3.23 Electrical, Optical, and Magnetic Properties of Materials

Fall 2007

3.23 Fall 2007 – Lecture 5

THE HYDROGEN ECONOMY

Last time

1. Commuting operators, Heisenberg principle
2. Measurements and collapse of the wavefunction
3. Angular momentum and spherical harmonics
4. Electron in a central potential and radial solutions

Simultaneous eigenfunctions of L², L_z

$$\hat{L}_z Y_l^m(\theta,\varphi) = m\hbar Y_l^m(\theta,\varphi)$$

$$\hat{L}^2 Y_l^m(\theta,\varphi) = \hbar^2 l(l+1) Y_l^m(\theta,\varphi)$$

$$Y_l^m(\theta,\varphi) = \Theta_l^m(\theta)\Phi_m(\varphi)$$

An electron in a central potential

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

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

An electron in a central potential (III)

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

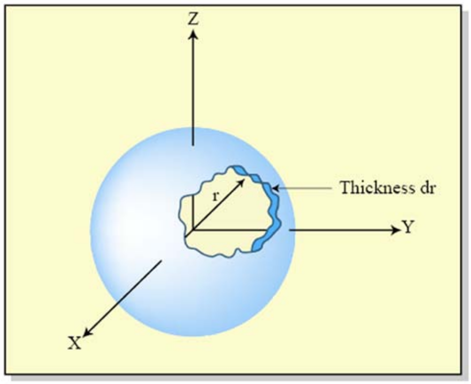
$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V_{eff}(r)\right]u_{nl}(r) = E_{nl}\,u_{nl}(r)$$

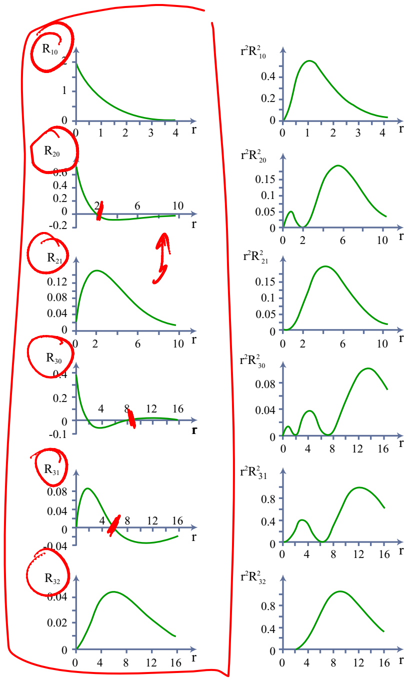
The Radial Wavefunctions for Coulomb V(r)

R_{nl}

Nodes:

$n - l - 1$





Radial functions $R_{nl}(r)$ and radial distribution functions $r^2R^2_{nl}(r)$ for atomic hydrogen. The unit of length is $a_m = (m/_m)\, a_0$, where a_0 is the first Bohr radius.

Figures by MIT OpenCourseWare.

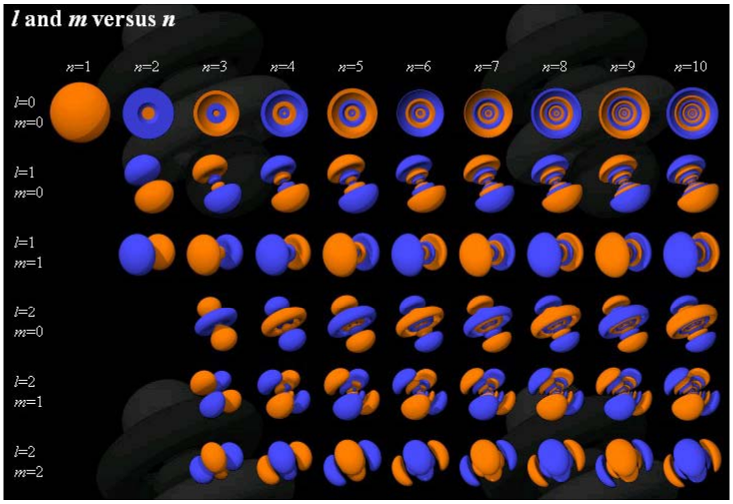
Solutions in a Coulomb Potential

5d 4f 5g

Images removed; please see any visualization of the 5d, 4f, and 5g hydrogen orbitals.

The Full Alphabet Soup

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



Courtesy of David Manthey. Used with permission. Source: http://www.orbitals.com/orb/orbtable.htm.

Good Quantum Numbers

- For an operator that does not depend on t:

$$\frac{d\langle A\rangle}{dt}=\frac{d\langle\Psi|\hat{A}|\Psi\rangle}{dt}=\left\langle\frac{\partial}{\partial t}\Psi\middle|\hat{A}\middle|\Psi\right\rangle+\cancel{\left\langle\Psi\middle|\frac{\partial}{\partial t}\hat{A}\middle|\Psi\right\rangle}+\left\langle\Psi\middle|\hat{A}\middle|\frac{\partial}{\partial t}\Psi\right\rangle=\ldots$$

$$\ldots \quad \hookrightarrow \frac{d}{dt}\int\psi^*(\hat{A}\psi) \quad \frac{1}{i\hbar}\langle\psi|AH-HA|\psi\rangle \quad =\frac{1}{ih}\left\langle\left[\hat{A},\hat{H}\right]\right\rangle$$

- Then, if it commutes with the Hamiltonian, its expectation value does not change with time (it's a constant of motion – if we are in an eigenstate, that quantum number will remain constant)

Three Quantum Numbers

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

ATOMIC NUMBER =

= CHARGE

$$E_n=-\frac{e^2}{8\pi\varepsilon_0}\frac{Z^2}{a_0n^2}=-(13.6058\text{ eV})\frac{Z^2}{n^2}=-(1\text{ Ry})\frac{Z^2}{n^2}$$

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

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

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

  m = -l,-l+1,…,l-1,l

How do you measure angular momentum ?

- Coupling to a (strong !) magnetic field $\vec{B}$

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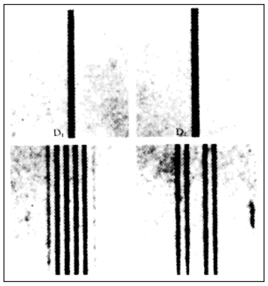
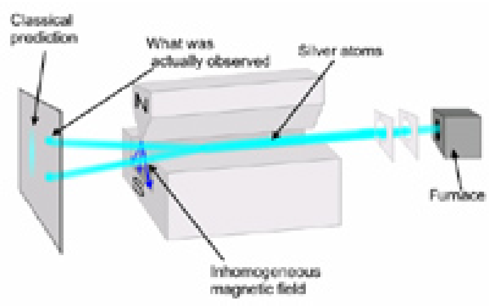
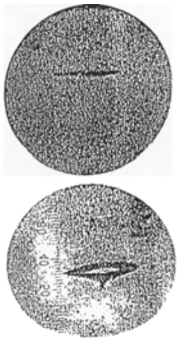
Please see any experimental setup
for observing the Zeeman Effect.



Right experiment – wrong theory (Stern-Gerlach)

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





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

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

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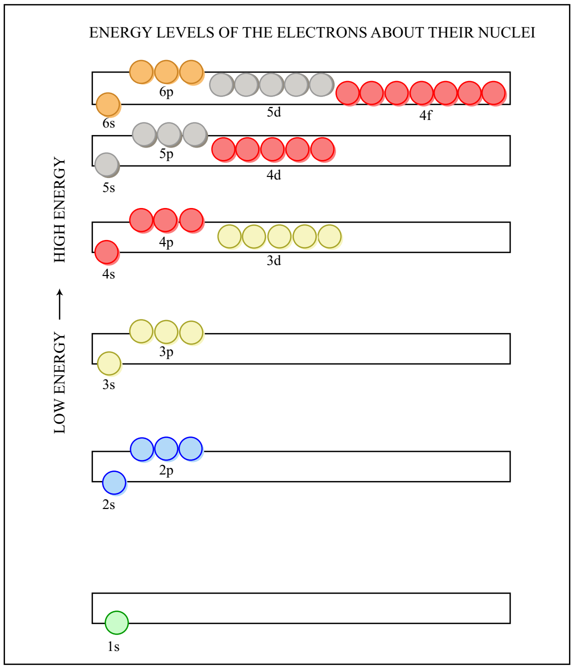
Auf-bau



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