Quantum Mechanics

- Erwin Schrödinger developed a mathematical solution where the electron is described as a wave.
- Mathematically derived the probability of finding an electron in a given region of space. This is known as the 'electron density'. The electrons are here 90% of the time.
- The region of space where the electron (of a given energy) is most probably located is known as ‘orbital’.

The 'quantum numbers’ \(n, l, m_l\) are derived from Schrodinger’s eqn.

Quantum Mechanics

- The wave equation is designated with a lower case Greek psi (\(\psi\)).
- The square of the wave equation, \(\psi^2\), gives a probability density map of where an electron has a certain statistical likelihood of being at any given instant in time.
- From the ‘uncertainty principle’ we cannot determine the location of an electron of any given energy.

Quantum Numbers

- Solving the wave equation gives a set of wave functions, or orbitals, and their corresponding energies.
- Each orbital describes a spatial distribution of electron density.
- An orbital is described by a set of three quantum numbers \((n, l, m_l)\)

<table>
<thead>
<tr>
<th>Value of (l)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of orbital</td>
<td>(s)</td>
<td>(p)</td>
<td>(d)</td>
<td>(f)</td>
</tr>
</tbody>
</table>

- \(n\), the Principal Quantum Number = 1, 2, 3, …infinity
  - Gives the primary electron shell for the electron. Analogous to Bohr’s value of \(n\). \(E_n = -\frac{\hbar^2}{2m}\).
  - (‘bigger’ \(n\) value means ‘bigger’ orbitals, and ‘higher’ energy)

- \(l\), the Angular Momentum Quantum Number = 0, 1, 2, …\(n-1\)  This quantum number defines the shape of the orbital. Gives the electron subshell or orbital the electron can be found in. Allowed values of \(l\) are 0 to \((n-1)\).

  - Bigger \(l\) higher the energy of the orbital

- \(m_l\), the Magnetic Quantum Number = \(-l, -l+1, \ldots, 0, \ldots, l-1, l\)  The orientation of the orbital in space.

  - Bigger \(m_l\) higher the energy of the orbital
Magnetic Quantum Number, $m_l$

- Describes the three-dimensional orientation of the orbital.
- Values are integers ranging from -$l$ to $l$.

<table>
<thead>
<tr>
<th>$l$</th>
<th>possible values of $m_l$</th>
<th># orbitals in this subshell</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>-1, 0, +1</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>-2, -1, 0, +1, +2</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>-3, -2, -1, 0, +1, +2, +3</td>
<td>7</td>
</tr>
</tbody>
</table>

Spin Quantum Number, $m_s$

- In the 1920s, it was discovered that two electrons in the same orbital do not have exactly the same energy.
- The “spin” of an electron describes its magnetic field, which affects its energy.
- The spin quantum number, $m_s$ has values of +1/2 and −1/2.

In summary....

<table>
<thead>
<tr>
<th>$n$</th>
<th>Possible Values of $l$</th>
<th>Subshell Designation</th>
<th>Possible Values of $m_l$</th>
<th>Number of Orbitals in Subshell</th>
<th>Total Number of Orbitals in Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1s</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2s</td>
<td>1, 0, −1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>3s</td>
<td>1, 0, −1</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>4s</td>
<td>1, 0, −1</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>3p</td>
<td>1, 0, −1</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>4p</td>
<td>1, 0, −1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>3d</td>
<td>2, 1, 0, −1, −2</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>4d</td>
<td>2, 1, 0, −1, −2</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>5f</td>
<td>3, 2, 1, 0, −1, −2, −3</td>
<td>7</td>
<td>16</td>
</tr>
</tbody>
</table>

Observing a graph of probabilities of finding an electron versus distance from the nucleus, we see that s orbitals possess $n−1$ nodes, or regions where there is 0 probability of finding an electron. s orbitals have a zero $l$ value.
**p orbitals**

- Has an imaginary plane (nodal surface) that divides the region of electron density in half. Zero probability of finding an e- here.
- Occurs when \( l = 1 \) (dumb-bell shaped orbitals, one nodal surface)
- When \( l = 1 \), \( m_l \) values are \(-1, 0, +1\) (corresponds to \( p_x, p_y \) and \( p_z \))

**d orbitals**

- Occurs when \( l = 2 \), orbitals have two nodal surfaces, four regions of e- density. Five orbitals, corresponding to \( m_l \) quantum number. \((d_{x^2-y^2}, d_{xz}, d_{yz}, d_{xy}, d_z)\)

**Orbital Energy Levels of Hydrogen**

For the Hydrogen atom, each subshell with the same ‘n’ has same energy.

We say that the orbitals are **degenerate**.

For \( n = 2 \), 2s and 2p orbitals are **degenerate** (possess the same energy).

* Recall at \( n = 1, E = 0 \)

**Energy levels in a non-Hydrogen atom**

- As the number of electrons increases, though, so does the repulsion between them.
- Therefore, in many-electron atoms, orbitals on the same energy level are no longer degenerate
Pauli Exclusion Principle

- two electrons cannot share the same set of quantum numbers within the same system, i.e. no two electrons in the same atom can have identical sets of quantum numbers. 
  \((n, l, m_l\text{ and } m_s)\)

- Example: An electron in a 3d orbital might have the following four quantum numbers, \(n = 3, l = 2, m_l = 0, m_s = +1/2\).
  A second electron in the same 3d orbital would have the following quantum numbers, \(n = 3, l = 2, m_l = 0, m_s = -1/2\).

Electron Configurations

- Number denotes the energy level, \(n=4\)
- \(4p^5\) Denotes the subshell ‘p’ orbital
- \(4p^5\) Denotes number of e\(^{-}\) in the orbital

Orbital Notations

- Each box denotes an orbital
- The half arrows denote an e
- The up and down arrows denote differences of e\(^{-}\) spin

Li

\[
\begin{array}{ll}
1s & 2s \\
\end{array}
\]

Hund’s Rule

- Every orbital in a subshell is singly occupied with one e\(^{-}\) before any one orbital is doubly occupied.
- All electrons in singly occupied orbitals have the same spin.
- This configuration helps attain the lowest energy configuration within degenerate orbitals

\[
\begin{array}{llll}
1s & 2s & 2p \\
\end{array}
\]

Which element is this?

\(1s^22s^22p^4\)
To write spdf notation, read the periodic table from left to right, row by row, and fill in with e- starting from the lowest energy orbital available! (this is Aufbau principle)

Anomalies...

• Some exceptions to Hund’s rule occur for the transition elements, as 4s and 3d orbitals are very close in energy.
• Occurs in f block elements as well
Exceptions to the rule

A $d$ subshell that is half-filled or full (i.e., 5 or 10 electrons) is more stable than the $s$ subshell of the next shell.

This is because it takes less energy to maintain an electron in a half-filled $d$ subshell than a filled $s$ subshell. For instance, copper (atomic number 29) has a configuration of $[\text{Ar}]4s^1\ 3d^{10}$ NOT $[\text{Ar}]4s^2\ 3d^9$ as one would expect.

Chromium (atomic number 24) has a configuration of $[\text{Ar}]4s^1\ 3d^5$, not $[\text{Ar}]4s^2\ 3d^4$. $[\text{Ar}]$ : configuration for argon.