## CHEM 103 Spectroscopy and the Quantum Mechanical Model

Lecture Notes April 6, 2006 Prof. Sevian





### Agenda

- Emission spectroscopy
- How the quantum mechanical model explains it
- Where quantum mechanics breaks down

# 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?

### Spectroscopy

#### Macroscopic observations

- When energy enters atoms, atoms give off light at discrete wavelengths (line emission spectrum)
- Line emission is fingerprint of an element
- Entire periodic table at

http://jersey.uoregon.edu/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
- See http://www.avogadro.co.uk/light/bohr/spectra.htm

#### Symbolic representation (mathematical 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  $hcR_{H} = 2.18 \times 10^{-18} J$ 

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.

$$\Delta E_{3 \to 2} = -2.18 \times 10^{-18} \left( \frac{1}{2^2} - \frac{1}{3^2} \right) J$$
$$= -2.18 \times 10^{-18} \left( \frac{1}{4} - \frac{1}{9} \right) J$$
$$= -3.03 \times 10^{-19} J$$
Exothermic

Release of 182.2 kJ/mol

$$\Delta E_{4\to3} = -2.18 \times 10^{-18} \left( \frac{1}{3^2} - \frac{1}{4^2} \right) J$$
$$= -2.18 \times 10^{-18} \left( \frac{1}{9} - \frac{1}{25} \right) J$$
$$= -1.55 \times 10^{-19} J$$

Exothermic

Release of 93.3 kJ/mol

Where in the electromagnetic spectrum are these energies?





### **Example continued**

Where in the electromagnetic spectrum are these energies?





### **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<sup>+</sup> ion, H<sub>2</sub><sup>+</sup> ion, Li<sup>2+</sup> 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



$$H\psi_{nlm}(\theta,\phi,r) = E_n \psi_{nlm}(\theta,\phi,r)$$

where 
$$H\left|\psi(t)
ight
angle=\mathrm{i}\hbarrac{\partial}{\partial t}\left|\psi(t)
ight
angle$$

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

 $\psi_{nlm}$  are a set of functions that are mathematical solutions in threedimensional space (radial coordinates  $\theta$ ,  $\phi$ , *r* instead of Cartesian coordinates *x*, *y*, *z*) that depend on three quantum numbers *n*, *l*, *m* 

$$a_o$$
 is the "Bohr radius" given by  $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = \frac{\hbar}{m_e c\alpha}$ 

 $\rho, L$  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<sub>l</sub>, which are interdependent

### The Game of Quantum Numbers



Principal quantum number ( $n = 1, 2, 3, ...\infty$ ) Specifies energy of the electron Sometimes called "shell", in reference to Bohr model  $E_n = -Rhc/n^2$  (same as Bohr/Rydberg)

Azimuthal (angular momentum) quantum number (l = 0, 1, 2, ..., n-1) Specifies 3-D shape of probability map of electron density Sometimes called subshell Often coded by letters corresponding to different values for ll = 0, 1, 2, 3, ... corresponds to s, p, d, f, ...

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











# 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





#### Magnetism of Materials Macroscopic Evidence



- 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 AINiCo) can set up permanent magnetic character
- Atomic emission spectra of paramagnetic substances show splitting of spectral lines

#### 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



In presence of magnetic field



Magnetic field absent







Ferromagnetism

From http://cwx.prenhall.com/petrucci/medialib/media\_portfolio/24.html



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



Electrons are mathematical wave functions (orbitals) specified by:

- 1. Principal quantum number, n
  - Can take values 1, 2, 3, 4, ...
  - Radial distance from the nucleus (shell #)
- 2. 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.)
- 3. Magnetic quantum number,  $m_1$ 
  - Can take values ranging from -l up to +l
  - Orientation of the orbital
- 4. Spin quantum number,  $m_s$ 
  - Can take one of two values (+½ or -½), does not depend on other quantum numbers

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



- Study pp. 232-233 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*) are allowed and which combinations are not allowed
- Given a particular electron address, determine a set of quantum numbers (*n*, *l*, *m<sub>j</sub>*) that correspond to it
- Given an atom with a specific number of electrons, determine the electronic "ground state" configuration

# How to find <u>ground state</u> electron configuration for an element



Aufbau ("building up/assembly") principle

Add electrons sequentially from lowest energy orbitals on upward.

2. Pauli exclusion principle

Electrons are uniquely specified. If two electrons have the same first three quantum numbers (same orbital), then their fourth quantum number  $(m_i)$  must differ.

3. Hund's rule

Electrons that are in the same subshell (same l value) tend to distribute so that they are in different orbitals (different  $m_l$  values) and have parallel spin (same  $m_s$  values).







#### Aufbau (Building) Elements

















## Book's representation

Element	Total Electrons	Orbital Diagram	Electron Configuration
Li	3	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$1s^2 2s^1$
Be	4	11 11	$1s^2 2s^2$
В	5	11 11 1	$1s^2 2s^2 2p^1$
С	6	11 11 1	$1s^2 2s^2 2p^2$
N	7	11 11 1 1	$1s^2 2s^2 2p^3$
Ne	10	11 11 11 11 1	$1s^2 2s^2 2p^6$
Na	11	11 11 11 11 1	$1s^2 2s^2 2p^6 3s^1$



Aufbau (Building) Elements



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#### Aufbau (Building) Elements





### Periodic Table Structure





## **Two Notable Exceptions**

Chromium [Ar] 4s<sup>1</sup> 3d<sup>5</sup> Copper [Ar] 4s<sup>1</sup> 3d<sup>10</sup>

because it turns out that a half-full or a full *d*-subshell is more stable

Generally, complete subshells lend stability.