Quantum Mechanics and Atomic Physics

Lecture 22:
Multi-electron Atoms

http://www.physics.rutgers.edu/ugrad/361

Prof. Eva Halkiadakis
Atoms with 2 or more electrons have a new feature:

- Electrons are indistinguishable!
- There is no way to tell them apart!

Any measurable quantity (probability, expectation value, etc.) must not depend on which electron is labeled 1, 2, etc.
Last Time: Pauli Exclusion Principle

- Principle was formulated by Wolfgang Pauli in 1925.
- “Weak form”:
  - In an atom, no two electrons can be in the same quantum state, i.e. the same set of quantum numbers: $n, \ell, m_\ell, m_s$
Last Time: Pauli Exclusion Principle

- Suppose electrons 1 and 2 are in the same quantum state A. Then:

\[ \Psi_{\text{symm}} = \frac{1}{\sqrt{2}} \left[ \Psi_{A} (1) \Psi_{A} (2) + \Psi_{A} (1) \Psi_{A} (2) \right] \]

\[ = \sqrt{2} \Psi_{A} (1) \Psi_{A} (2) = 0 \]

- So, \( \Psi_{\text{symm}} \) permits 2 electrons in the same state.
- So, \( \Psi_{\text{symm}} \) violates the Pauli exclusion principle!

\[ \Psi_{\text{anti}} = \frac{1}{\sqrt{2}} \left[ \Psi_{A} (1) \Psi_{A} (2) - \Psi_{A} (1) \Psi_{A} (2) \right] = 0 \]

- So \( \Psi_{\text{anti}} \) obeys the Pauli exclusion principle!
Pauli Exclusion Principle

“Strong” form of Pauli Exclusion Principle:

- A multi-electron system must have an antisymmetric total eigenfunction.
- “Strong” because it also incorporates indistinguishability.
- All particles of half-integer spin (1/2, 3/2, …) have antisymmetric total eigenfunctions and are called “Fermions”, obeying Fermi-Dirac statistics
  - Electrons, protons, neutrons
- All particles of integer spin (0, 1, 2, …) have symmetric total eigenfunctions, and are called “Bosons”, obeying Bose-Einstein statistics.
  - Photons, alpha, W and Z particles

\[ \Psi_{tot} \propto \Psi_A(1)\Psi_B(2) \pm \Psi_A(2)\Psi_B(1) \]

- Required for Bosons
- Required for Fermions
Helium Example

■ Normal Helium \((^4_2 \text{He})\)
  ■ 2 protons, 2 neutrons and 2 electrons
  ■ Even number of spin \(\frac{1}{2}\) constituents
  ■ Is a Boson

■ Helium-3 \((^3_2 \text{He})\)
  ■ 2 protons, 1 neutrons, 2 electrons
  ■ Odd number of spin \(\frac{1}{2}\) constituents
  ■ Is a Fermion
Total Fermion Eigenfunction

- So, for Fermion, total eigenfunction must be antisymmetric
- Can write:
  \[ \psi_{\text{Anti}} = \psi_{\text{space}} \psi_{\text{spin}} \]
- So, \( \psi_{\text{space}} \) and \( \psi_{\text{spin}} \) must have opposite symmetry in order for \( \psi_{\text{Anti}} \) to be antisymmetric
- We had used A and B as abbreviations for particular sets of \( n, \ell, m_\ell, m_s \)
- Now let’s use a and b as abbreviations for particular sets of \( n, \ell, m_\ell \)
  - i.e. just the space part
Space and Spin Eigenfunctions

\[ \Psi_{\text{symm}}(\text{space}) = \frac{1}{\sqrt{2}} \left[ \Psi_a(1) \Psi_b(2) + \Psi_b(1) \Psi_a(2) \right] \]

\[ \Psi_{\text{anti}}(\text{space}) = \frac{1}{\sqrt{2}} \left[ \Psi_a(1) \Psi_b(2) - \Psi_b(1) \Psi_a(2) \right] \]

- The space wavefunctions are analogous to R\(\Theta\)F for Hydrogen

- Spin wavefunctions are matrices
  - Symbolically,
Spin Eigenfunctions

- Let’s write this such that $\chi$ has a definite symmetry.

- So, the antisymmetric $\chi$, corresponding to $\Psi_{\text{Symm}}(\text{space})$ (singlet state):
  \[ \chi_{\text{Anti}} = \frac{1}{\sqrt{2}} \left( \chi(+1/2,-1/2) - \chi(-1/2,+1/2) \right) \]

- The symmetric $\chi$, corresponding to $\Psi_{\text{Anti}}(\text{space})$; there are three ways to do it (triplet state):
  \[ \chi_{\text{Symm}} = \begin{cases} \chi (+1/2,+1/2) \\ \frac{1}{\sqrt{2}} \left[ \chi(+1/2,-1/2) + \chi(-1/2,+1/2) \right] \\ \chi (-1/2,-1/2) \end{cases} \]
Spin Angular Momentum

- In a two electron atom (Helium) the spin angular momentum of the two electrons couple to give the total spin:

\[ S' = S_1 + S_2 \]

\[ S' = |S'| = \sqrt{s'(s'+1)} \hbar \]

\[ S'_\parallel = m_s \hbar \]

\[ m_{s'} = -s', -s'+1, \ldots, s' \]

- But what is $s'$?

\[ s_1 = s_2 = \frac{1}{2} \]

\[ s' = |s_1 - s_2|, |s_1 - s_2| + 1, \ldots, (s_1 + s_2) \]

\[ = 0 \text{ or } 1 \]
Spin Angular Momentum

- If $s'=0$, $m_{s'} = 0$ only, and this is the singlet state, which is antisymmetric.
  - We have opposite spins, and $S'=0$

- If $s'=1$, $m_{s'} = -1, 0, +1$, and this is why we get the triplet state which is symmetric.
  - We have parallel spins
Parallel Spins

- For parallel spins:
  - $s' = 1$
  - triplet state in Helium
  - $\chi$ symmetric
  - $\Psi$(space) antisymmetric.

- Suppose electrons get close, so $a = b$ (same spacial quantum numbers):

\[
\Psi_{\text{anti (space)}} = \frac{1}{\sqrt{2}} \left[ \Psi_a(1) \Psi_a(2) - \Psi_a(1) \Psi_a(2) \right] = 0
\]

- Low probability for electrons to have similar coordinates
- Parallel-spin electron repel each other, over and above the Coulomb repulsion.
- This “exchange” force mainly reflects the exclusion principle
Antiparallel Spins

- For antiparallel spins:
  - $s' = 0$
  - Singlet state in Helium
  - $\chi$ antisymmetric
  - $\Psi$(space) symmetric

- Suppose electrons get close, so $a = b$ (same spacial quantum numbers):

\[
\Psi_{\text{symm}}(\text{space}) = \frac{1}{\sqrt{2}} \left[ \Psi_a(1) \Psi_a(2) + \Psi_a(1) \Psi_a(2) \right] = \sqrt{2} \Psi_a(1) \Psi_a(2)
\]

- This is large, so antiparallel-spin electrons attract each other via the “exchange” force.
Summary:

- Multi-electron atoms and Pauli’s exclusion principle
- Electrons are Fermions (spin 1/2), are indistinguishable and have an antisymmetric total eigenfunction

\[ \Psi_{\text{anti}} = \Psi(\text{space}) \Psi(\text{spin}) \]

- Helium:
  - For antiparallel spins:
    - \( s' = 0 \)
    - Singlet state in Helium
    - \( \chi \) antisymmetric
    - \( \Psi(\text{space}) \) symmetric
  - For parallel spins:
    - \( s' = 1 \)
    - triplet state in Helium
    - \( \chi \) symmetric
    - \( \Psi(\text{space}) \) antisymmetric.
Example

If we put 5 electrons (fermions!) in an infinite square well, what is the ground state energy?

Recall the energies for an infinite square well are:

\[ E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = n^2 E_1, \text{ where } E_1 = \frac{\pi^2 \hbar^2}{2mL^2} \]

Since electrons are fermions, 2 electrons will populate \( n=1 \), 2 in \( n=2 \), and 1 in \( n=3 \).

So, the ground state energy of this system is:

\[ E = 2 \cdot (E_1) + 2 \cdot (4E_1) + 1 \cdot (9E_1) = 19E_1 \]

What if we put 5 bosons in the well?

All 5 bosons can go into \( n=1 \)!

So ground state energy is \( E=5E_1 \)
Complex Atoms

- For complex atoms, S.E. is solved numerically (we’ll see this in Reed Chapter 10) using:
  - the potential between each electron and the nucleus,
  - and the potential between each electron and all the others.
- Atomic energy levels and chemical properties are then obtained!

Each value of \( n \) corresponds to a shell:

| \( n \) | 1 | 2 | 3 | 4 | ...
| --- | --- | --- | --- | --- | --- |
| Shell | K | L | M | N | ...

Each \( n \) and \( \ell \) constitute a subshell:

| \( \ell \) | 0 | 1 | 2 | 3 | 4 | ...
| s | p | d | f | g | ... |
# Population of Shells

<table>
<thead>
<tr>
<th>Shell</th>
<th>n</th>
<th>(\ell)</th>
<th>(m_\ell)</th>
<th>(m_s)</th>
<th>Sub-shell</th>
<th>Max. Sub-shell population</th>
<th>Max. Shell population</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>(\pm 1/2)</td>
<td>1s</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>L</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>(\pm 1/2)</td>
<td>2s</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>0, (\pm 1)</td>
<td>(\pm 1/2)</td>
<td>2p</td>
<td>6</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>(\pm 1/2)</td>
<td>3s</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>0, (\pm 1)</td>
<td>(\pm 1/2)</td>
<td>3p</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>0, (\pm 1, \pm 2)</td>
<td>(\pm 1/2)</td>
<td>3d</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

For each \(\ell\), there are \((2\ell+1)\) values of \(m_\ell\) and 2 values of \(m_s\), so the maximum subshell population is \(2(2\ell+1)\)
Maximum Shell Population

- For each $n$, $\ell = 0, 1, \ldots (n-1)$
- So the maximum shell population is:

\[
\sum_{\ell=0}^{n-1} 2(2\ell+1) = \sum_{\ell=0}^{n-1} (4\ell+2)
\]

\[
= 4 \left( \frac{(n-1)n}{2} + 2n \right) = 2n^2 - 2n + 2n = 2n^2
\]
Chemical properties of atoms are (mostly) determined by the outermost electrons.

Outer electrons do not feel the full nuclear charge, because inner electrons partially shield the nucleus.

This is called **shielding** or **screening**.

Also radii of complex atoms are within a factor of two of hydrogen!

- The inner electrons get pulled in closer to the nucleus.
Ionization Energy

- The ionization energy: the energy necessary to remove an electron from the neutral atom.
- Ionization energy of hydrogen: 13.6 eV
- Other atoms: 5-25 eV
- So within a factor of two or so of hydrogen.
- It is a minimum for the atoms (alkali metals) which have a single electron outside a closed shell.
- It generally increases across a row on the periodic table.
  - maximum for the noble gases which have closed shells.
Energy of Complex Atoms

- Hydrogen atom:
  - In Schrödinger theory, H atom exhibits $\ell$-degeneracy
  - In Dirac theory: energy depends on $n$ and $j$

- For complex atoms:
  - For a given $n$, the energy increases with $\ell$
  - Mainly a consequence of screening.

2 electrons in 1s
1 electron in 2s

Penetration of 2s and 2p states inside first Bohr radius.

So 2s is lower than 2p
Energy Levels of Helium

- In Helium one electron is presumed to be in the ground state of a helium atom, the 1s state.

- An electron in an upper state can have spin antiparallel to the ground state electron (s’=0, singlet state) or parallel to the ground state electron (s’=1, triplet state).

- This gives us two sets of states for Helium:
  1. **Parahelium:**
     - electrons have antiparallel spins, s’=0, singlet spin eigenfunctions, antisymmetric \( \chi \), symmetric \( \Psi \) (space), attractive exchange force, electrons close.
  2. **Orthohelium:**
     - electrons have parallel spins, s’=1, triplet spin eigenfunctions, symmetric \( \chi \), antisymmetric \( \Psi \) (space), repulsive exchange force, electrons generally far apart.
It is observed that the orthohelium states \((s' = 1)\) are lower in energy than the parahelium states \((s' = 0)\).
Features of Helium Energy Levels

1. For an $n$, energy increases with $\ell$.
   - Mainly due to increasing shielding as $\ell$ increases.

2. Triplet states have a little less energy than corresponding singlet state.
   - Mainly because electrons are farther apart due to exchange forces.
   - Energy of $e^- e^-$ interaction is:

$$\frac{1}{4\pi\varepsilon_0} \frac{(-e)(-e)}{r} = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r}$$
Features of Helium Energy Levels

3. **Most important**: $1^3S$ state does not exist!
   - That’s because it would violate Pauli exclusion principle: $n=1$, $\ell=0$, $m_\ell=0$, parallel spins ($s=1$).

4. Parahelium: $s’=0$, so $j’=\ell$. So singlet states are: $1^1S_0$, $2^1S_0$, $2^1P_1$, etc.
   Orthohelium: $s’=1$, so if $\ell=0$, $j’=s’=1$. So, $2^3S_1$ really is a singlet. But $2^3P$ is truly a triplet ($\ell=1$, $j’=0$, 1, 2): $2^3P_0$, $2^3P_1$, $2^3P_2$ (Note that the degeneracy would be lifted by a magnetic field.)
Features of Helium Energy
Levels

5. Transitions between triplet and singlet states are rare. They would require spin flip, which in general occurs only when an atom collides with another.

6. The $1^1S$ state is very tightly bound. The ionization energy is 24.6eV, the largest of all atoms!
Build-up of Periodic Table

- Electrons fill subshells in order of increasing energy:
  - 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s ....

- Note that the \( \ell \) dependence of energy becomes more and more important as \( Z \) increases.

- Each element is described by giving its electron configuration, i.e. the population of each subshell.

Element | Population
---|---
H | \( +1 \)
He | \( +2 \)
Li | \( +3 \)
Be | \( +4 \)
B | \( +5 \)
C | \( +6 \)
N | \( +7 \)
O | \( +8 \)
F | \( +9 \)
Ne | \( +10 \)
Na | \( +11 \)
Mg | \( +12 \)

Subshell full \( \Rightarrow \) Inert gas
Alkali metal; electron in 2s mostly determines chemistry of Li
Another inert gas
Summary/Announcements

- **Next time:**
  - Multi-electrons continued, and in a B field
  - Approximation Methods (I)

- **HW 10 due today.**

- **HW 11 due on Wed Dec 5. (note extended deadline)**

- **Final exam: Wed. Dec 19th 8-11am room SEC 118**
  - More details to come soon

- **Please fill out SIRS:** [http://ctaar.rutgers.edu/sirs/current-surveys](http://ctaar.rutgers.edu/sirs/current-surveys)
  - Survey runs Monday, November 29 through Friday, December 14