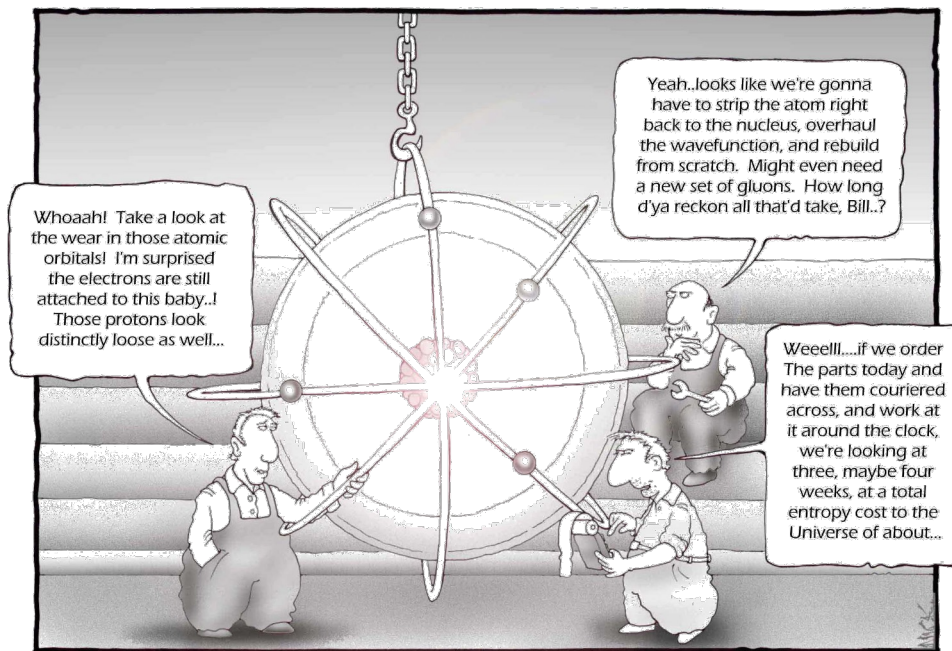


ORBITALS

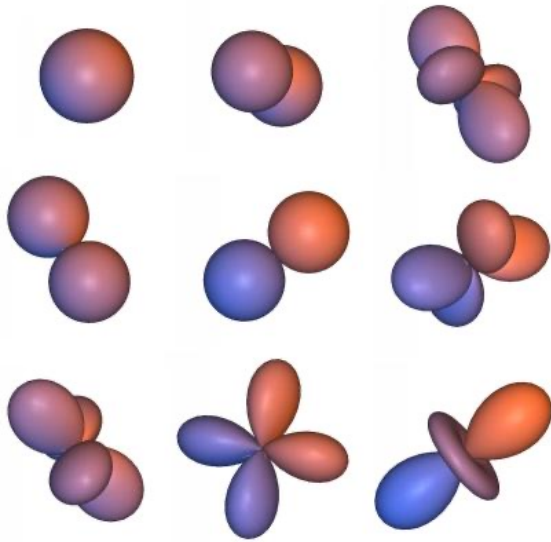


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Last week: the mechanics of quantum mechanics

- 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
- Spherical harmonics

Spherical Harmonics in Real Form



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

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

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

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

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

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

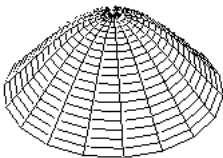
$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(Y_2^2 + Y_2^{-2}) = \sqrt{\frac{15}{16\pi}} \sin^2 \theta \cos 2\phi$$

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

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Same as a beating drum...

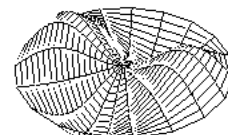
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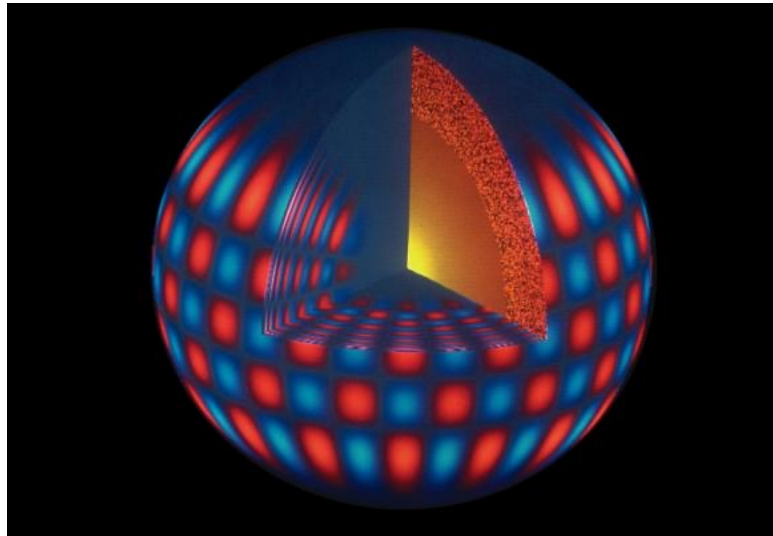


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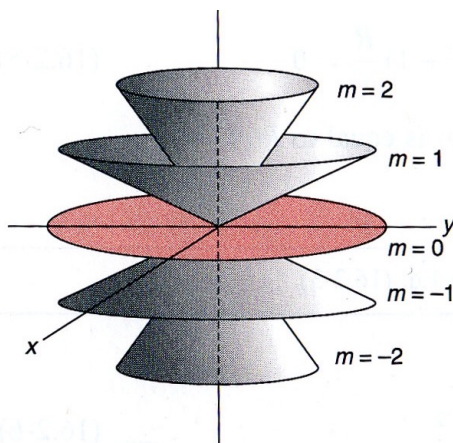
...for the career helioseismologist



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

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Angular Momentum, then...



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

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

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.

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An electron in a central potential (I)

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \quad \nabla^2 \text{ needs to be in spherical coordinates}$$

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

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

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An electron in a central potential (II)

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

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

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An electron in a central potential (III)

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

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An electron in a central potential (IV)

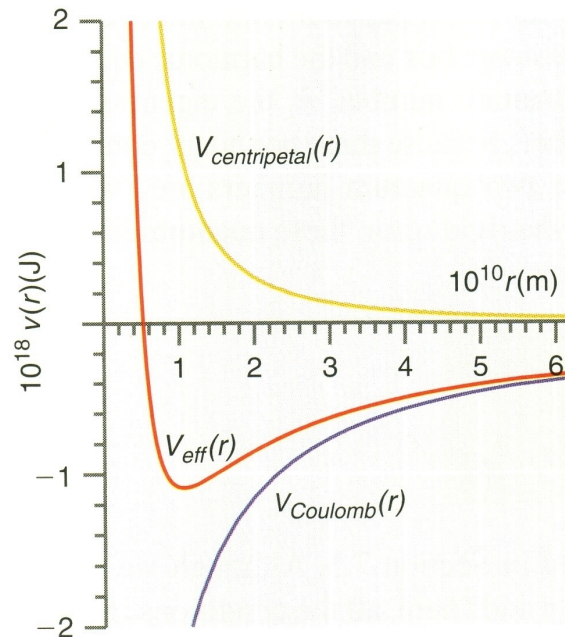
$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right] R_{nlm}(r) = E_{nlm} R_{nlm}(r)$$

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

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

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

$$V_{\text{eff}}(r) = \frac{\hbar^2}{2\mu} \frac{l(l+1)}{r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$



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Summary

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

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

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

$$V_{\text{eff}}(r) = \frac{\hbar^2}{2\mu} \frac{l(l+1)}{r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

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The Radial Wavefunctions for Coulomb $V(r)$

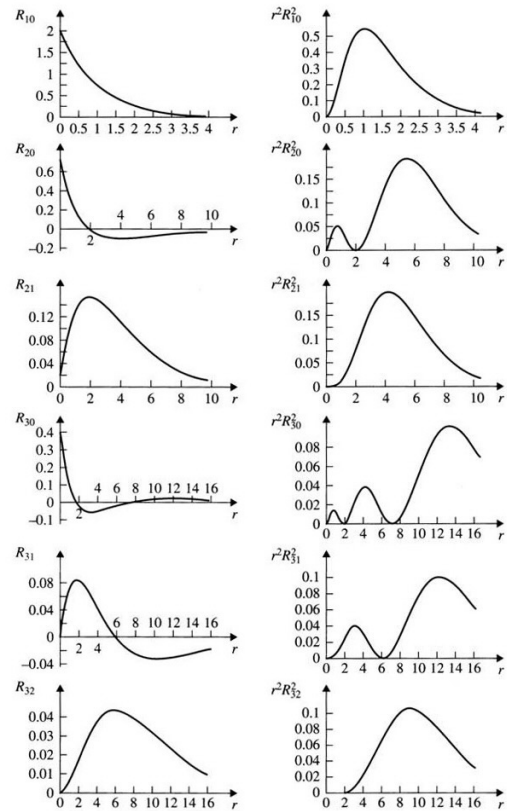
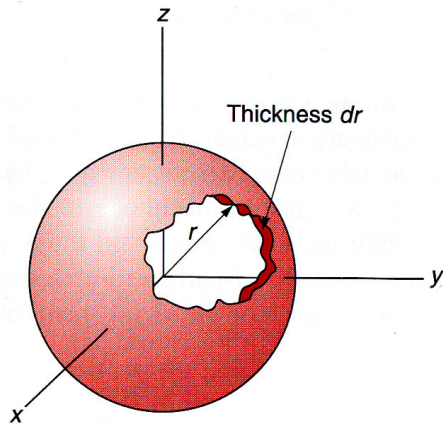
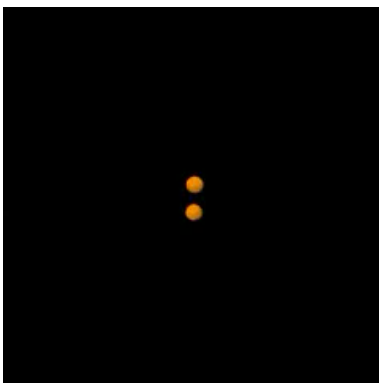


Figure 7.9 Radial functions $R_{nl}(r)$ and radial distribution functions $r^2 R_{nl}^2(r)$ for atomic hydrogen. The unit of length is $a_0 = (\hbar^2 / \mu e^2)$, where a_0 is the first Bohr radius (1.66).

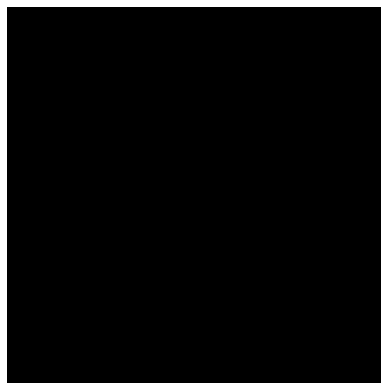
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Solutions in the central Coulomb potential

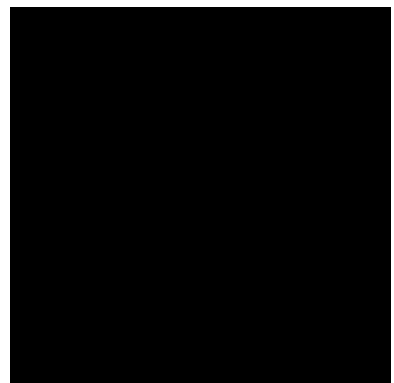
5d



4f



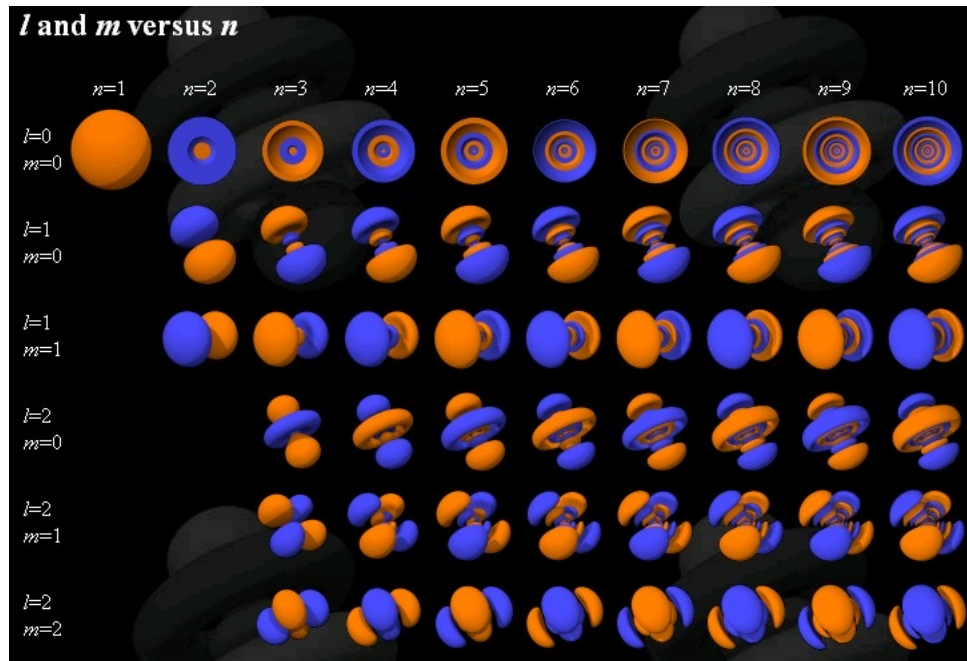
5g



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The Full Alphabet Soup

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



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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 $a_0 = 4\pi\epsilon_0\hbar^2/me^2$ 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 <i>n l m</i>			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 _{±1}	$\mp \frac{1}{8\sqrt{\pi}} (Z/a_0)^{3/2} (Zr/a_0) \exp(-Zr/2a_0) \sin \theta \exp(\pm i\phi)$
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 _{±1}	$\mp \frac{2}{27\sqrt{\pi}} (Z/a_0)^{3/2} (1 - Zr/6a_0) (Zr/a_0) \exp(-Zr/3a_0) \sin \theta \exp(\pm i\phi)$
	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 _{±1}	$\mp \frac{1}{81\sqrt{\pi}} (Z/a_0)^{3/2} (Z^2r^2/a_0^2) \exp(-Zr/3a_0) \sin \theta \cos \theta \exp(\pm i\phi)$
	3	2	±2	3d _{±2}	$\frac{1}{162\sqrt{\pi}} (Z/a_0)^{3/2} (Z^2r^2/a_0^2) \exp(-Zr/3a_0) \sin^2 \theta \exp(\pm 2i\phi)$

Three Quantum Numbers

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

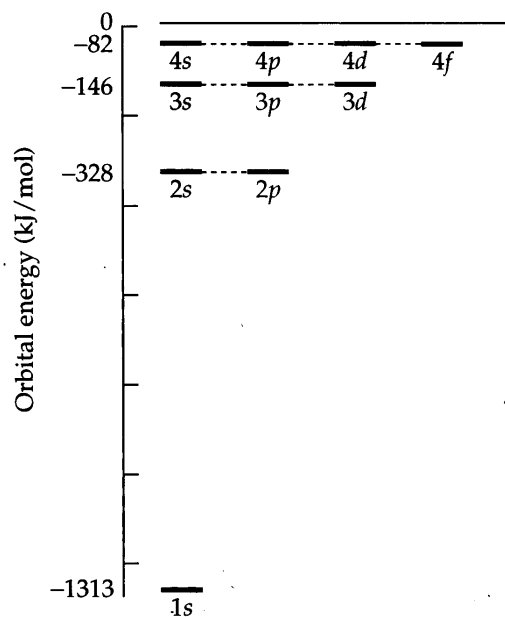
$$E_n = -\frac{e^2}{8\pi\epsilon_0} \frac{Z^2}{a_0 n^2} = -(13.6058 \text{ eV}) \frac{Z^2}{n^2} = -(1 \text{ Ry}) \frac{Z^2}{n^2}$$

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

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

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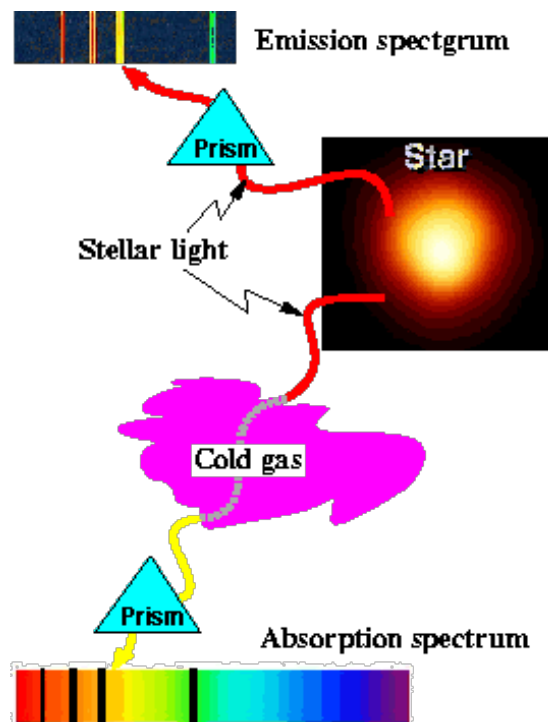
Orbital levels in hydrogenoid atoms



(a) Hydrogen

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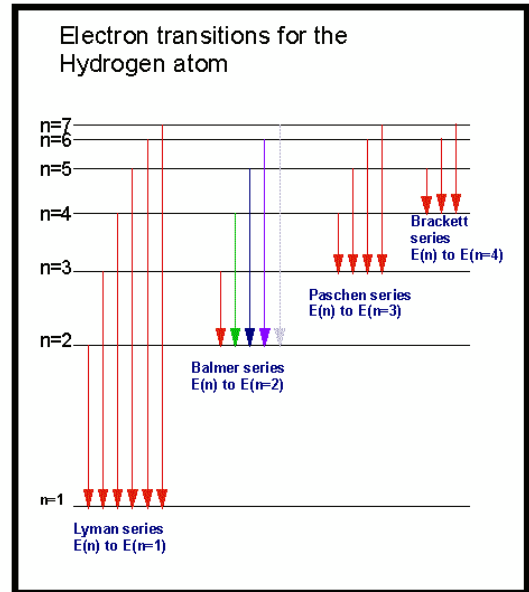
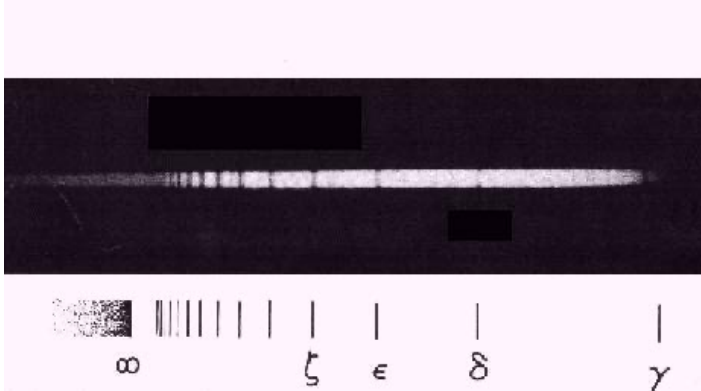
Emission and absorption lines



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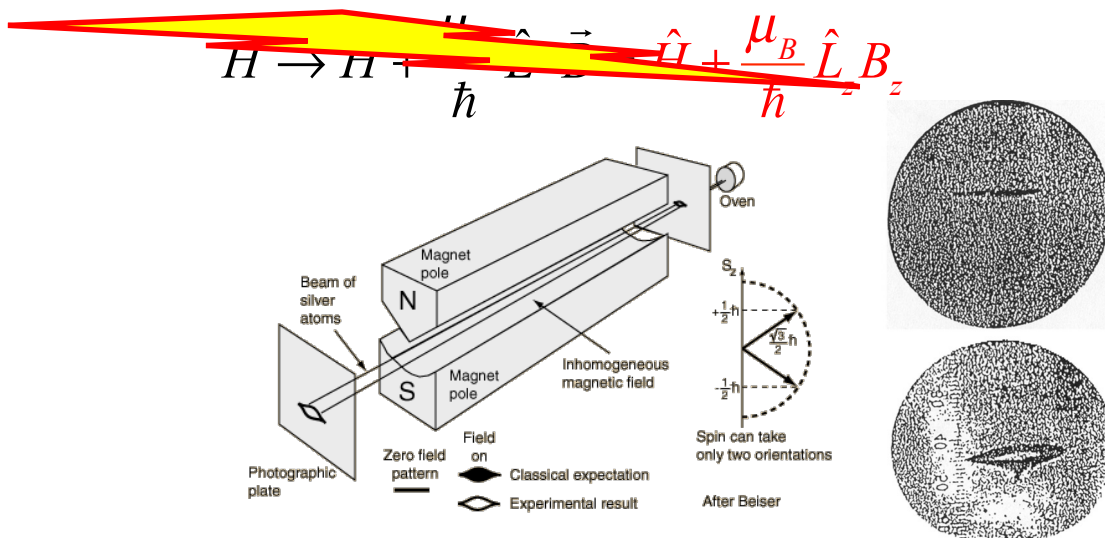
Solar spectrum in the 7000 Å (top)
to 4000 Å (bottom) region

Balmer lines in a hot star



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Right experiment – wrong theory (Stern-Gerlach)



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

Goudsmit and Uhlenbeck

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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

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

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Spin Eigenvalues/Eigenfunctions

- Norm (s integer $\rightarrow$ bosons, half-integer $\rightarrow$ 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

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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

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Atomic Units

$$m_e=1, e=1, a_0 \text{ (Bohr radius)}=1, \quad \hbar = 1$$

$$\epsilon_0 = \frac{1}{4\pi}$$

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

$$(1 \text{ atomic unit of energy} = 1 \text{ Hartree} = 2 \text{ Rydberg} = 27.21 \text{ eV})$$

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