### Atomic Structure

**Chapter 8**

#### Periodic Table of Elements

<table>
<thead>
<tr>
<th>Period</th>
<th>Group 1 (IA)</th>
<th>Group 2 (IIA)</th>
<th>Group 13 (IIIA)</th>
<th>Group 14 (IVA)</th>
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</table>

*Legend - click to find out more...*

- **H** - gas
- **Li** - solid
- **Be** - liquid
- **Na** - gas
- **Mg** - gas
- **Ca** - gas
- **Sr** - gas
- **Ba** - gas
- **Ra** - gas
- **Ac** - gas
- **Th** - gas
- **Pa** - gas
- **U** - gas
- **Pu** - gas
- **Am** - gas
- **Cm** - gas
- **Bk** - gas
- **Cf** - gas
- **Es** - gas
- **Fm** - gas
- **Md** - gas
- **No** - gas
- **Lr** - gas
- **Rf** - gas
- **Db** - gas
- **Sg** - gas
- **Bh** - gas
- **Hs** - gas
- **Mt** - gas
- **Ds** - gas
- **Rg** - gas

**Non-Metals**

**Transition Metals**

**Rare Earth Metals**

**Halogens**

**Alkaline Metals**

**Alkaline Earth Metals**

**Other Metals**

**Inert Elements**
Overview

To understand atomic structure requires understanding a special aspect of the electron - spin and its related magnetism - and properties of a collection of identical quantum particles.

The magnetic properties of electrons were discovered in studies of atoms in which the electric charge of the electron is neutralized.

Pauli invented the Exclusion Principle which requires electrons occupy different states, which together with an understanding of hydrogen is the key to atomic structure.
Magnetic dipoles

Recall a current loop generates a magnetic field. The orientation and strength of the field is at large distances that of a point magnetic dipole characterized by

\[ \vec{\mu} = iA\hat{n} = \text{magnetic dipole moment} \]
Orbital magnetic moment

For a circular orbit or radius \( r \), period \( T \), and velocity \( v \), the time average magnetic dipole moment is related to the orbital angular momentum

\[
\mu = iA = \frac{q}{T} (\pi r^2)
= q \frac{v}{2\pi r} \pi r^2 = \frac{q}{2m} mvr
= \frac{q}{2m} L
\]
Magnetic torque

A magnetic moment in a uniform external magnetic field $\mathbf{B}$ is subject to a torque

$$\mathbf{\tau} = \mathbf{\mu} \times \mathbf{B}$$

Work is required to alter the angle between the magnetic moment and external field and the magnetic potential energy is

$$U = -\mathbf{\mu} \cdot \mathbf{B}$$
Bohr magneton

The z component of orbital angular momentum of an atomic electron is a multiple of Planck’s constant and the corresponding magnetic moment is

\[ \mu_B = \frac{e}{2m_e} \hbar \]
\[ = 9.27 \times 10^{-24} J/T \]
\[ = 5.788 \times 10^{-5} eV/T \]

The magnetic moment is expressed in terms of the associated magnetic energy. Laboratory magnetic fields are at most a few T and magnetic energy is small compared to electric binding energy.
Normal Zeeman Effect

Consider the atomic electron in hydrogen. In a s-state like the ground state, l=m=0 - there is no magnetic moment, no magnetic energy.

For a p-state, l = 1 and m= +1,0,-1. These states have orbital magnetic moment

$$\mu_z = -\mu_B, 0, +\mu_B$$

Note sign: the charge of the electron is -e
Normal Zeeman Effect

In an external B field, the magnetic energy shifts of the $m = +1, 0, -1$ by

$$\Delta E = \mu_Z B = -\mu_B B, 0, +\mu_B B$$

Spectral lines are expected to split.
Normal Zeeman Effect

Very high resolution spectroscopy shows evidence for the energy shifts due to the (diamagnetic) magnetic moments of atomic electrons.

The effect on the wave functions is negligible, just a precession.
Electron Spin

Additional magnetic effects reveal a structure of sorts to an electron. The electron behaves a bit like a tiny spinning charged sphere with corresponding spin angular momentum and magnetic moment.
Electron Spin

The electron spin and magnetic moment are however NOT any value anticipated classically.

\[ |\vec{S}| = \hbar \sqrt{s(s+1)} \]
where \( s = 1/2 \)
and \( m_s = +\frac{1}{2}, -\frac{1}{2} \)
\[ \vec{\mu}_e = g \frac{q}{2m_e} \vec{S} \]
with
\[ g \approx 2 \]

“Half integer” spin and a g-factor of 2
Stern-Gerlach Experiment

The magnetic moment of a free electron is difficult to observe because the electric and magnetic forces due to the electronic charge are large.

Evidence appeared in experiments with neutral atoms.
Stern-Gerlach Experiment

A beam of silver atoms is directed through an inhomogeneous (not uniform) magnetic field and the deflections observed.

A neutral atom is deflected if it has a magnetic moment.
Stern-Gerlach Experiment

Think of a magnetic dipole as a north pole and south pole. In an inhomogeneous field, the pole in the stronger part of the B field suffers a larger force so the net force depends on orientation of the magnetic moment.
Stern-Gerlach Experiment

Atoms are deflected not through a smooth distribution as would be expected for random classical orientations, but into two distinct bands corresponding to two opposite magnetic moment values.
Stern-Gerlach Experiment

Stern boldly deduced that the electron behaves in effect as if it carries bi-valued spin angular momentum and magnetic moment:

$$|\vec{S}| = \hbar \sqrt{s(s + 1)}$$

where $s = 1/2$

and $m_s = +\frac{1}{2}, -\frac{1}{2}$

$$\vec{\mu}_e = g \frac{q}{2m_e} \vec{S}$$

with

$g \approx 2$

(The angular momentum and moments of all but one electron cancel in pairs. )
The Dirac equation

The spin of the electron was explained by Paul Dirac who extended the Schrödinger equation to the relativistic case.

A photon is a quantum of a wave field of entangled E and B fields (six real wave fields). The photon carries energy, momentum and spin angular momentum depending on polarization.

A relativistic electron is the quantum of four entangled complex matter waves (eight real wave fields) and carries energy, momentum, spin angular momentum depending on polarization, and (unlike the photon) charge and effective magnetic moment.
Photon polarization

A right or left handed electromagnetic wave is one in which the electric field vector tip traces out a right or left handed screw.

Such a wave is a combination of a wave linearly polarized along one axis plus another polarized along an orthogonal axis and out of phase.

The wave and associated photons carry angular momentum aligned with the direction of propagation.

http://www.optics.arizona.edu/jcwyant/JoseDiaz/Polarization-Circular.htm
Pauli Equation

In the non-relativistic limit (which does not exist for photons), two of Dirac’s four complex fields are non-vanishing and the equations for an electron in a magnetic field are:

\[
\begin{align*}
    i\hbar \frac{\partial}{\partial t} \psi_1 &= -\frac{\hbar^2}{2m_e} \nabla^2 \psi_1 + \frac{e\hbar}{m_e} (B_z \psi_1 + (B_x + iB_y) \psi_2) \\
    i\hbar \frac{\partial}{\partial t} \psi_2 &= -\frac{\hbar^2}{2m_e} \nabla^2 \psi_2 + \frac{e\hbar}{m_e} (-B_z \psi_2 + (B_x - iB_y) \psi_1)
\end{align*}
\]

The last terms on the right couple the two wave functions together so the amount of each depends on time. These are the electron equivalent of L and R circular polarization states of light.
Pauli Equation

If we choose the z-axis along B, the two wave functions are independent but offset in energy.

\[ i\hbar \frac{\partial}{\partial t} \psi_1 = -\frac{\hbar^2}{2m_e} \nabla^2 \psi_1 + \frac{e\hbar}{m_e} B_z \psi_1 \]
\[ i\hbar \frac{\partial}{\partial t} \psi_2 = -\frac{\hbar^2}{2m_e} \nabla^2 \psi_2 - \frac{e\hbar}{m_e} B_z \psi_2 \]

In general, the two wave functions are linked. Spin polarization represents the amount of each. Mixtures are the equivalent of elliptically polarized light.
Zeeman effect with spin

The total angular momentum of an atomic electron is

\[ \vec{J} = \vec{L} + \vec{S} \quad |\vec{J}| = \hbar \sqrt{j(j+1)} \]

\[ m_j = -j, \ldots, +j \]

The total magnetic moment of an atomic electron is

\[ \vec{\mu} = \vec{\mu}_L + \vec{\mu}_S = \frac{-e}{2m_e} [\vec{L} + g \vec{S}] \]

The total magnetic energy of an atomic electron is

\[ U = -\vec{\mu} \cdot \vec{B} = \frac{e}{2m_e} B [L_z + g S_z] \]

\[ = \mu_B B [m_l + m_s] \]
Including spin, we expect twice the number of states and a corresponding multiplicity of lines in spectroscopy.
Spin-Orbit Interaction

Complication:

The orbital motion and spin are coupled. The spin magnetic moment likes to be aligned with the magnetic field resulting from the orbital motion of the proton in the electron rest frame.
Spin-Orbit Interaction

The magnetic field of the proton in the electron’s instantaneous rest frame is according to relativity

\[ B = \frac{v \times E}{c^2} \]

and \( E \sim \frac{r}{|r|^3} \) so

\[ B \sim r x v \sim r x p / m \sim L \]

and the spin magnetic energy is

\[ U \sim S \cdot L \]
Total angular momentum

In the absence of spin orbit coupling, $\mathbf{L}$ and $\mathbf{S}$ are each conserved. The states of sharp energy are characterized by $l, m_l, s, m_s$. The spin-orbit coupling produces mixtures of different $m_l$ and $m_s$ with sharp energy.

Total angular momentum is conserved and the states of sharp energy are states of sharp total angular momentum

$$\vec{J} = \vec{L} + \vec{S}$$
Addition of angular momenta

The values of a sum of angular momenta like \( J = L + S \) are obtained by adding the various values of the \( z \) components.

\[
\begin{align*}
j &= l + s \\
l + s - 1 & \quad \ldots \\
l - s + 1 & \\
l - s & 
\end{align*}
\]

Vector model
Vector model

Example: Combining 3 orbital states of \( l=1 \) and \( m_l = +1,0,-1 \) with 2 spin states of \( s=1/2 \) and \( m_s = +1/2, -1/2 \) yields 6 states which have the following values for total angular momentum and z component:

\[ j = 3/2, m_j = +3/2, +1/2, -1/2, -3/2 \]
\[ j = 1/2, m_j = +1/2, -1/2 \]
Spectroscopic notation

The spin orbit interaction implies that the sharp energy states of the electron in hydrogen are

$\nu' \ L' \ J' =$

- $1S_{1/2}$, The two 1s ground states are $j=1/2$
- $2S_{1/2}$, The two 2s states are $j=1/2$
- $2P_{3/2}$, The six 2p states form two groups, four are $j=3/2$, two are $j=1/2$
- $2P_{1/2}$
Spin-orbit splitting in hydrogen

Note two groups of 2p states with energy different from the 2s!

\[ \Delta E \approx 2\mu B = 5 \times 10^{-5} \text{ eV} \]

The spin orbit splitting is only 5e-5 eV yet important!
Sodium has a core of 10 electrons and an outer electron typically in the 3s. Excitation and de-excitation to 3p states split by the spin-orbit interaction yields two slightly different yellow wavelengths.
Two particles

Two spinless particles correspond to two matter waves. Each obeys a Schrodinger equation. (For relativistic electrons, two Dirac equations!)

\[ i\hbar \frac{\partial}{\partial t} \psi_1(x_1) = -\frac{\hbar^2}{2m_1} \nabla^2 \psi_1(x_1) + V \psi_1(x_1) \]
\[ i\hbar \frac{\partial}{\partial t} \psi_2(x_2) = -\frac{\hbar^2}{2m_2} \nabla^2 \psi_2(x_2) + V \psi_2(x_2) \]

These two waves are NOT the two in Pauli’s equation!
Two particle wave function

Cross multiply and combine into a product wave function

\[ i\hbar \psi_2 \frac{\partial}{\partial t} \psi_1 = -\frac{\hbar^2}{2m_1} \psi_2 \nabla_1^2 \psi_1 + \psi_2 V_1 \psi_1 \]
\[ i\hbar \psi_1 \frac{\partial}{\partial t} \psi_2 = -\frac{\hbar^2}{2m_2} \psi_1 \nabla_2^2 \psi_2 + \psi_1 V_2 \psi_2 \]
\[ i\hbar \frac{\partial}{\partial t} (\psi_1 \psi_2) = -\frac{\hbar^2}{2m_1} \nabla_1^2 (\psi_1 \psi_2) - \frac{\hbar^2}{2m_2} \nabla_2^2 (\psi_1 \psi_2) \]
\[ + (V_1 + V_2) \psi_1 V \psi_2 \]

\[ i\hbar \frac{\partial}{\partial t} \psi(x_1, x_2) = -\frac{\hbar^2}{2m_1} \nabla_1^2 \psi(x_1, x_2) - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi(x_1, x_2) \]
\[ + (V_1 + V_2) \psi(x_1, x_2) \]
\[ \psi(x_1, x_2) \equiv \psi_1 \psi_2 \]
Identical Particles

If two quantum particles are identical (equal masses, potential energy symmetric under $1 \leftrightarrow 2$, and interacting, the combined wave function has a symmetric and anti-symmetric part

\[ \psi_S(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi(x_1, x_2) + \psi(x_2, x_1)] \]
\[ \psi_A(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi(x_1, x_2) - \psi(x_2, x_1)] \]

Identical particles do not exist classically, just similar particles. Identical means if you look away then back, you can not tell in principle if the two are interchanged.
Pauli Principle

A new principle: (a rose is a rose is a rose)

Electrons exist exclusively in quantum states anti-symmetric under interchange of particle labels. For states of spin and coordinate wave A and B,

$$\psi_{A}(1, 2) = \frac{1}{\sqrt{2}} [\psi_{1}^{A}\psi_{2}^{B} - \psi_{2}^{A}\psi_{1}^{B}]$$

This vanishes identically if A=B. Two electrons can not be in the same quantum state!
Bosons and Fermions

Generalization (Bose, Einstein, Fermi):

All collections of identical spin 1/2 particles/systems exist only in antisymmetric states. These are called fermions. Examples are electrons, protons, neutrons. More generally, half integer spin particles (S=1/2,3/2,5/2…) are fermions.

All collections of identical integral spin (0,1,2…) particles/systems exist only in symmetric states. These are called bosons. Examples are deuterons (S=1), pions (S=0), photons (S=1).
In scattering of non-identical particles, the amplitudes (a) and (b) for angle theta and pi - theta are different. For identical bosons/fermions, the amplitude is proportional to (a) +/- (b)! The probablilty is proportional to |a|^2 + |b|^2 +/-(a) (b)^* +/-(a)^*(b)
# Periodic Table

## Periodic Table of Elements

<table>
<thead>
<tr>
<th>IA</th>
<th>IIA</th>
<th>IIA</th>
<th>IIIA</th>
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<td>02</td>
<td>03</td>
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</tbody>
</table>

* Lanthanide Series
+ Actinide Series

### Legend - click to find out more...

- **H - gas**
  - Non-Metals
  - Alkali Metals

- **Li - solid**
  - Transition Metals
  - Alkali Earth Metals

- **Br - liquid**
  - Rare Earth Metals
  - Other Metals

- **Tc - synthetic**
  - Halogens
  - Inert Elements

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**October 09**

**Modern Physics**
Atomic structure

Consider assembling an atom of atomic number Z. The first electron goes into a 1s state for that Z. The 1s state partially shields the nucleus. The 2nd goes into a 1s state and the orthogonal spin state. (Ignore e-e repulsion) These partially shield the nucleus. The 2s state has smaller radius on average than the 2p so lower energy. The 3rd and 4th electrons occupy the 2s. The next 6 electrons occupy 2p states. The next two occupy the 3s...

## Periodic Table

<table>
<thead>
<tr>
<th>Atom</th>
<th>1s</th>
<th>2s</th>
<th>2p</th>
<th>Electron configuration</th>
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<tbody>
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<td>↑</td>
<td>↑</td>
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Qualitative properties

Adding electrons to a partially empty shell leads to increasing stability, ever larger ionization energy.

A single electron in a shell is relatively energetic, easy to remove or exchange, and the atom relatively reactive.
# Electronic Configurations

## Table 9.2 Electronic Configurations of the Elements

<table>
<thead>
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<th>Z</th>
<th>Symbol</th>
<th>Ground Configuration</th>
<th>Ionization Energy (eV)</th>
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Ionization Energy

![Graph showing ionization energy vs. atomic number for different elements. The graph displays the ionization energy (eV) on the y-axis and atomic number (Z) on the x-axis. Notable elements include He, Ne, Ar, Kr, Xe, Hg, and Rn. Peaks and valleys indicate variations in ionization energy across the periodic table.]
The X-ray spectra of the elements reveals the validity of the picture we have developed. If an inner shell electron is dislodged, an outer shell electron may make a transition to fill it producing an X-ray.
Moseley’s law

The inner shell energies in the cores of atoms behave as expected as functions of atomic number assuming partial shielding.