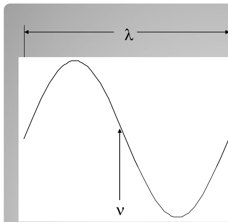
Quantum Chemistry

Light

- Electromagnetic radiation
- Waves
- Parts of the spectrum
  - Radio, microwave, IR
  - Visible
  - UV, X-rays, cosmic rays

Waves



- λ stands for wavelength
  - Measured in meters
- ν stands for frequency
  - Measured in s^{-1} or Hz

$$\lambda \nu = c = 2.998 \times 10^{8} \text{ m s}^{-1}$$

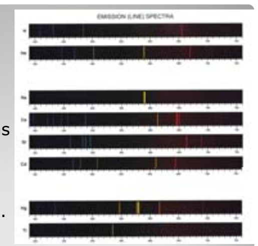
- c is the speed of light

Energy and waves

- Unlike water waves or sound waves, the energy of a light wave depends on the frequency of the wave.
- Planck proposed that: $E = nh\nu$
  - E is the energy
  - n is an integer
  - h is a constant called Planck's constant and is equal to 6.626×10^{-34} J s.

Light and atoms

- Emission spectra
  - Results when atoms absorb and then release energy
  - Classical physics cannot explain this.



Bohr and the atom

- Niels Bohr's explanation
  - The electron can have only particular energy values in the atom.
  - The emission spectrum results from transitions between these energy levels.
  - The energy of a given level is: $E_n = -\frac{R_H}{n^2}$
  - R_H is 2.180×10^{-18} J
  - n can only be positive integers

Bohr and the emission spectrum

- Applying what we know:
  - The emissions spectrum results from the energy emitted (as light) when an electron loses energy to drop from one energy level to another. We can state this mathematically as:

$$\Delta E = E_i - E_f = \left(-\frac{R_H}{n_i^2}\right) - \left(-\frac{R_H}{n_f^2}\right) = -\frac{R_H}{n_i^2} + \frac{R_H}{n_f^2} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

continued

- But we also know that energy is related to frequency which is related to wavelength.

$$E = h\nu \qquad \nu = \frac{c}{\lambda} \qquad E = \frac{hc}{\lambda}$$

$$\Delta E = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = \frac{hc}{\lambda} \qquad \frac{1}{\lambda} = \frac{R_H}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Explaining emission spectra

$$\frac{1}{\lambda} = \frac{R_H}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

- This equation is valid only for Hydrogen.
- n_f and n_i are integers (exact numbers).
- Slight modification needed to account for Hydrogen-like ions (ions with one electron).

Calculation

- What is the wavelength, in nm, of the light emitted when an electron drops from the 5th to the 2nd energy level?

Hydrogen-like ions

- These are ions with one electron
  - Li^{2+}, C^{5+}, O^{7+}, etc.
- We need a slight modification to take into account the higher nuclear charge

$$\frac{1}{\lambda} = \frac{Z^2 R_H}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

- Where Z is the atomic number.

Calculate

- The Helium ion undergoes a transition from n=5 to n=3, what is the wavelength of the emitted light?

A Step Beyond Energy Levels

- Quantum Mechanics
  - Mathematical representation of the microscopic world.
  - Not intuitive
  - Gives accurate predictions of experimental outcomes

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One of the predictions

- Quantum mechanics deals with the probability of finding a particular value, such as the position of an electron.
- When we solve the equations of QM we get numbers that are called quantum numbers

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Quantum numbers

- There are 4 quantum numbers that come out of the mathematics.
  - n – the principle quantum number – tells us which energy lever we are in. It can range from 1 to ∞.
  - l – the azimuthal quantum number – it can range from 0 to n-1. It tells us which sub-level we are in. The sub-levels are labeled with the letters s, p, d, and f.

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Quantum Numbers

- m_l – the magnetic quantum number – it can range from –l to +l. It tells us which orbital we are in.
- m_s – the spin quantum number – it has either the value +1/2 or -1/2. More on this one later.

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Energy levels and sub-levels

n value	Energy level	Available sub-levels
1	1	s
2	2	s, p
3	3	s, p ,d
4	4	s, p, d, f

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Energy levels and sub-levels

- This table makes sense when we look at the quantum numbers.
  - If n=1 then l can only be 0. That corresponds to what we call the s sub-level in the first energy level.
  - If n=2 then l can be 0 or 1. That corresponds to the s and p sub-levels in the second energy level.

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Sub-levels and orbitals

l value	sub-level	Number of orbitals	shape
0	s	1	spherical
1	p	3	dumb-bell
2	d	5	4-lobed + 1
3	f	7	8-lobed + 1

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Sub-levels and orbitals

- Again, it all makes sense with the quantum numbers.
  - If it's an s sub-level, then l = 0 and m_l is also 0 (it goes from –l to +l or -0 to +0, which is just 0). Because l has only one value, there is only one orbital.
  - If it's a p sub-level, then l = 1 and m_l is either -1, 0 or +1, which means there are 3 orbitals.

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What are orbitals?

- orbitals are mathematical constructs that help us to explain the behavior of electrons in atoms.
- According to QM, orbitals can hold at most two electrons (this is where the spin quantum number, m_s, comes in).
  - s orbital = 2 electrons (2 electrons in 1 orbital)
  - p orbitals = 6 electrons (2 in each of 3 sub-levels)
  - d orbitals = 10 electrons (2 in each of 5 sub-levels)
  - f orbitals = 14 electrons (2 in each of 7 sub-levels)

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Where are the electrons?

- The easy answer is "In the orbitals."
- But where is each electron in the atom?
  - The electron configuration tells us where they are.
  - What is an electron configuration?

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Electron configurations?

- We can get a clue to electron configurations by looking at the periodic table.

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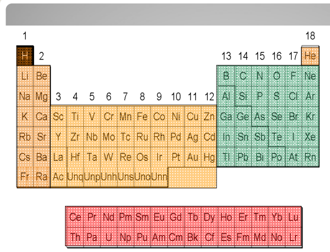
The periodic table



Why is the periodic table colored this way?

It gives us a clue to where the electrons are.

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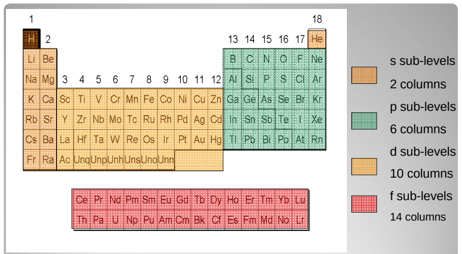
Electron configurations…



Electron configurations

- To create the electron configuration we just read across the periodic table.
  - H 1s^1
  - He 1s^2
  - C 1s^2 2s^2 2p^2
  - Fe 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6

Write electron configurations

- P
- Na
- Ru

Shorthand method

- Relies on noble gases
- Look at the EC for P and Ne
  - P 1s^2 2s^2 2p^6 3s^2 3p^3
  - Ne 1s^2 2s^2 2p^6
- The difference is in the outer energy level. Everything else is the same.
- We could then write the EC for phosphorus as
  - P [Ne] 3s^2 3p^3
  - This means use the EC for Neon plus the 3s^2 3p^3.

Use the Shorthand method

- Rh
- Ni
- Pm

Orbital Diagrams

- Related to EC's
- More specific for each electron
- Must take into account another electron property

New electron property

- Called spin and is from the spin quantum number, m_s.
  - a misnomer because the electron is not really spinning.
  - m_s can have values of +1/2 or -1/2 which are also called up and down

New rules

- Pauli Exclusion rule
  - No two electrons in the same orbital can have the same spin which basically means that no two electrons in an atom can have the same set of quantum numbers.
- Hund's rule
  - When two or more electrons have to go into two or more orbitals with the same energy (i.e., a set of p orbitals), they do so singly with the same spin until all the orbitals are occupied then they pair up.

Pauli's exclusion rule

- We cannot have two up electrons or two down electrons in an orbital.
- Allowed possibilities:
  - [↑↓]
  - [↑] (the electron could also be down)
  - [ ]

Hund's Rule

- Allowed possibilities (example assume 2 electron and 3 orbitals):
  - [↑][↑][ ]
  - [↑][ ][↑]
  - [ ][↑][↑]

Orbital Diagrams

- First find the EC
- Then set up the correct number of sub-levels for each sublevel in the EC
- Place the correct number of electrons into each sub-levels with the proper spin.

Orbital Diagrams

- Find the OD for Fe
  - EC
    - Fe $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$
  - Set up orbitals
    - [ ] [ ] [ ][ ][ ] [ ] [ ][ ][ ] [ ] [ ][ ][ ][ ][ ]
      1s 2s 2p 3s 3p 4s 3d
  - Fill in electrons
    - [↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑↓][↑][↑][↑][↑]
      1s 2s 2p 3s 3p 4s 3d
- Be sure to label the orbitals as shown here.

Write orbital diagrams (use the shorthand method)

- S
- Mo
- Gd

Periodic Properties

- Atomic radius
  - increases as we move down as group
  - decreases as we move across a period
- Ionization Energy (IE)
  - $A \rightarrow A^+ + e^-$
  - decreases as we move down a group
  - increases as we move across a period
- Electron Affinity Energy (EAE)
  - $A + e^- \rightarrow A^-$
  - increases as we move down a group
  - decreases as we move across a period