Chemistry 1B Lectures 5-6
Fall 2013

2012 Nobel in QUANTUM physics

many-electron atoms and Schrödinger Equation (ppn557-558)

Although the Schrödinger equation for polyelectronic atoms (and molecules) cannot be solved exactly (mathematically), numerical computer calculations give solutions that agree perfectly with experiment but are very complex.

We can (and will!!) use the hydrogen-like orbitals as a very good approximation to the exact solutions of the Schrödinger equation for many-electron atoms.

Chemistry 1B Lectures 5-6: many electron atoms

- electron spin, “the 4th quantum number and the Pauli exclusion principle
- effective nuclear charge, \( Z_{\text{eff}} \)
- knowledge of the principal quantum number (\( n \)) and \( Z_{\text{eff}} \) for an atom’s valence electrons leads to an understanding of:
  - \( E_2s < E_2p \)
  - \( E_3p < E_3d \)
  - \( E_3d \) vs \( E_4s \)
- Hund’s Rule and electron configuration in many-electron atoms: the Aufbau Principle

new considerations for many-electron atoms
(somewhat different ‘order’ of presentation than Zumdahl)

- how does increased atomic number (\( Z \)) and the presence of other electrons affect orbital energies?
- how does one “fill up” the available orbitals in many-electron atoms

the spin quantum number

- Stern-Gerlach experiment (fig. 8-1 Silberberg)
Pauli exclusion principle (PEP) (sec 12.10)

no two electrons can have the same four quantum numbers:

\[ n = 1 \]
\[ \ell = 0 \]
\[ m_\ell = 0 \]
\[ m_s = \pm \frac{1}{2} \]

many-electron atoms

He, Li, Be, B, C, N, O, F, Ne ………

• greater nuclear charge (Z) than hydrogen (Z=1)

• more electrons than hydrogen (one-electron)

what we will need to figure out

How do the energies of the various hydrogen-like orbitals change when we take into account the effects of increased Z and the other electrons present ?????

in hydrogen \[ E_{2s} = E_{2p} \]

in boron why \[ E_{2s} < E_{2p} \] ????

where we are heading !!! chapter 12

• Quantum mechanics describes many-electron atoms by filling hydrogen-like orbitals with the atom’s electrons in a manner consistent with the Pauli Exclusion Principle.

• This description allows us to understand the energies of electrons in atoms and ions, the relative sizes of atoms and ions, and the chemical reactivity and other properties of various elements.
orbital energies in many-electron atoms

- Energy dependence on n and Z
  \[ E_n = -\frac{\alpha^2}{n^2} \]

- Holds EXACTLY for 1-electron atoms and ions: H, He\(^+\), Li\(^2+\), Be\(^3+\), ...
  Here \( Z \) is “regular” nuclear charge with \( Z=1, 2, 3, 4, ... \)

16

17

energy and average radius of electron in a hydrogen orbital

Energy of \( H\) 1s vs \( He^+\) 1s vs \( Li\(^2+\)\) 1s (still 1 electron)

- Increase \( Z \)
- More attraction
- Lower (more negative) energy (i.e., higher IE)
- Smaller \( r_{av} \)

Silberberg Figure 8.3
Energy of \( H\) 1s vs \( He^+\) 1s vs \( Li\(^2+\)\) 1s (still 1 electron)

Ionization energy (section problem S3)

Ionization energy (IE): the energy required to remove an electron from an atom, ion, or molecule in the gas phase

\[ X (g) + IE \rightarrow X^+ (g) + e^- \] (absorbs energy endothermic, \( \uparrow \) sign for energetics)

Similar to the work function \( \Phi \) in the photoelectric effect, except IE refers to gas phase ionization where \( \Phi \) refers to removal of electron from the solid

Z and Ionization Energies
IE = \( 2.18 \times 10^{-18} \) J \( \frac{Z^2}{n^2} \)

Z (He\(^+\) 1s) > Z (H1s)

Energy of \( H\) 1s vs \( He^+\) 1s (HO 12.1)

Increase \( Z \)
- More attraction
- Lower energy (i.e., higher IE)
- Smaller average radius

18

19

20
what happens when other electrons are present: effective nuclear charge (p. 546)

**Important Facts in Understanding Effective Nuclear Charge**

- Energy dependence on \( n \) and \( Z_{\text{eff}} \)
  \[ E_n = -(2 \times 10^{-18} \text{ J}) \]

- \( Z_{\text{eff}} \) and shielding
  \[ Z_{\text{eff}} = Z - (\text{shielding of other electrons}) \]
  \[ Z_{\text{eff}} = Z - (\text{effect of electron repulsions}) \]

- Electrons in same shell:
  \[ \text{He}^+ \, 1s \, \text{vs} \, \text{He} \, 1s^2 \]
  The two 1s electrons shield one another from the \( Z=+2 \) nuclear pull.

**Energy of \( \text{He} \, 1s^2 \) vs \( \text{He}^+ \, 1s \) (HO fig 12.2)**

\[ Z_{\text{eff}} \, (\text{He}^+ \, 1s) > Z_{\text{eff}} \, (\text{He} \, 1s^2) \]

\[ \text{IE} = 3.8 \times 10^{-18} \text{ J} \]

\[ Z_{\text{eff}} \approx 1.34 \] (1.20)

**He\(^+\) vs He (what positive charge does a 1s electron 'see'?)**

- Less attraction (more shielded)
  \[ 2^{nd} \, 1s \text{ electron (e\(^-\))} \]

He\(^+\) 1s

He 1s\(^2\)

**He\(^+\) vs He (what net positive charge does a 1s electron 'see'?)**

- Shielding of electron by 2nd 1s electron
  \[ 1 < Z_{\text{eff}} < 2 \]

He\(^+\) 1s

He 1s\(^2\)

**Silberberg figure 8.4A: energy of \( \text{He} \, 1s^2 \) vs \( \text{He}^+ \, 1s \) (same shell shielding) Zumdahl (p. 556-8)**

- One \( e^- \) makes the other \( e^- \) easier to remove
- This orbital is less stable
- \( \text{He} \, 1s \) actual He atom
- \( \text{Zumdahl's 'hypothetical' He atom} \)

- This \( e^- \) is harder to remove
- This orbital is more stable
- \( \text{He}^+ \, 1s \)
Energy dependence on n and $Z_{\text{eff}}$

$E_n = -(\frac{2}{18} \times 10^{-18}) \frac{Z_{\text{eff}}}{n}$

$Z_{\text{eff}}$ and shielding

$Z_{\text{eff}} = Z - \text{shielding of other electrons}$

$Z_{\text{eff}} = Z - (\text{effect of electron repulsions})$

Electrons in different shells

$\text{Li}^{2+} \ 2s$ vs $\text{Li}^{[1s^2]} \ 2s$

$Z_{\text{eff}}$ for $2s$ electron in $\text{Li}^{[1s^2]} \ 2s$

$Z_{\text{eff}}$ of $\text{Li}^{[1s^2]} \ 2s$

$Z=+3$

shielding by $1s^2$ electrons

$Z_{\text{eff}} \approx 1.26$

$\text{IE}=3.8 \times 10^{-18} \text{J}$

$Z_{\text{eff}} \approx 1.34$ (1.20)

$\text{IE}=4.9 \times 10^{-18} \text{J}$

$Z_{\text{eff}} = Z = 3$

$\text{IE}=0.86 \times 10^{-18} \text{J}$

$Z_{\text{eff}} \approx 1.26$

This is approximate way to calculate $Z_{\text{eff}}$

Other techniques give slightly different numbers

Figure 8.4 B (Silb) shielding by inner shell electrons

How do the energies of the 2s and 2p orbitals compare in many-electron atoms?

In 1-electron atoms (H-atom) and 1-electron ions, the 2s and 2p orbitals have the SAME... energies

$Z_{\text{eff}}$

And the effect of penetration of inner shell electron density by electrons in the same shell
Z\textsubscript{eff} for 2s vs 2p: 2p and 2s have SAME energy in 1-electron ion

\begin{itemize}
    \item 'penetration' by 2s electron of 1s\textsuperscript{2} shielding GIVES INCREASED \textit{Z\textsubscript{eff}}
\end{itemize}

\begin{itemize}
    \item 2s electron
    \item shielding by 1s\textsuperscript{2}
    \item \textbf{Li 1s\textsuperscript{2}2s}
    \item \textbf{Z\textsubscript{eff} \approx 1.26}
    \item actual 2s electron density (one radial node; one inner maximum in radial probability)
\end{itemize}

Z\textsubscript{eff} for 2s vs 2p

\begin{itemize}
    \item no (less) 'penetration' of 1s\textsuperscript{2} shielding by 2p electron GIVES relatively smaller \textit{Z\textsubscript{eff}}
\end{itemize}

\begin{itemize}
    \item 2p electron
    \item shielding by 1s\textsuperscript{2}
    \item \textbf{Li 1s\textsuperscript{2}2p}
    \item \textbf{Z\textsubscript{eff} for 2s > Z\textsubscript{eff} for 2p}
    \item \textbf{E_2s < E_2p}
\end{itemize}

Z\textsubscript{eff} for 2s vs 2p (handout fig. 12.4)

\begin{itemize}
    \item more penetration of inner shell electron density, electron see's more +Z and has greater Z\textsubscript{eff}
\end{itemize}

Energy of Li [1s\textsuperscript{2}] 2s vs Li [1s\textsuperscript{2}] 2p (HO Fig. 12.5): penetration

\begin{itemize}
    \item \textbf{Z\textsubscript{eff} (Li[1s\textsuperscript{2}] 2s) > Z\textsubscript{eff} (Li[1s\textsuperscript{2}] 2p)}
\end{itemize}

\begin{itemize}
    \item \textbf{IE=4.8 \times 10^{-18} J}
    \item \textbf{Zeff \approx 1.26}
    \item \textbf{IE=0.86 \times 10^{-18} J}
    \item \textbf{Zeff \approx 1.02}
    \item \textbf{IE=0.6 \times 10^{-18} J}
    \item \textbf{Zeff \approx 1.02}
\end{itemize}

how do the energies of the 2s and 2p orbitals compare in many-electron atoms?

\begin{itemize}
    \item Configurations and valence-level orbital diagrams
    \item Hund's rule
    \item 2\textsuperscript{nd} row aufbau fig 8.8 (Sil)
\end{itemize}

3s, 3p, 3d, 4s orbital energy ordering

\begin{itemize}
    \item Increasing \textit{Z\textsubscript{eff}} due to increasing penetration effects (figure HO 12Z.6);
    \item \textbf{(Z\textsubscript{eff})_3s > (Z\textsubscript{eff})_3p > (Z\textsubscript{eff})_3d}
    \item \textbf{(E)_3s < (E)_3p < (E)_3d}
    \item 4s vs 3d (Z\textsubscript{eff} vs n)
    \item Orbital energy ordering fig 8.6 (Silb) (figure 8.13, Silb)
\end{itemize}
configurations

- Hund’s rule
  - Energy ordering
  - Unambiguous (closed shell, 1e, (n-1)e’s)
  - Ambiguous (e.g., p^2, p^3, p^4, d^2 → d^8)

- Examples (periodic table)
  - ground state
  - excited state
  - not allowed configuration
  - transition metal cations
  - “exceptions”

unpaired electrons and magnetic properties (Gouy balance)

Diamagnetic
- pushed out of magnet
- no unpaired electrons

Paramagnetic
- pulled into magnet
- unpaired electrons

Gouy Balance

\[ \text{IE} = 3.8 \times 10^{-18} \text{ J} \]

\[ Z_{eff} \approx 1.34 \quad (1.20) \]

\[ Z_{eff} = Z = 1. \]

\[ Z_{eff} = Z = 2. \]

\[ \text{IE} = 0.6 \times 10^{-18} \text{ J} \]

\[ Z_{eff} \approx 1.02 \]

\[ \text{IE} = 0.86 \times 10^{-18} \text{ J} \]

\[ Z_{eff} \approx 1.26 \]

\[ \text{IE} = 4.9 \times 10^{-18} \text{ J} \]

\[ Z_{eff} = Z = 3. \]

\[ \text{IE} = 0.86 \times 10^{-18} \text{ J} \]

\[ Z_{eff} \approx 1.26 \]

\[ \text{IE} = 4.9 \times 10^{-18} \text{ J} \]

\[ Z_{eff} = Z = 3. \]

\[ \text{IE} = 0.86 \times 10^{-18} \text{ J} \]

\[ Z_{eff} \approx 1.26 \]

end of lectures 5-6

the Periodic Table

Silberberg figure 8.8

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.
Figure HO 8.6: penetration of 3s vs 3p vs 3d; radial nodes = n-\ell-1

3s: 2 radial nodes
2 “inner electron density maxima”

3p: 1 radial node
1 “inner maxima”

3d: 0 radial nodes
0 “inner maxima”

less penetration
smaller Z_{eff}
higher energy

more penetration
larger Z_{eff}
lower energy

screening by n=2 electrons

Zumdahl figure 12.29

Why B (He) 2s 2p^1 is ‘unambiguous’ ground state configuration

Experimental spectrum (states) of B

Only one energy state
(gamma 2S vs 1S)
Why C [He] 2s^2 2p^2 is 'ambiguous' ground state configuration

Experimental spectrum (states) of C

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Term</th>
<th>J</th>
<th>Level</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s^2 2p^2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6.85</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>14.81</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>43.73</td>
</tr>
<tr>
<td>2s^2 2p^2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>30.382 (43)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>21.446 (46)</td>
</tr>
<tr>
<td>2s^2 2p^2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>18.750 (57)</td>
</tr>
<tr>
<td>2s^2 2p^2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>60.355 (13)</td>
</tr>
<tr>
<td>2s^2 2p^2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>60.355 (14)</td>
</tr>
</tbody>
</table>

Ground energy state (ignore 0 vs 1 vs 2)

Excited states with same [He] 2s^2 2p^2 configuration

Why B [He] 2s^1 2p^2 is 'unambiguous' ground state configuration

Experimental spectrum (states) of B

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Term</th>
<th>J</th>
<th>Level</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s^1 2p^2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.85</td>
</tr>
<tr>
<td>2s^1 2p^2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>13.81</td>
</tr>
<tr>
<td>2s^1 2p^2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>43.73</td>
</tr>
<tr>
<td>2s^1 2p^2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>30.382 (43)</td>
</tr>
<tr>
<td>2s^1 2p^2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>21.446 (46)</td>
</tr>
<tr>
<td>2s^1 2p^2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>18.750 (57)</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>60.355 (13)</td>
</tr>
<tr>
<td>2s^1 2p^2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>60.355 (14)</td>
</tr>
</tbody>
</table>

Only one energy state (ignore 3/2 vs 1/2)

Excited states have excited [He] 2s^1 2p^2 configuration