Where Are We Going…?

- **Week 10: Orbitals and Terms**
  - Russell-Saunders coupling of orbital and spin angular momenta
  - Free-ion terms for $p^2$
- **Week 11: Terms and ionization energies**
  - Free-ion terms for $d^2$
  - Ionization energies for $2p$ and $3d$ elements
- **Week 12: Terms and levels**
  - Spin-orbit coupling
  - Total angular momentum
- **Week 13: Levels and ionization energies**
  - $j-j$ coupling
  - Ionization energies for $6p$ elements

Revision – Atomic Orbitals

- For any 1 e⁻ atom or ion, the Schrödinger equation can be solved
- The solutions are atomic orbitals and are characterized by $n$, $l$, and $m_l$ quantum numbers

\[ H\psi = E\psi \]

- $E$ is energy of the orbital $\psi$
- $H$ is the 'Hamiltonian' - describing the forces operating:
  - Kinetic energy due to motion \( \frac{1}{2} mv^2 \)
  - Potential energy due attraction to nucleus \( -\frac{Ze}{r} \)
  - Total Hydrogen-like Hamiltonian \( H_{\text{H-like}} \)
Atomic Orbitals - Quantum Numbers

- For any 1-e- atom or ion, the Schrödinger equation can be solved
- The solutions are **atomic orbitals** and are characterized by \( n, l \) and \( m_l \) quantum numbers
  - Principal quantum number, \( n = 1, 2, 3, 4, 5, 6, \ldots \)
  - Orbital quantum number, \( l = n-1, n-2, n-3, 0 \) = number of nodal planes
  - Magnetic quantum number, \( m_l = l, l-1, l-2, \ldots, -l \)

\[ l = 0: \text{s} \quad l = 1: \text{p} \quad l = 2: \text{d} \]

Orbital Quantum Number

- Orbital quantum number, \( l = n-1, n-2, n-3, 0 \) = number of nodal planes
- Magnetic quantum number, \( m_l = l, l-1, l-2, \ldots, -l \) = orientation of orbital
  - e.g. \( l = 2 \) gives \( m_l = 2, 1, 0, -1, -2 \); so \( 2l+1 = 5 \) d-orbitals

Magnetic Quantum Number

- Orbital quantum number, \( l = n-1, n-2, n-3, 0 \) = number of nodal planes
- Magnetic quantum number, \( m_l = l, l-1, l-2, \ldots, -l \) = orientation of orbital
  - related to magnitude of orbital angular momentum
  - related to direction of orbital angular momentum

\[ l = 2 \]

\[ m_l = 2 \quad m_l = 1 \quad m_l = 0 \quad m_l = -1 \quad m_l = -2 \]
Spin Quantum Number

- All electrons have spin quantum number, \( s = \frac{1}{2} \)
- Magnetic spin quantum number, \( m_s = s, s - \frac{1}{2} \) or \( -\frac{1}{2}, 2s + 1 = 2 \) values

Many Electron Atoms

- For any 2-e⁻ atom or ion, the Schrödinger equation cannot be solved
- The H-like approach is taken for every electron

\[
H_{\text{H-like}} = \sum_i \frac{1}{2} mv_i^2 + \sum_i -\frac{Ze}{r_i}
\]

- Treatment leads to configurations
  - for example: \( \text{He} \ 1s^2 \)
  - \( \text{C} \ 1s^2 2s^2 2p^2 \)

- Neglects interaction between electrons
  - \( e^- e^- \) repulsion is of the same order of magnitude as \( H_{\text{H-like}} \)

Many Electron Atoms – \( p^1 \) Configuration

- A configuration like \( p^1 \) represents 6 electron arrangements with the same energy
  - there are three \( p \)-orbitals to choose from as \( l = 1 \)
  - electron may have up or down spin

<table>
<thead>
<tr>
<th>( m_l )</th>
<th>( m_s )</th>
<th>microstate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+( \frac{1}{2} )</td>
<td>1 ( (1) )</td>
</tr>
<tr>
<td>-1</td>
<td>-( \frac{1}{2} )</td>
<td>0 ( (1) )</td>
</tr>
<tr>
<td>0</td>
<td>+( \frac{1}{2} )</td>
<td>-1 ( (1) )</td>
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<td>-1 ( (1) )</td>
</tr>
</tbody>
</table>
Many Electron Atoms – $p^2$ Configuration

- A configuration like $p^2$ represents even more electron arrangements
- Because of $e^-/e^-$ repulsion, they do not all have the same energy:
  - electrons with parallel spins repel one another less than electrons with opposite spins
  - electrons orbiting in the same direction repel one another less than electrons with orbiting in opposite directions

\[ \begin{array}{c|c}
1 & 0 \\
-1 & -1 \\
\end{array} \]

\[ \begin{array}{c}
\downarrow & \downarrow \\
\downarrow & \downarrow \\
\end{array} \]

lower in energy than

\[ \begin{array}{c|c}
1 & 0 \\
-1 & -1 \\
\end{array} \]

\[ \begin{array}{c}
\uparrow & \uparrow \\
\downarrow & \downarrow \\
\end{array} \]

lower in energy than

Many Electron Atoms – $L$

- For a $p^2$ configuration, both electrons have $l = 1$ but may have $m_l = 1, 0, -1$
- $L$ is the total orbital angular momentum

\[ L_{\text{max}} = l_1 + l_2 = 2 \]
\[ L_{\text{min}} = l_1 - l_2 = 0 \]
\[ L = l_1 + l_2, l_1 + l_2 - 1, \ldots, l_1 - l_2 \]
\[ = 2, 1, 0 \]

For each $L$, $M_l = L, L-1, \ldots, -L$

$L$: 0, 1, 2, 3, 4, 5, 6 ...
code: S, P, D, F, G, H, I ...

Many Electron Atoms – $S$

- Electrons have $s = \frac{1}{2}$ but may have $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$
- $S$ is the total spin angular momentum

\[ S_{\text{max}} = s_1 + s_2 = 1 \]
\[ S_{\text{min}} = s_1 - s_2 = 0 \]
\[ S = s_1 + s_2, s_1 - s_2, \ldots, s_1 - s_2 \]
\[ = 1 \text{ and } 0 \]

For each $S$, $M_s = S, S-1, \ldots, -S$
Many Electron Atoms – p²

- L = 2, 1, 0
  - for each L: \( M_L = L, L - 1, L - 2, \ldots -L \)
  - for each L, there are \( 2L + 1 \) functions
- S = 1, 0
  - for each S: \( M_S = S, S - 1, S - 2, \ldots -S \)
  - for each S, there are \( 2S + 1 \) functions

Wavefunctions for many electron atoms are characterized by \( L \) and \( S \) and are called terms with symbol: 

\[ L \text{ and } S \]

\( 2S + 1 \)

- singlets: \( ^1D, ^1P, ^1S \)
- triplets: \( ^3D, ^3P, ^3S \)

Microstates – p²

- For example, \( ^3D \) has \( L = 2 \) and \( S = 1 \) so:
  - \( M_L = 2, 1, 0, -1, -2 \) and \( M_S = 1, 0, -1 \)
  - five \( M_L \) values and three \( M_S \) values: \( 5 \times 3 = 15 \) wavefunctions with the same energy

\[ \left( \frac{+/-}{M_{l_1}, M_{l_2}} \right) \]

\[ M_L = m_{l_1} + m_{l_2} \]

\[ M_S = m_{s_1} + m_{s_2} \]
Pauli Principle and Indistinguishability

- The Pauli principle forbids two electrons having the same set of quantum numbers. Thus for $p^2$
  - Microstates such as $(1, 1)$ and $(-1, -1)$ are not allowed
- Electrons are indistinguishable
  - Microstates such as $(1, -1)$ and $(-1, 1)$ are the same
  
- Microstates such as $(1, -1)$ and $(1, -1)$ are different
- For example, for $p^2$
  - 6 ways of placing 1st electron, 5 ways of placing 2nd electron (Pauli)
  - Divide by two because of indistinguishability: \( \frac{6 \times 5}{2} = 15 \)

<table>
<thead>
<tr>
<th>Microstate</th>
<th>$M_L$</th>
<th>$M_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>((1, 1))</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>((1, 0))</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>((-1, 0))</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>((-1, 1))</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>((-1, 2))</td>
<td>-2</td>
<td>-1</td>
</tr>
</tbody>
</table>

Working Out Allowed Terms

1. Pick highest available $M_L$; there is a term with $L$ equal to this $M_L$
   - Highest $M_L = 2 \rightarrow L = 2 \rightarrow$ D term
2. For this $M_L$; pick highest $M_S$; this term has $S$ equal to this $M_S$
   - Highest $M_S = 0 \rightarrow S = 0 \rightarrow 2S+1 = 1$: D term
3. Term must be complete:
   - For $L = 2$, $M_L = 2, 1, 0, -1, -2$ for each value of $M_S$, strike out microstates with these $M_L$ values
   - For $S = 0$, $M_S = 0$
4. Repeat 1-3 until all microstates are used up
   a. Highest $M_L = 1 \rightarrow L = 1 \rightarrow$ P term
   b. Highest $M_S = 1 \rightarrow S = 1 \rightarrow 2S+1 = 3$: P term
   c. Strike out 9 microstates ($M = 1, 0, -1$ for each $M_L = 1, 0, -1$)
   d. Left with $M_L = 0 \rightarrow L = 0 \rightarrow$ S term
   e. This has $M_L = 0 \rightarrow S = 0 \rightarrow 2S+1 = 1$: S term
Check

• The configuration \( p^2 \) gives rise to 15 microstates
• These give belong to three terms:
  - \( ^1D \) is composed of 5 states (\( M_S = 0 \) for each of \( M_L = 2, 1, 0, -1, -2 \))
  - \( ^3P \) is composed of 9 states (\( M_S = 1, 0, -1 \) for each of \( M_L = 1, 0, -1 \))
  - \( ^1S \) is composed of 1 state (\( M_S = 0, M_L = 0 \))
  - \( 5 + 9 + 1 = 15 \)
• The three terms differ in energy:
  - Lowest energy term is \( ^3P \) as it has highest \( S \) (unpaired electrons)

Summary

Configurations
• For many electron atoms, the \( H_{\text{tttot}} \) gives rise to configurations
• Each configuration represents more than one arrangements
Terms
• The arrangements or microstates are grouped into terms according to \( L \) and \( S \) values
• The terms differ in energy due to interelectron repulsion
Next week
• Hund’s rules and ionization energies
Task!
• Work out allowed terms for \( d^2 \)