**Atomic Structure**

**Topics:**
- 7.1 Electromagnetic Radiation
- 7.2 Planck, Einstein, Energy, and Photons
- 7.3 Atomic Line Spectra and Niels Bohr
- 7.4 The Wave Properties of the Electron
- 7.5 Quantum Mechanical View of the Atom
- 7.6 The Shapes of Atomic Orbitals
- 7.7 Atomic Orbitals and Chemistry

**Standing Waves**

- Two or more points of zero amplitude
- Distance between consecutive nodes = \( \lambda / 2 \)
- Standing waves must have a distance between fixed ends = \( n \lambda / 2 \), where \( n \) is an integer.

**Standing Waves**

- Node
- Distance / cm
- Amplitude
- Displacement / cm

**Speed of light \((m \cdot s^{-1})\)**

\[
\begin{align*}
\text{Speed of light} &= 2.99792458 \times 10^8 \text{ m/s} \\
\mathbf{c} &= \mathbf{\lambda} \times \nu \\
\text{Wavelength (m)} &\quad \text{Frequency (s}^{-1}) \\
\text{(or Hz or 1/s)}
\end{align*}
\]
Example Problem (7.1):
The line shown here is 10cm long:

a) Draw a standing wave with one node between the ends. What is the wavelength of this wave?
b) Draw a standing wave with three evenly spaced nodes between the ends. What is its wavelength?
c) If the wavelength of the standing wave is 2.5cm, how many waves fit within the boundaries? How many nodes are there between the ends?

\[ \text{a) } 10 \text{cm} \quad \text{b) } 5 \text{cm} \quad \text{c) } \frac{10}{2.5} = 4 \text{ waves; 7 nodes} \]

Electromagnetic radiation is self-propagating (i.e. it doesn’t require a medium to travel through. It can travel through the vacuum of space.)

Example Problem (7.2):

a) Which color in the visible spectrum has the highest frequency? Which has the lowest frequency?
b) Is the frequency of the radiation used in a microwave oven higher or lower than that from a FM radio station broadcasting at 91.7MHz?
c) Is the wavelength of x-rays longer or shorter than that of ultraviolet light?

Answers:

a) Blue/violet has the highest frequency. Red has the lowest frequency (longest wavelength).
b) Microwaves are higher in frequency (shorter wavelength) than FM station 91.7MHz.
c) X-ray wavelengths are shorter (higher frequency) than that of UV light.

Max Planck (1900): Vibrations in atoms are quantized (i.e. Only certain vibrations with certain frequencies are allowed)
The Photoelectric Effect

**Assumption:** Energy is carried on the amplitude of a wave (as in classical waves).

**Prediction:** Since the amplitude of an EM wave correlates with the brightness of the light, light of high enough intensity irradiating a metal for a long enough period of time should be able to eject electrons from the surface of a metal.

**Reality:** It was the frequency of the light that determined whether or not electrons were ejected regardless of the time of irradiation. The brightness (amplitude) only determined how many were ejected per unit time once ejection started occurring.

Einstein (1905) incorporated Planck's equation with the idea that light had (massless) particle properties (photon). These photons are "packets" of energy where $E$ depends on the frequency of the photon ($E = h\nu$).

Example: A 60W, monochromatic laser beam gives off photons of wavelength 650nm. How long does it take for 2.5 moles of these photons to be given off?

Answer:

\[
E = \frac{hc}{\lambda} = \left(6.626 \times 10^{-34} \text{ Js}\right) \left(3.0 \times 10^8 \text{ m/s}\right) / 6.50 \times 10^{-7} \text{ m} = 3.06 \times 10^{-19} \text{ J/photon}
\]

\[
(3.06 \times 10^{-19} \text{ J/photon}) (6.022 \times 10^{23} \text{ photons/mol}) (2.5 \text{ mol}) = 4.60 \times 10^5 \text{ J}
\]

\[
4.60 \times 10^5 \text{ J} / (60 \text{ J/s}) = 7673.4 \text{ s} / (3600 \text{ s/hr}) = 2.13 \text{ hr}
\]
Example Problem (7.3):

Compare the energy of a mole of photons of orange light (625nm) with the energy of a mole of photons of microwave radiation having a frequency of 2.45GHz ($1\text{GHz} = 10^9\text{s}^{-1}$). Which has the greater energy? By what factor is one greater than the other?

Answer:

$$E = (6.626 \times 10^{-34} \text{Js})(3.00 \times 10^8 \text{m/s})/(6.25 \times 10^{-7} \text{m}) = 3.18 \times 10^{-19} \text{J}\,$$

$$E = (6.626 \times 10^{-34} \text{Js})(2.45 \times 10^9 \text{Hz}) = 1.623 \times 10^{-24} \text{J}\,$$

$$1.9 \times 10^{19} / 9.7 \times 10^{-1} = 1.96 \times 10^5$$
Example Problem (7.4)
Calculate the energy of the n=3 state of the H atom in a) joules per atom and b) kilojoules per mole.

\[ R_h = 2.179 \times 10^{-18} \text{ J/atom or } 1312 \text{kJ/mol} \]

Answer:
\[ E = -\frac{R_h}{n^2} = -2.179 \times 10^{-18} \text{ J/atom} / 3^2 = -1.86 \times 10^{-19} \text{ J} \]
\[ E = -1312 \text{kJ/mol} / 3^2 = -145.8 \text{kJ/mol} \]

Example Problem (7.5):
The Lyman series of spectral lines for the H atom occurs in the ultraviolet region. They arise from transitions from higher levels to n=1. Calculate the frequency and wavelength of the least energetic line in this series.

Answer:
\[ \Delta E = -\frac{R_h}{n^2} \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = -2.179 \times 10^{-18} \text{ J/atom} \left( 1 - \frac{1}{4} \right) = -1.634 \times 10^{-18} \text{ J} \]
\[ E = \frac{h \nu}{c} = \frac{1.634 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} = 2.46 \times 10^{15} \text{ Hz} \]
\[ \lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{2.46 \times 10^{15} \text{ Hz}} = 1.216 \times 10^{-7} \text{ m} = 121.6 \text{ nm} \]
Example:
Calculate the wavelength associated with a neutron having a mass of 1.675x10^-27 kg and a kinetic energy of 6.21x10^-24 J. (Recall that the kinetic energy of a moving particle is \( E = \frac{1}{2} mv^2 \).)

Answer:
\[
KE = \frac{1}{2} mv^2 = 6.21 \times 10^{-24} J = \frac{1}{2} (1.67 \times 10^{-27} \text{kg}) (v^2)
\]
\[
v = 2727.11 \text{ m/s}
\]
\[
\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-24} \text{Js})}{(1.67 \times 10^{-27} \text{kg})(2727.11 \text{ m/s})}
\]
\[
= 1.45 \times 10^{-10} \text{ m} = 1.45 \text{ angstroms} = .145 \text{ nm}
\]
The principal quantum number (n): This number is related to the overall energy of an orbital (roughly the average distance from the nucleus). The number n, can take on integer values n = 1, 2, 3, 4,...

The angular momentum (azimuthal) quantum number (l): (Subshell) This number is related to the shape of the sub-orbitals (i.e. shape of the 90% probability region) that an orbital may possess. The value of l can take on numbers from 0 to n-1

The magnetic quantum number (m_l): This number is related to the spatial orientation of the sub-orbital (subshell orbital). Its numbers range from m_l = -l...0...+l

The spin quantum number (m_s): This number relates to the spin orientation of an electron in a given orbital. The electron does not have a true "spin" in the classical sense, but is used to account for spectral lines that are produced in the presence of an external magnetic field. The spin quantum number can possess values of m_s = ±½. Therefore only 2 values are possible. (Covered in the next chapter)

With regard to the angular momentum quantum number, l, scientists have assigned letters that correspond to the numerical values that l can have. This comes from the days of spectroscopy (spectral analysis) and are as follows:

<table>
<thead>
<tr>
<th>Value of l</th>
<th>Corresponding Subshell Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>s (sharp)</td>
</tr>
<tr>
<td>1</td>
<td>p (principal)</td>
</tr>
<tr>
<td>2</td>
<td>d (diffuse)</td>
</tr>
<tr>
<td>3</td>
<td>f (fine)</td>
</tr>
</tbody>
</table>

For l equal to:

- 0 → s (sharp)
- 1 → p (principal)
- 2 → d (diffuse)
- 3 → f (fine)

For l equal to 4 and beyond the letters g, h, i,... and so on are used, skipping the letters that have already been used.

Table 7.1: Summary of the Quantum Numbers, Their Interrelationships, and the Orbital Information Considered

<table>
<thead>
<tr>
<th>Principal Quantum Number</th>
<th>Subshell Number</th>
<th>Magnetic Quantum Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>Number of Subshells</td>
<td>Values of m_l</td>
</tr>
<tr>
<td>n</td>
<td>n²</td>
<td>n² - n</td>
</tr>
<tr>
<td>(n²)</td>
<td>2n</td>
<td>2n²</td>
</tr>
</tbody>
</table>

Note the following:
- n = the number of subshells in a shell
- 2n² = total electrons possible in a shell

Interpretation of an s orbital

Middle Image: Plot of surface density (radial distribution plot) = Probability of finding an electron in a thin shell at a given distance from the nucleus.

Y-axis: Plot of \(4\pi r^2|\psi|^2\) in units of 1/distance

Maximum amplitude of electron wave at 0.0529nm.

The spherical surface (right image) is the 90% probability region (boundary surface)

p and d Orbitals, Nodal Surfaces and Spherical Nodes

p-orbital (left) and typical d-orbital (right)

Note that the whole shape is a single orbital
Surfaces (planes in these cases) that represent zero probability regions for electrons in those orbitals.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Number of Nodal Surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0</td>
</tr>
<tr>
<td>p</td>
<td>1</td>
</tr>
<tr>
<td>d</td>
<td>2</td>
</tr>
<tr>
<td>f</td>
<td>3</td>
</tr>
</tbody>
</table>