Quantum mechanics and electron structure

- The missing link in Bohr’s model was the quantum nature of the electron
- Quantum mechanics yields a viable model for electronic structure in all elements
- Quantum mechanics replaced the particle by the wave
- The extent to which it is physical reality or an abstract mathematical model remains a fascinating, complex and unresolved argument
Learning objectives

- Describe the quantum numbers and predict allowed values
- Describe properties of atomic orbitals
The Quantum Mechanics

- Schrödinger's wave equation:
  \[ \hat{H} \Psi = E \Psi \]

- Obtain *orbital* picture of the electrons
  - P.S. the electrons don’t “orbit”

- Electrons are not particles with precise location, but waves with probability of being in some region of the atom – the orbital

- This result impossible with the *classical* mechanics of Newton which is based on linear forces between particles
Wave functions and probability

- Solutions to the Schrödinger equation are wave functions ($\Psi_i$)
- $\Psi_i^2$ is a measure of the probability of finding the electron in space
- In the atomic orbital $\int \Psi_i^2 \, dV = 1$
- Orbitals are described by quantum numbers ($n, l, m_l$)
Probability density and radial distribution function

- **Probability density:** \( \psi_i^2 \)
  - Probability per unit volume
  - Approaches infinity at \( r = 0 \)

- **Radial distribution function:** Total radial probability at radius \( r = \) Probability per unit volume \( \times \) volume of shell at \( r \)
  - Goes through a maximum
  - Goes to 0 at \( r = 0 \)
The quantum numbers:
Principle quantum number $n$

- Determines size and energy of orbital
- Positive integer:

$n = 1, 2, 3, \ldots$
Angular momentum quantum number $l$

- Defines shape of the orbital
- Integer that has all values between 0 and $(n - 1)$
  - For $n = 1$, $l = 0$
  - For $n = 2$, $l = 0$ or 1
  - For $n = 3$, $l = 0$, 1 or 2
- For historic reasons associated with spectroscopy $l$ values are described by letters:
  - $l = 0$ ($s = \text{sharp}$);
  - $l = 1$ ($\rho = \text{principal}$);
  - $l = 2$ ($d = \text{diffuse}$);
  - $l = 3$ ($f = \text{fundamental}$)
Magnetic quantum number $m_l$

- Defines the spatial orientation of the orbitals.
- For given value of $l$, $m_l$ has integer values from $-l$ to $+l$.
- There are $2l + 1$ different spatial orientations for given $l$.

- $l = 0$, $m_l = 0$ (total 1)
- $l = 1$, $m_l = -1, 0, 1$ (total 3)
- $l = 2$, $m_l = -2, -1, 0, 1, 2$ (total 5)
## Hierarchy of the quantum numbers

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>$m_l$</th>
<th>Orbital notation</th>
<th>No of orbitals in subshell</th>
<th>No of orbitals in shell (same $n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1s</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2s</td>
<td>1</td>
<td>4</td>
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<tr>
<td>1</td>
<td>-1</td>
<td>-1,0,1</td>
<td>2p</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>3s</td>
<td>1</td>
<td>9</td>
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<tr>
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<td>-1</td>
<td>-1,-1</td>
<td>3p</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
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<td>-2</td>
<td>-2,-1,0,1,2</td>
<td>3d</td>
<td>5</td>
<td>9</td>
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<tr>
<td>4</td>
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<td>0</td>
<td>4s</td>
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<td>16</td>
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<tr>
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<td>-1,0,1</td>
<td>4p</td>
<td>3</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>-2</td>
<td>-2,-1,0,1,2</td>
<td>4d</td>
<td>5</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>-3</td>
<td>-3,-2,-1,0,1,2,3</td>
<td>4f</td>
<td>7</td>
<td>16</td>
</tr>
</tbody>
</table>
Sally sells subshells...

- All orbitals with same $n$ value form a **shell** (level)
  - Orbitals in the shell have roughly same energy and size

- All orbitals with same $n$ and $l$ value form a **subshell** (sublevel)

- We will relate the shells and subshells to the periodic table
Orbital energies are (filthy) degenerate (same energy) in H only

A) Hydrogen

B) Multielectron atom
Meet the orbitals

The Orbitron: a gallery of atomic orbitals and molecular orbitals
Getting from the orbitals to the elements

- All elements have the same set
- Atomic number dictates how many are filled – how many electrons are added
- Filling orbitals follows a fixed pattern: lowest energy ones first
- But need to know... how many electrons in an orbital?
Electron spin and the fourth quantum number

The property of electron spin was deduced from splitting of beam of Ag atoms in magnetic field.

Conceptually we can describe it as a spinning magnetic: clockwise or anticlockwise - but this is a classical picture of a quantum-mechanical phenomenon.
Spin angular momentum quantum number $s (m_s)$

- $S (m_s) = = \frac{1}{2}$ or $- \frac{1}{2}$

Pauli Exclusion Principle:
- No two electrons can have the same four quantum numbers

Each electron has a unique identifying code of four quantum numbers

Consequence for orbital filling:
- Only two electrons per orbital