

CHEM 115

Spectroscopy and the Quantum Mechanical Model

Lecture 18
Prof. Sevian



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Agenda

- Exams will be returned at the end of class today
- Emission spectroscopy as evidence for quantization of electron energies (quantization requires wave explanation for electrons)
 - Observe hydrogen emission spectrum through diffraction grating
 - Other elements' emission spectra
 - Models that explain the emission spectrum of hydrogen
- How the quantum mechanical model explains electrons in atoms
 - Four parameters in the equations that describe electron wave functions
 - Principal quantum number, n
 - Azimuthal quantum number, l
 - Magnetic quantum number, m_l
 - Spin quantum number, m_s

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Key points from last lecture

- Waves can be described by three interrelated measurements: wavelength, speed and frequency
 - These are related by $c = \lambda \cdot \nu$
 - Remember to pay attention to units
 - Wavelength in nm vs. m
 - Frequency has units s^{-1} or Hz
- Energy of a wave is proportional to frequency
 - These are related by $E = h \cdot \nu$
- Some properties of light are explained by wave behavior (e.g., diffraction)
- Other properties of light are explained by particle behavior (e.g., photoelectric effect)

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Does Wave-Particle Duality Apply to Electrons?

Photoelectric effect:

Photons (particles of light) cause electrons to be ejected from atoms

Can converse work?

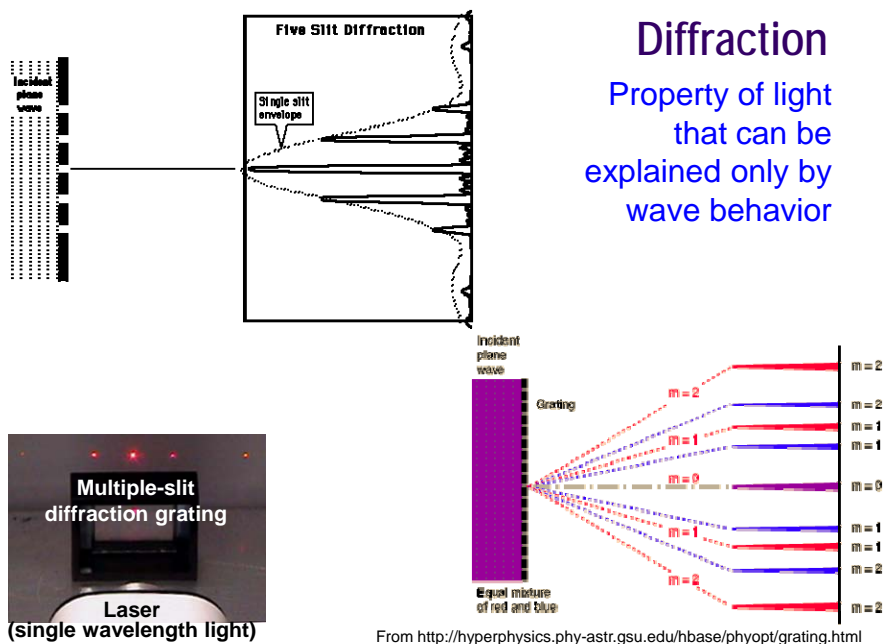
Can electrons moving cause photons to be ejected from atoms?

Light behaves as waves sometimes and particles sometimes

So...

What about electrons, which are very small particles?

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A simulation of the hydrogen emission spectrum

Physics Education Technology (PhET) at CU Boulder

http://phet.colorado.edu/new/simulations/sims.php?sim=Models_of_the_Hydrogen_Atom

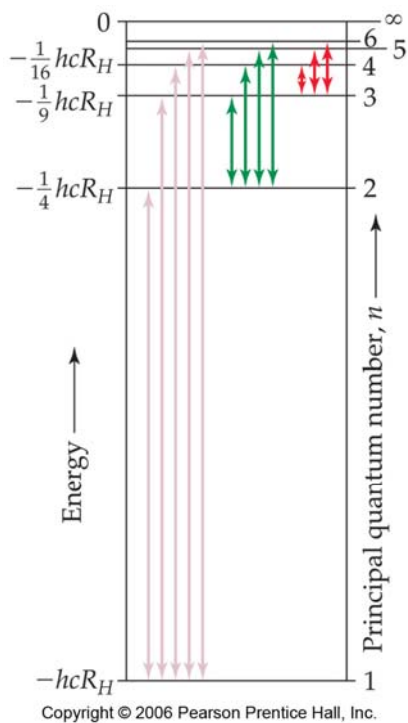
You may want to play with this on your own time also.

Here are some ideas to consider:

- Which model most closely matches experiment?
- Which model does the Rydberg equation come from?
- How are other elements different from hydrogen?

Models to describe the hydrogen emission spectrum

(write down some notes here about each model)



Emission Spectrum of Hydrogen

Bohr Theory

Bohr first thought to mathematically model electrons as in orbit around nucleus, and when “quantization postulate” applied, Bohr’s model correctly predicts hydrogen spectrum that is experimentally seen

Rydberg equation:

$$\Delta E = -hcR_H \left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2} \right)$$

where $hcR_H = 2.18 \times 10^{-18} \text{ J}$

See equation 6.5, p. 226

Using the Rydberg equation

Example:

Compare the $n=3 \rightarrow n=2$ transition with the $n=4 \rightarrow n=3$ transition.

$$\begin{aligned}\Delta E_{3 \rightarrow 2} &= -2.18 \times 10^{-18} \left(\frac{1}{2^2} - \frac{1}{3^2} \right) J \\ &= -2.18 \times 10^{-18} \left(\frac{1}{4} - \frac{1}{9} \right) J \\ &= -3.03 \times 10^{-19} J \text{ per atom}\end{aligned}$$

Exothermic

Using N_A to convert to per mol:
Release of 182.2 kJ/mol

$$\begin{aligned}\Delta E_{4 \rightarrow 3} &= -2.18 \times 10^{-18} \left(\frac{1}{3^2} - \frac{1}{4^2} \right) J \\ &= -2.18 \times 10^{-18} \left(\frac{1}{9} - \frac{1}{25} \right) J \\ &= -1.55 \times 10^{-19} J \text{ per atom}\end{aligned}$$

Exothermic

Using N_A to convert to per mol:
Release of 93.3 kJ/mol

Where in the electromagnetic spectrum are these energies?

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Converting energy to wavelength

- Energy equation

$$E = h\nu$$

- Wavelength equation

$$c = \lambda\nu \quad \Rightarrow \quad \nu = \frac{c}{\lambda}$$

- Substituting

$$E = h\nu = h \left(\frac{c}{\lambda} \right) = \frac{hc}{\lambda}$$

- Solving for wavelength

$$\lambda = \frac{hc}{E}$$

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Example continued

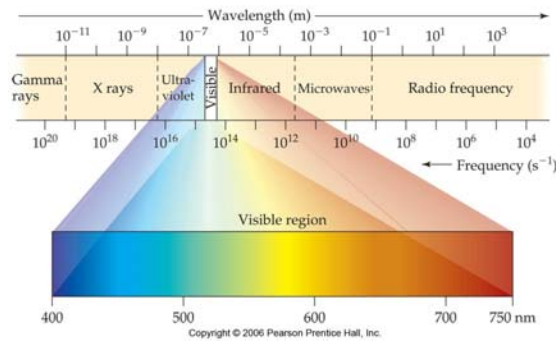
Where in the electromagnetic spectrum are these energies?

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{3.03 \times 10^{-19} \text{ J}}$$

$$= 6.57 \times 10^{-7} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 657 \text{ nm} \quad \text{RED}$$

$$\lambda = \frac{hc}{E} = \frac{hc}{1.55 \times 10^{-19} \text{ J}}$$

$$= 1.28 \times 10^{-6} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 1280 \text{ nm} \quad \text{Infra-RED}$$



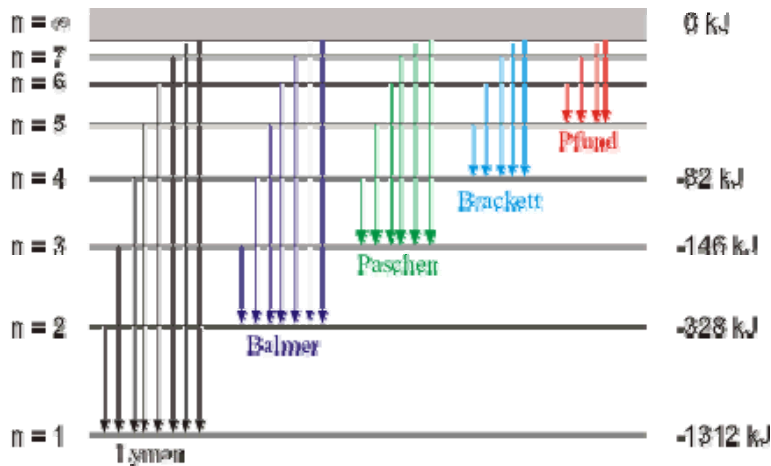
Infra-RED

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Emission Spectrum of Hydrogen

$$\Delta E = -hcR_H \left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2} \right)$$

where $hcR_H = 1312 \text{ kJ/mol}$



See http://www.ktf-split.hr/glossary/image/emission_spectrum_of_hydrogen.gif



Clicker question #1

Which emission line in an atomic emission spectrum would be expected to have the longest wavelength?

- (A) $n = 3$ to $n=1$
- (B) $n = 4$ to $n = 2$
- (C) $n = 10$ to $n = 5$
- (D) $n = 1$ to $n = 2$
- (E) $n = 4$ to $n = 10$

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Spectroscopy

Macroscopic observations

- When energy enters atoms, atoms give off light at discrete wavelengths (line emission spectrum)
- Line emission is fingerprint of an element (demonstrations in class)
- Entire periodic table at <http://jersey.uoregon.edu/vlab/elements/Elements.html>

Particle level explanation

- Electrons are so small that their quantum mechanical properties become important (Heisenberg uncertainty principle)
- Electrons can reside in various different quantum mechanical potential energy states, only one of which is the lowest energy ground state
- For a very nice, short summary explanation with helpful pictures, see <http://www.avogadro.co.uk/light/bohr/spectra.htm>

Symbolic representation (mathematical model)

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Quantum Mechanical Theory

- Bohr model correctly predicts hydrogen spectrum, but no theoretical basis for “quantization postulate” needed in the mathematical model
- de Broglie uses converse of Einstein’s “light can be described as a particle” to say “a very small particle like an electron can be described as a wave.”
- Schrödinger equation models hydrogen spectrum and quantization occurs as a mathematical solution, resulting from the wavelike behavior of electrons.
- Schrödinger equation involves electromagnetic interaction between a single electron and a positive point charge at the nucleus
- Therefore, Schrödinger equation can be solved exactly only when there is a single electron (H atom, He⁺ ion, H₂⁺ ion, Li²⁺ ion)
- However, Schrödinger equation serves as a good first approximation for other elements (ch. 7 and structure of the Periodic Table)

The Schrodinger equation and wave functions that obey it

$$H\psi_{nlm}(\theta, \phi, r) = E_n\psi_{nlm}(\theta, \phi, r) \quad \text{where } H|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$

$$\psi_{nlm}(\theta, \phi, r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{l,m}(\theta, \phi)$$

ψ_{nlm} are a set of functions that are mathematical solutions in three-dimensional space (radial coordinates θ, ϕ, r instead of Cartesian coordinates x, y, z) that depend on three quantum numbers n, l, m

$$a_0 \text{ is the "Bohr radius" given by } a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = \frac{\hbar}{m_e c \alpha}$$

ρ, L and Y are just special functions that depend on the parameters shown

Implications of Quantum Mechanical Model

- Energy of electron is quantized (only certain states are allowed)
- Due to Heisenberg uncertainty principle, it is impossible to identify both position of electron and its energy, so if energy is given by the S equation, then equation can only predict *probability* of locating electron within a given region of space (orbital), also called electron density
- Orbitals (solutions to S equation) are specified mathematically by quantum numbers: n, l, m_l , which are interdependent

The “Game” of Quantum Numbers

Principal quantum number ($n = 1, 2, 3, \dots \infty$)

Meaning: Specifies energy of the electron

Sometimes called “shell”, in reference to Bohr model

$$E_n = -Rhc/n^2 \text{ (same as Bohr/Rydberg)}$$

Azimuthal (angular momentum) quantum number ($l = 0, 1, 2, \dots n-1$)

Meaning: Specifies 3-D shape of probability map of electron density

Sometimes called subshell

Often coded by letters corresponding to different values for l

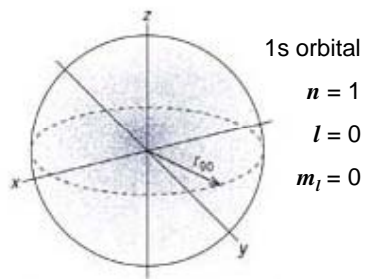
$$l = 0, 1, 2, 3, \dots \text{ corresponds to } s, p, d, f, \dots$$

Magnetic quantum number ($m_l = 0, \pm 1, \pm 2, \pm 3, \dots \pm l$)

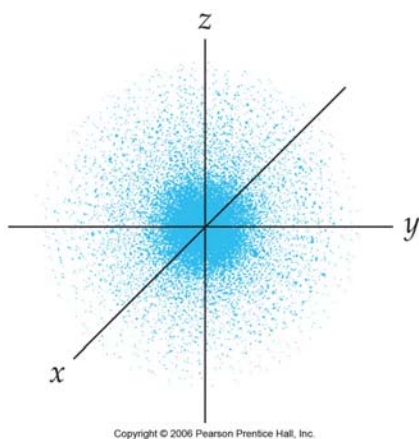
Meaning: Orientation of orbitals (mathematical solutions to S equation) within a subshell

What Orbitals Are

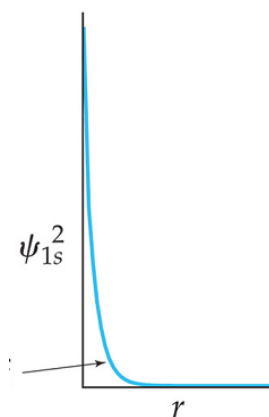
- Electron cloud pictures
- Probability density describing where electron is located
- Proportional to the square of the wave function with specific quantum numbers (wave function symbolized by Greek letter ψ)
- Think of a bird at a bird feeder, and a time-lapse photo



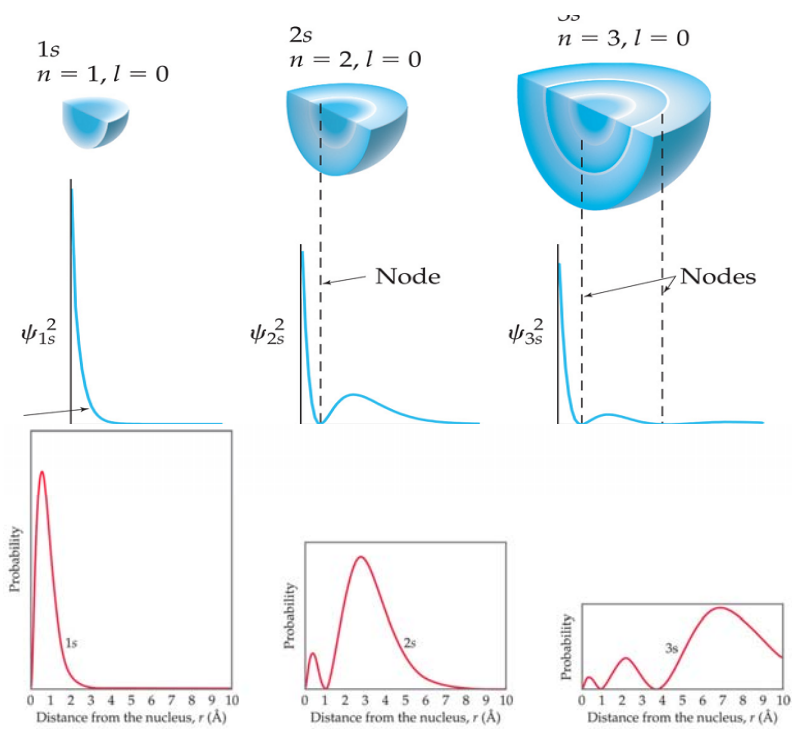
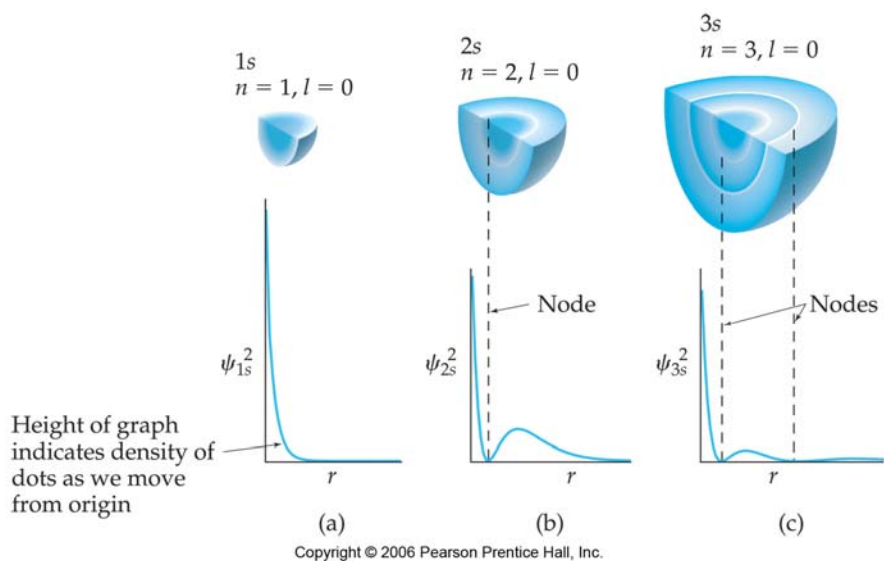
The 1s orbital



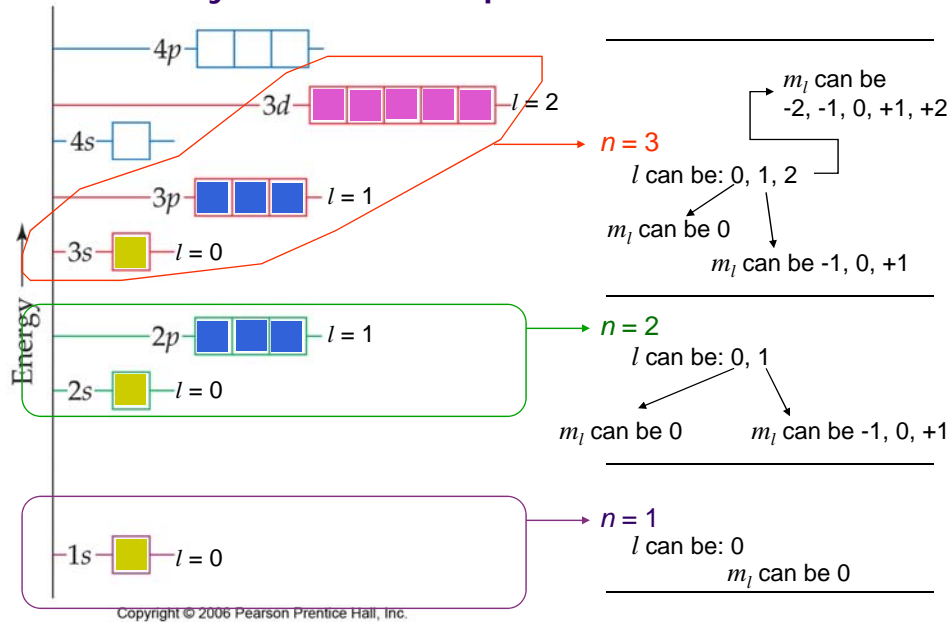
1s
 $n = 1, l = 0$



Comparing 1s, 2s, and 3s orbitals



Summary of the first 3 quantum numbers

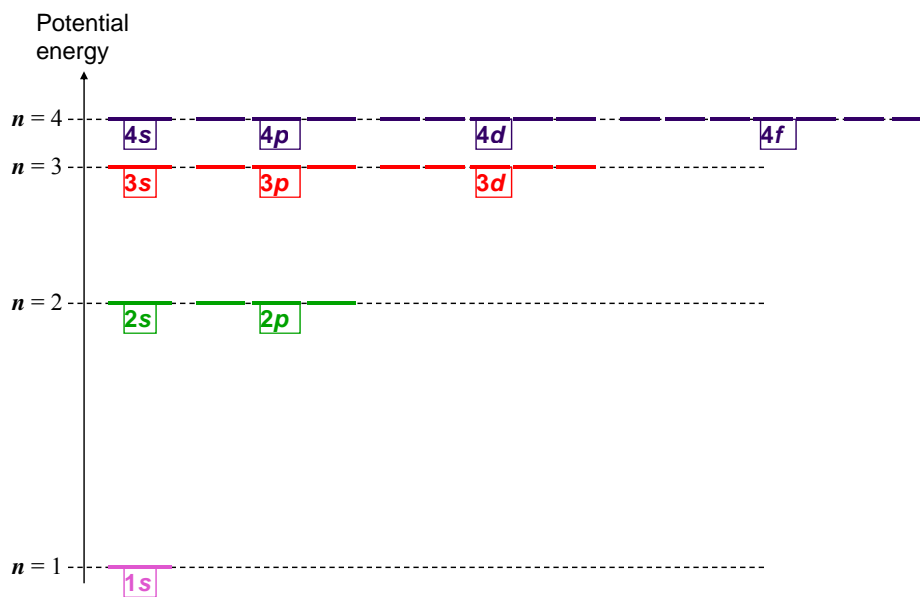


How do the Bohr model and the Quantum Mechanical model compare?

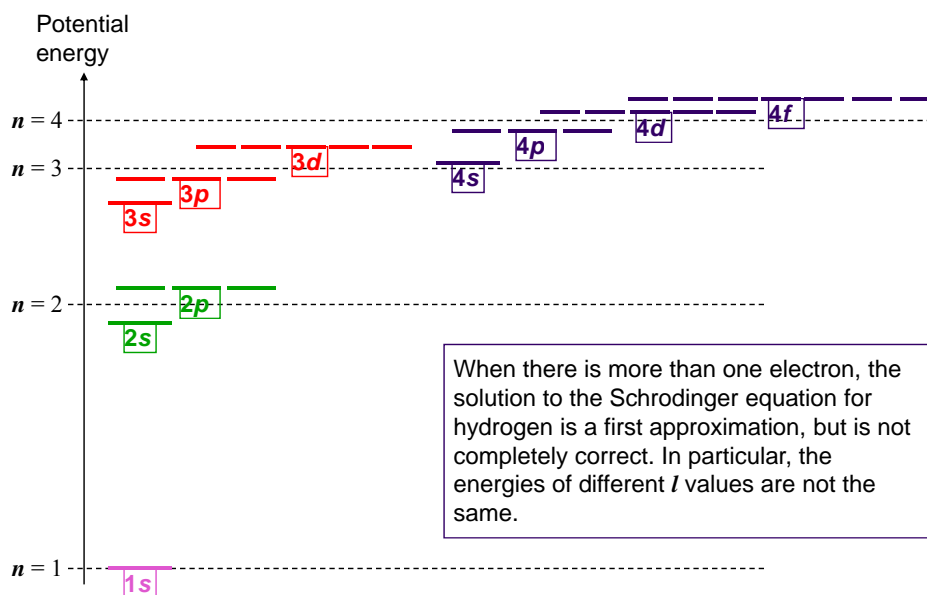
- Both quantitatively predict hydrogen emission spectrum
- Bohr model is completely wrong for atoms with more than one electron
- Quantum mechanical model is impossible to solve exactly for atoms with more than one electron, but:
 - Qualitatively predicts correct atomic emission spectra
 - Explains arrangement of atoms in the periodic table
 - Approximate mathematical solutions come close to correct quantitative predictions for atomic emission spectra

Orbital Energies in Hydrogen (Only)

How QM model simplifies to the Bohr model



Orbital Energies in Multielectron Atoms



Magnetism of Materials

Macroscopic Evidence for a 4th Quantum Number

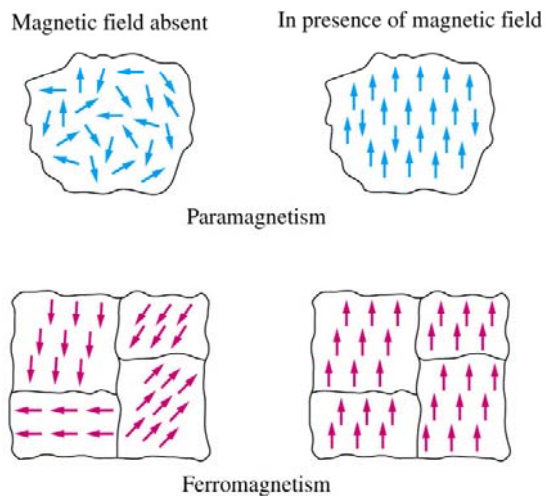
- Substances are either:
 1. Diamagnetic: slightly repelled by a strong magnet
 2. Paramagnetic: attracted to a magnetic field
- Usually undetectable unless strong field
- Some paramagnetic substances (iron, cobalt, nickel) are ferromagnetic (strongly attracted to a magnetic field)
- Some ferromagnetic substances (particularly mixtures, such as AlNiCo) can set up permanent magnetic character
- Atomic emission spectra of paramagnetic substances show splitting of spectral lines

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Magnetism of Materials

Particle Level Behavior


- Ferromagnets contain regions of magnetic “strength” in the material
- Some regions have slightly different magnetic moments than other regions




From http://cwx.prenhall.com/petrucci/medialib/media_portfolio/24.html

Magnetism of Materials

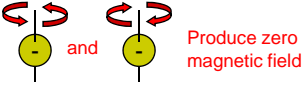
Symbolic/Mathematical Representation

- Recall that an electric field in motion creates a magnetic field, and vice versa
- Electron is charged particle that spins 
- Two spins possible, therefore two directions of magnetic field possible

Some unpaired electrons

- If spins of two electrons are aligned, then magnetic field strengthened 

All electrons are paired

- If spins of two electrons are opposed, then magnetic field cancelled 

- Define a fourth quantum number: magnetic spin, m_s , which can take two possible values $+\frac{1}{2}$ or $-\frac{1}{2}$

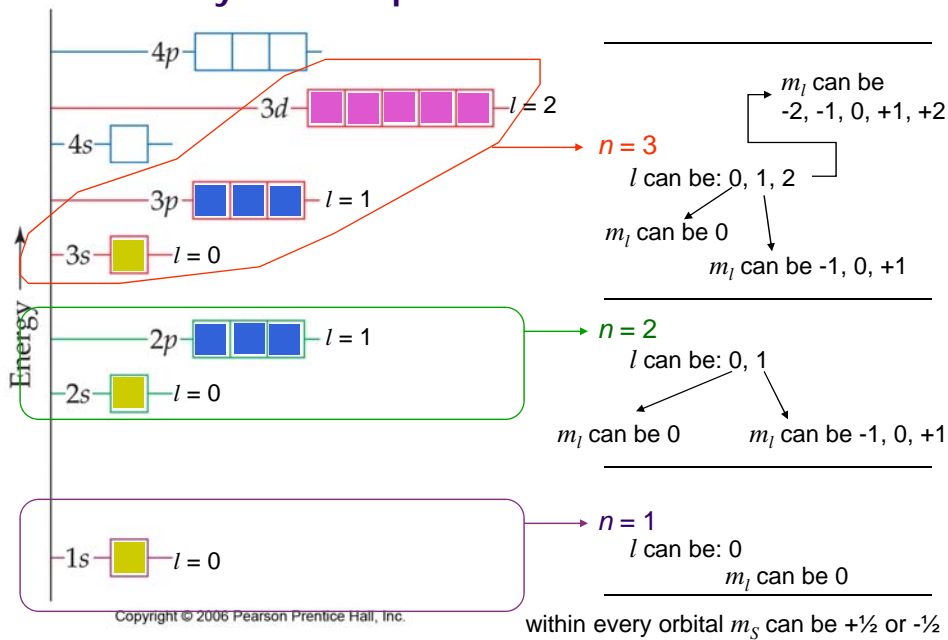
Adding a fourth quantum number: magnetic spin of the electron, m_s

Electrons are mathematical wave functions (orbitals) specified by:

- Principal quantum number, n
 - Can take values 1, 2, 3, 4, ...
 - Radial distance from the nucleus (shell #)
- Azimuthal quantum number, l
 - Can take values up to but not including n value
 - Shape of orbital (when $l=0$ has s -shape, when $l=1$ has p -shape, when $l=2$ has d -shape, etc.)
- Magnetic quantum number, m_l
 - Can take values ranging from $-l$ up to $+l$
 - Orientation of the orbital
- Spin quantum number, m_s
 - Can take one of two values ($+\frac{1}{2}$ or $-\frac{1}{2}$), does not depend on other quantum numbers

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Summary of all 4 quantum numbers



The "game" of QM: What you need to know

- Study pp. 232-233 (10th ed.) or pp. 226-227 (11th ed.) in the text to learn the rules
- Know the difference between s, p, d and f orbitals (these are "l" values of 0, 1, 2 and 3)
- Be able to tell which combinations of quantum numbers (n , l , m_l) are allowed and which combinations are not allowed
- Given a particular electron address, determine a set of quantum numbers (n , l , m_l) that correspond to it
- Given an atom with a specific number of electrons, determine the electronic "ground state" configuration

