In the late 19th century, a Russian Chemist, Dmitri Mendeleev discovered that when the elements are ordered according to their atomic weight, they organize themselves so that their chemical properties "repeat" in periods. This led to the famous "Periodic Table of the Elements." Some 50 years later, the explanation of these periods began to become clear with the application of Schrödinger's wave equations to atomic structure.
The key to the periodic table lies in the way electron waves can fit into the "box" defined by the attractive Coulomb potential of the nucleus. For a hydrogen atom this potential is

\[ U(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \]

The specific form of the electron waves that can form in an atom are parameterized by a set of "QUANTUM NUMBERS". In the case of a particle in a three-dimensional box, there were three quantum numbers \( n_x = 1, 2, 3 \) etc., \( n_y = 1, 2, 3 \ldots \) & \( n_z = 1, 2, 3 \ldots \). Similarly for the hydrogen atom there are three quantum numbers.
They are labelled \( n, \ell, \text{ and } m_\ell \). These are as follows

\[
\begin{align*}
  n &= 1, 2, 3, \ldots & \text{Principal quantum number} \\
  \ell &= 0, 1, \ldots, n-1 & \text{Orbital quantum number} \\
  m_\ell &= -\ell, -\ell+1, \ldots, \ell-1, \ell & \text{Magnetic quantum number}
\end{align*}
\]

To these we will later add the spin angular momentum quantum number \( s_z = \pm \frac{1}{2} \). Remarkably, these quantum numbers are closely related to Mendeleev's table. In other words, the waves of an electron about an atom determine chemistry.

To understand how this works, we must first go back and look at the quantum models for the atom—the historical (and educational) Bohr atom, and the Schrödinger model of the atom.
39.5  **THE HYDROGEN ATOM.**

- Bohr Model and spectral lines
- Schrödinger wavefunction
- \( n=1 \) & \( n=2 \) wavefunctions

**i) THE BOHR MODEL**

An early quantum model of the atom.

Led to important insights (quantized energy levels) and later de Broglie's hypothesis that electrons are matter waves. Fortuitously gave the right energy levels

\[
2\pi r = n\lambda \quad \text{(de Broglie)}
\]

\[
\Rightarrow \frac{p}{\lambda} = \frac{hn}{2\pi r} = \frac{\hbar}{r} n
\]

\[
\Rightarrow rp = mvr = \frac{L}{\hbar} = n\hbar
\]

Bohr's angular momentum quantization
The total energy is

\[ E = \frac{1}{2} mv^2 + \left( -\frac{\frac{e^2}{4\pi\epsilon_0}}{r} \right) \]

Now since \( mvr = h = nk \) \( \Rightarrow \) \( \frac{1}{2} mv^2 = \frac{1}{2} \left( \frac{mvr}{r^2} \right)^2 = \left( \frac{nk}{2mr^2} \right)^2 \)

\[ E = \frac{n^2 \frac{h^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}}{1} \]

The radius will adjust to minimize the energy, so that

\[ \frac{\delta E}{\delta r} = 0 = -\left( \frac{nk}{mr^2} \right) + \frac{e^2}{4\pi\epsilon_0 r^2} = 0 \quad \Rightarrow \quad r = n^2 \left( \frac{\frac{h^2}{4\pi\epsilon_0}}{me^2} \right) \]

\[ = n^2 a \]

Where

\[ a = \frac{h^2}{4\pi\epsilon_0 me^2} = \frac{\frac{h^2}{me^2}}{\text{Time}^2} = 5.291 \times 10^{-10} \text{m} = 52.92 \text{pm} \]

(Alternatively, we could have set \( \frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2} \), then gotten

\[ \left( \frac{mvr}{mr^2} \right) = \left( \frac{nk}{mr^2} \right) = \frac{e^2}{4\pi\epsilon_0 r^2} \quad \Rightarrow \quad r = n^2 a \text{ again} \)
Since \( \frac{e^2}{4\pi\varepsilon_0 r} = \left(\frac{\hbar}{mr}\right)^2 \), it follows that

\[
E_n = -\frac{1}{2} \left( \frac{e^2}{4\pi\varepsilon_0 \alpha} \right) \times \frac{1}{n^2}
\]

\[
E_n = -\left( \frac{m_e e^4}{8\varepsilon_0 \hbar} \right) \times \frac{1}{n^2}, \quad n = 1, 2, 3, \ldots
\]

\[
E_n = -\frac{2.18 \times 10^{-18} \text{J}}{n^2} = -13.61 \text{eV}
\]

Energy levels of the hydrogen atom.

**The Hydrogen Spectrum**

\[
R = \frac{m_e e^4}{8\varepsilon_0 h^2 c} = 1.097 \times 10^7 \text{m}^{-1}
\]

"Rydberg Const"
Schrödinger Equation for the H-Atom

\[
\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + \frac{2m}{\hbar^2} \left( E + \frac{e^2}{4\pi\varepsilon_0 r} \right) \psi = 0
\]

3 dimensional kinetic Energy

\[U(r) = -\frac{e^2}{4\pi\varepsilon_0 r}\]

"electron in a Coulomb box"

The solution of the Schrödinger equation for the H-atom \(\psi_{n,\ell, m_s}\) depends on three quantum numbers

| \(n\) | principle quantum number | 1, 2, 3 |
| \(\ell\) | orbital quantum number | 0, 1, 2, ... \(n-1\) |
| \(m\) | Orbital magnetic q. no | \(-\ell, -\ell+1, 2-\ell, \ldots\) |
Wave function of the H-atom's ground state

\[ \psi(r) = \frac{1}{\sqrt{\pi a^3/2}} e^{-r/a} \]

solution of 3D Schrödinger equation

\[
\left( \frac{\text{Probability of detecting}}{\text{in volume } dV} \right) = \left( \frac{\text{probability of density } \psi^2(r)}{\text{at radius } r} \right) \times \text{volume } dV
\]

\[
= \int_0^{2\pi} \int_0^\infty \int_0^\infty 4\pi r^2 \psi^2(r) dr d\theta d\phi
\]

\[
= \int_0^\infty \psi^2(r) dr = \frac{4}{a^3} e^{-2r/a} r^2 dr
\]

\[
= P(r) dr
\]

\[
P(r) = \text{radial probability density} = \frac{4}{a^3} r^2 e^{-2r/a}
\]

Radial problem.

The probability of detecting an electron between radius \( r \) and \( r + dr \)

is then

\[
= \int_{r}^{r+dr} P(r) dr
\]

Note that \( \int_0^\infty dr P(r) = 1 \).

Volume probability density around nucleus.

"Fuzzy ball with no hint of orbits."
Hydrogen States with $n=2$

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>$m_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Note that as $n$ becomes large, one can make out the semiclassical orbits.
Example

The ground-state wavefunction of Hydrogen is

\[ \Psi_{2s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \]

\[ a_0 = \text{Bohr radius} = 5 \times 10^{-10} \text{m}. \]

a) Sketch the radial probability distribution function \( P(r) \)

b) Calculate the probability that the electron is more than one Bohr radius from the atom.

\[ P(r) \, dr = \text{probability inside shell between } r \text{ & } r + dr \]

\[ = |\Psi(r)|^2 \, dV \]

\[ = \left( \frac{1}{\pi a_0^3} e^{-2r/a_0} \right) 4\pi r^2 \, dr \]

\[ P(r) = \frac{4 \, r^2}{a_0^3} e^{-2r/a_0} \]
b) \[ P(r > a_0) = \text{area under curve with } r > a_0 \]

\[
= \int_{a_0}^{\infty} dr \, P(r)
\]

\[
= 4 \int_{a_0}^{\infty} dr \, \frac{r^2}{a_0^3} e^{-2r/a_0}
\]

\[
x = r/a_0 \quad \frac{dr}{a_0} = dx \quad \frac{r^2}{a_0^2} = x^2
\]

\[
P(r > a_0) = 4 \int_{1}^{\infty} dx \, x^2 e^{-2x} = 4 \left[ \left. \left( -\frac{x^3}{2} - \frac{x}{2} - \frac{1}{4} \right) e^{-2x} \right|_{1}^{\infty} \right]
\]

\[
= 5 e^{-2} = 0.677
\]
40.1 KEY PROPERTIES OF ATOMS

- Stable  The atoms in our world have survived for billions of years!

- Atoms combine with one another  They slide together to form molecules and stack together to form rigid solids.

- Atoms are mostly empty space  But you can stand on a floor without falling through it!

B. Periodicity of the Periodic Table

Chemistry & ionization energies depend periodically on $Z = \# \text{ of protons in the nucleus.}$

![Periodic Table Diagram]

All of this can be understood using Quantum Mechanics.
C. **Atoms Emit & Absorb Light**

\[ h\nu = E_{\text{high}} - E_{\text{low}} \]

D. **Atoms Have Angular Momentum and Magnetism**

\[ \vec{L} = m\vec{r} \times \vec{\nu} \quad \text{Angular Momentum} \]

\[ \vec{m} = i\vec{A} \quad \text{Magnetic dipole} \]

Because the electron is negatively charged, the magnetic dipole points in the **opposite** direction to the angular momentum.

Einstein de Haas Experiment.
The quantum numbers of the H atom also apply to electrons in more complex, multi-electron atoms.

<table>
<thead>
<tr>
<th>Quantum No</th>
<th>Symbol</th>
<th>Selection Rules</th>
<th>Related to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principal</td>
<td>n</td>
<td>1, 2, 3...</td>
<td>Distance from nucleus</td>
</tr>
<tr>
<td>Orbital</td>
<td>l</td>
<td>0, 1, 2, ... (n-1)</td>
<td>Orbital angular momentum</td>
</tr>
<tr>
<td>Orbital Magnetic</td>
<td>ml</td>
<td>0, ±1, ±2, ..., ±l</td>
<td>z-component of ( l )</td>
</tr>
<tr>
<td>Spin</td>
<td>s</td>
<td>( \frac{1}{2} )</td>
<td>Spin angular momentum</td>
</tr>
<tr>
<td>Spin Magnetic</td>
<td>( m_s )</td>
<td>( ±\frac{1}{2} )</td>
<td>z-component of ( l )</td>
</tr>
</tbody>
</table>

Schrödinger's eqn. tells us that the magnitude \( \ell \) and the z-component of \( \ell \) are quantized.

\[
\ell = \sqrt{\ell (\ell+1)} \hbar \quad (\ell = 1, 2, 3, \ldots)
\]

where \( \ell < n \), the principal quantum number while

\[
\ell_z = m_e \hbar \quad (m_e = 0, \pm 1, \pm 2, ..., \pm \ell)
\]

\[
\cos \theta = \ell_z / \ell
\]

( semiclassical angle)
e.g. How many quantum states of the H atom are there with \( n = 3 \) ?

<table>
<thead>
<tr>
<th>( n )</th>
<th>( l )</th>
<th>( m_l )</th>
<th>( m_s )</th>
<th>( n_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>( \pm \frac{1}{2} )</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-1,0,1</td>
<td>( \pm \frac{1}{2} )</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>-2,-1,0,1,2</td>
<td>( \pm \frac{1}{2} )</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>18</strong></td>
</tr>
</tbody>
</table>

This is the number of elements in the third row of the periodic table.
Magnetic Dipole Moment

Classically
\[ \vec{L} = \vec{r} \times \vec{p} \]
\[ m = \vec{L} \cdot \vec{r} \]

\[ i = \frac{e}{T} = \frac{ev}{2\pi r} \Rightarrow iA = \frac{ev}{2\pi r} \pi r^2 = \frac{e}{2} \]
\[ = \frac{e}{2\pi} \nu r \]

\[ L = m \nu r \]

\[ \Rightarrow \mu = iA = \frac{e L}{2m} \]

\[ \Rightarrow \mu_{\text{orb}} = -\frac{e L^2}{2m} \]

\[ \mu_{\text{orb}} = -me \frac{eK}{2m} = -meM_B \]

Where

\[ M_B = \frac{eK}{4\pi m} = \frac{e^2}{2m} = 9.274 \times 10^{-10} \text{ J} \]

Bohr Magnetron
G. Spin Angular Momentum & Magnetic Moment

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

\[ S_z = m_s \hbar \]

\[ m_s = \pm \frac{\sqrt{s(s+1)}}{2} \] "Half Integer"

\[ M_s = -\frac{e}{\hbar} \frac{S}{n} \]

\[ M_s = -2m_s \mu_B \]

An electron with \( m_s = \frac{1}{2} \) has

\[ M_{s, z} = -\mu_B \]

In other words, an electron carries one Bohr magneton of magnetic moment.