CHEM 1311

Course web page
http://web.chemistry.gatech.edu/~barefield/1311/chem1311a.html

Outline for first exam period

• Atomic structure and periodic properties
• Structures and bonding models for covalent compounds of p-block elements
  – Lewis Structures, Valence Shell Electron Repulsion (VSEPR) concepts and oxidation state
  – Hybridization
  – Composition and bond energies in binary p-block compounds
  – Molecular orbitals in homonuclear diatomics

First Exam – Friday, September 15
Atomic structure and periodic properties

- Early experiments concerning atomic structure and properties of electromagnetic radiation
- Bohr model of the hydrogen atom
- Demise of Bohr model
- Wave equation and wave model for atom
- Wave functions and properties
- Orbital representations
- Multielectron atoms
- Periodic properties and their origin

Properties of Atoms

- Consist of small positively charged nucleus surrounded by negatively charged electrons, some at large distances from the nucleus
- Nucleus consists of positively charged protons and neutral neutrons
- Charges of proton and electron are equal
- The atomic number (and nuclear charge) of an atom is equal to the number of protons in its nucleus.
- The mass number of an atom is equal to the number of protons plus the number of neutrons
- Isotopes are atoms with the same atomic number but different mass numbers, i.e., $^1\text{H}$, $^2\text{H}$, $^3\text{H}$ or $^{12}\text{C}$, $^{13}\text{C}$, $^{14}\text{C}$
**Atomic Spectra**

Irradiation from electronically excited atoms is not continuous

Visible region line spectra could be fitted to simple (empirical) formula

\[
\frac{1}{\lambda} = 1.097 \times 10^7 \text{ m}^{-1} \left( \frac{1}{2^n^2 - 1/n^2} \right)
\]

\[
E = \frac{hc}{\lambda} = 2.178 \times 10^{-18} \text{ J} \left( \frac{1}{2^n^2 - 1/n^2} \right)
\]

Later work showed several series of lines

\[
E = 2.178 \times 10^{-18} \text{ J} \left( \frac{1}{n_2^2 - 1/n_1^2} \right) \quad (n_2 < n_1)
\]

### Spectrum of Electromagnetic Radiation

<table>
<thead>
<tr>
<th>Region</th>
<th>Wavelength (Angstroms)</th>
<th>Wavelength (centimeters)</th>
<th>Frequency (Hz)</th>
<th>Energy (eV)</th>
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</thead>
<tbody>
<tr>
<td>Radio</td>
<td>&gt; 10^9</td>
<td>&gt; 10</td>
<td>&lt; 3 x 10^9</td>
<td>&lt; 10^{-5}</td>
</tr>
<tr>
<td>Microwave</td>
<td>10^6 - 10^9</td>
<td>10 - 0.01</td>
<td>3 x 10^9 - 3 x 10^{12}</td>
<td>10^{-6} - 0.01</td>
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<tr>
<td>Infrared</td>
<td>10^6 - 7000</td>
<td>0.01 - 7 x 10^{-5}</td>
<td>3 x 10^{12} - 4.3 x 10^{14}</td>
<td>0.01 - 2</td>
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<tr>
<td>Visible</td>
<td>7000 - 4000</td>
<td>7 x 10^{-5} - 4 x 10^{-5}</td>
<td>4.3 x 10^{14} - 7.5 x 10^{14}</td>
<td>2 - 3</td>
</tr>
<tr>
<td>Ultraviolet</td>
<td>4000 - 10</td>
<td>4 x 10^{-5} - 10^{-7}</td>
<td>7.5 x 10^{14} - 3 x 10^{17}</td>
<td>3 - 10^3</td>
</tr>
<tr>
<td>X-Rays</td>
<td>10 - 0.1</td>
<td>10^{-7} - 10^{-9}</td>
<td>3 x 10^{17} - 3 x 10^{19}</td>
<td>10^3 - 10^{5}</td>
</tr>
<tr>
<td>Gamma Rays</td>
<td>&lt; 0.1</td>
<td>&lt; 10^{-9}</td>
<td>&gt; 3 x 10^{19}</td>
<td>&gt; 10^5</td>
</tr>
</tbody>
</table>
Visible region of electromagnetic spectrum

Properties of Electromagnetic Radiation

\[ c = \lambda \nu \]

\[ c = 2.998 \times 10^8 \text{ m s}^{-1} \text{ (vacuum); } \lambda \text{ in meters; } \nu \text{ in cycles per sec or s}^{-1} \]

1 cycle per sec is 1 Hz (Hertz)

\[ E = h \nu = hc/\lambda \]

With Einstein's relationship \( E = mc^2 \)

\[ hc/\lambda = mc^2 \]

\[ \lambda = h/mc \]
**Bohr Model**

Rule 1. Electron can exist in stationary states; requires fixed energy.

Rule 2. Possible stationary states determined by quantization of angular momentum \((mvr)\) in units of \(\hbar/2\pi\) \((mvr = nh/2\pi)\)

Rule 3. Transitions between stationary states occur with emission or absorption of a quantum of energy, \(\Delta E = h\nu\)

For a stationary state to occur for the electron moving in a planetary orbital about the nucleus, the centripetal force must equal the electrostatic attraction of the electron by the nucleus

\[
\frac{mv^2}{r} = \frac{(Ze)e}{4\pi\varepsilon_0 r^2}
\]

Employing the expression for angular momentum from Rule 2:

\[
r = n^2\hbar^2 e/mZe^2 \quad \nu = Z\nu^2/2\hbar\varepsilon_0
\]

Note that radius of orbits increase with \(n^2\) and decrease with \(Z\)

Total Energy for atom \((E)\) = K.E. + P.E. = \(\frac{1}{2}mv^2 + (-Ze^2/4\pi\varepsilon_0 r)\)

from the previous slide \(mv^2 = Z\nu^2/2\pi\varepsilon_0\)

so that \(E = \frac{1}{2}(Ze^2/4\pi\varepsilon_0 r) - (Ze^2/4\pi\varepsilon_0 r) = -\frac{1}{2}(Ze^2/4\pi\varepsilon_0 r) = -Ze^2/8\pi\varepsilon_0 r\)

from the previous slide \(r = n^2\hbar^2 e/mZe^2\)

\[
E = -me^4Z^2/8\varepsilon_0 n^2\hbar^2
\]

\[
E = -(2.18 \times 10^{-18} \text{ J}) Z^2/n^2
\]

\[
E = -(13.6 \text{ eV}) Z^2/n^2
\]

**Constants**

\[
\begin{align*}
m & = 9.10939 \times 10^{-11} \text{ kg} \\
e & = 1.60218 \times 10^{-19} \text{ C} \\
c & = 8.8538 \times 10^{-12} \text{ C}^2 \text{ m}^{-1} \text{ J}^{-1} \\
h & = 6.62608 \times 10^{-34} \text{ J} \text{ s} \\
1 \text{ eV} & = 1.6022 \times 10^{-19} \text{ J}
\end{align*}
\]

\(\Delta E = \text{final energy – initial energy}\)

\(\Delta E = -13.6 Z^2 \text{ eV} \left(1/n_f^2 - 1/n_i^2\right)\)
Further evidence for unique properties of light

**Photoelectric Effect**

K.E.(ejected electrons) = hν(impinging light) - w(work function)

![Photoelectric Effect Diagram]

**Compton Effect**

Momentum and energy conserved in collisions of light (photons) with electrons

Demise of Bohr Model - Introduction of Wave Model

**Heisenberg Indeterminacy (Uncertainty) Principle**

\[ \Delta x \cdot \Delta (mv) \geq h/2\pi \]

Exact position and exact momentum cannot both be known simultaneously

**De Broglie's Hypothesis**

\[ \lambda = h/mv \]

Particles have wave lengths; proof came from diffraction of electron beam

**Schroedinger's Wave Equation**

\[ \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\Psi = 0 \quad (H\Psi=E\Psi) \]

Solution of this equation requires conversion to spherical polar coordinates and the introduction of three constants, which are what we know as quantum numbers, n, ℓ, m_ℓ.
Each combination of \( n \), \( \ell \), and \( m \), value corresponds to an orbital

\( n \) values relate to the energy and size of the orbitals. \( n = 1, 2, 3 \cdots \)

\( \ell \) values specify the total angular momentum of the electron and determines the angular shape of the orbital. \( \ell \)'s have letter equivalents: \( \ell = 0 \) (s), 1 (p), 2 (d), 3 (f), 4 (g), etc. \( \ell = 0 \cdots n-1 \)

\( m \), specifies the orientation of the orbitals in space and the angular momentum with respect to direction. \( m = -\ell \cdots 0 \cdots +\ell \)

With introduction of the fourth quantum number, \( m_s = +1/2, -1/2 \) and the Pauli principle, which states that no two electrons in a given atom can have the same four quantum numbers, the development of electron configurations for multielectron atoms is straight-forward.

\[
E = -\frac{me^4Z^2}{8\varepsilon_0^2n^2h^2} = -13.6 \text{ eV } \frac{Z^2}{n^2} \text{ Same as for Bohr model!!!!}
\]

\[\text{Wave Functions}\]

\[
\Psi_{n,\ell,m\ell}(r,\theta,\phi) = R_{n,\ell}(r)\Theta_{\ell,m\ell}(\theta)\Phi_{m\ell}(\phi)
\]

\[
R_{n,\ell}(r) = \left[\frac{4Z^2(n-\ell-1)!}{n^2a_0^3[(n+\ell)!]^3}\right]^{1/2}\left(\frac{2Zr}{na_0}\right)e^{-Zr/a_0}\frac{L_{\ell+1}}{L_n}\]

\[
R_{1,0}(r) = 2Z^{3/2}a_0^{-3/2}e^{-Zr/a_0}.
\]

\[
R_{2,0}(r) = (1/2\sqrt{2})Z^{3/2}a_0^{-3/2}(2-Zr/a_0)e^{-Zr/2a_0}.
\]

\[
R_{2,1}(r) = (1/\sqrt{6})Z^{3/2}a_0^{-3/2}(Zr/a_0)e^{-Zr/2a_0}.
\]

\[
R_{3,0}(r) = (1/\sqrt{3})Z^{3/2}a_0^{-3/2}(27-18Zr/a_0+2Z^2r^2/9a_0^2)e^{-Zr/3a_0}.
\]

\[
\Theta_{\ell,m\ell}(\theta) = \sin^{\ell+1}P^\ell(\cos \theta)
\]

\[
\Phi_{m\ell}(\phi) = (1/\sqrt{2\pi})e^{im\phi}
\]

<table>
<thead>
<tr>
<th>( \ell )</th>
<th>( m_\ell )</th>
<th>( \Theta )</th>
<th>( \phi )</th>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1/\sqrt{2}</td>
<td>1/\sqrt{2}\pi</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>(\sqrt{3}/2)\cos \theta</td>
<td>1/\sqrt{2}\pi</td>
</tr>
<tr>
<td>1</td>
<td>\pm 1</td>
<td>(\sqrt{3}/2)\sin \theta</td>
<td>1/\sqrt{2}\pi e^{\mp \phi}</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>(\sqrt{5}/8)(3\cos^2\theta-1)</td>
<td>1/\sqrt{2}\pi</td>
</tr>
</tbody>
</table>
Representations of orbitals

$s$ Radial functions

\[ R_{1,s}(r) = 2a_o^{-3/2}e^{-r/a_o} \]
\[ R_{1,0}^2(r) = 4a_o^{-3}e^{-2r/a_o} \]
\[ r^2R_{1,0}^2(r) = 4a_o^{-3}r^2e^{-2r/a_o} \]
**2s Radial functions**

\[ R_{2s}(r) = \frac{1}{2\sqrt{2}} a_o^{-3/2} (2-r/a_o) e^{-r/a_o} \]

\[ R_{2s}^2(r) = \frac{1}{8} a_o^{-3} (4-2r/a_o + r^2/a_o) e^{-r/a_o} \]

\[ r^2 R_{2s}^2(r) = (1/8) a_o^{-3} (4-2r/a_o + r^2/a_o) r^2 e^{-r/a_o} \]

**Comparison of ns radial distribution functions**

1s

2s

3s
Comparison of 1s, 2s and 2p radial distribution functions

Angular functions as contour maps

- Angular nodes
- Radial nodes
- Relative size
Contour plots of H 2p and C 2p

Contour lines are set at 0.316 of maximum values of $\Psi^2(r,\theta,\phi)$

Multi-electron atoms; Aufbau Principle

<table>
<thead>
<tr>
<th></th>
<th>n=1</th>
<th>n=2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>H</td>
<td>___</td>
<td>___</td>
</tr>
<tr>
<td>He</td>
<td>___</td>
<td>___</td>
</tr>
<tr>
<td>Li</td>
<td>[He]</td>
<td>___</td>
</tr>
<tr>
<td>Be</td>
<td>[He]</td>
<td>___</td>
</tr>
<tr>
<td>B</td>
<td>[He]</td>
<td>___</td>
</tr>
<tr>
<td>C</td>
<td>[He]</td>
<td>___</td>
</tr>
<tr>
<td>N</td>
<td>[He]</td>
<td>___</td>
</tr>
<tr>
<td>O</td>
<td>[He]</td>
<td>___</td>
</tr>
<tr>
<td>F</td>
<td>[He]</td>
<td>___</td>
</tr>
<tr>
<td>Ne</td>
<td>[He]</td>
<td>___</td>
</tr>
</tbody>
</table>
More on multi-electron atoms

- Electron configurations in the third period (n=3) mirror those for the second period.
- In the fourth period (n=4) the 3d orbital energies are lower than the 4p so that these orbitals fill before the 4p. The elements with d electrons are referred to as transition elements.
- Electron configurations of the first transition element series are 4s²3dⁿ except for Cr and Cu, which are 4s¹3d⁶ and 4s¹3d¹⁰, respectively. These irregularities are a result of lower electron-electron repulsion energies.
- Transition metal cations have dⁿ electron configurations.

Periodic properties

- Ionization energy
- Atomic and ionic radii
- Electron Affinity
- Electronegativity
Ionization energy

Ionization energy is the minimum energy required to remove an electron from a gaseous atom (or other species). $E = E^+ + e^-$

Effective nuclear charge

$s & p$ orbital energies vs $Z$

$Z_{\text{eff}} = Z - \text{shielding constant}$

Effective nuclear charges

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>He</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.69</td>
</tr>
<tr>
<td>2s</td>
<td>1.28</td>
<td>1.91</td>
<td>2.58</td>
<td>3.22</td>
<td>3.85</td>
<td>4.49</td>
<td>5.13</td>
<td>5.76</td>
<td></td>
</tr>
<tr>
<td>2p</td>
<td></td>
<td></td>
<td>2.42</td>
<td>3.14</td>
<td>3.83</td>
<td>4.45</td>
<td>5.10</td>
<td>5.76</td>
<td></td>
</tr>
</tbody>
</table>
Atomic and ionic radii

Radial distribution functions for alkali metal ions
**Electron affinity**

Electron affinity is the energy change associated with addition of an electron to a atom or ion. \( E + e^- = E^- \)

![Graph showing electron affinity values for different elements]

Note that EA’s have been historically recorded as the negative of the energy associated with the electron attachment reaction.

---

**Electronegativity**

Electronegativity is the attraction of an atom for electron density in a chemical bond.

**Pauling electronegativities**

<table>
<thead>
<tr>
<th></th>
<th>H 2.20</th>
<th>Li 0.98</th>
<th>Be 1.57</th>
<th>B 2.04</th>
<th>C 2.55</th>
<th>N 3.04</th>
<th>O 3.44</th>
<th>F 3.98</th>
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<tbody>
<tr>
<td>Na</td>
<td>Mg 1.31</td>
<td>Al 1.61</td>
<td>Si 1.90</td>
<td>P 2.19</td>
<td>S 2.58</td>
<td>Cl 3.16</td>
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</tr>
<tr>
<td>K  0.82</td>
<td>Ca 1.00</td>
<td>Ga 1.81</td>
<td>Ge 2.01</td>
<td>As 2.18</td>
<td>Se 2.55</td>
<td>Br 2.96</td>
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<tr>
<td>Rb 0.82</td>
<td>Sr 0.95</td>
<td>In 1.78</td>
<td>Sn 1.96</td>
<td>Sb 2.05</td>
<td>Te 2.10</td>
<td>I 2.66</td>
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<tr>
<td>Cs 0.79</td>
<td>Ba 0.89</td>
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