Atomic Structure

Continued..

Chemistry is just ~10eV electron Physics...

Building up larger atoms

- In multi-electron atoms the subshells and orbitals look very similar to hydrogen, but their energies are different because the extra e⁻'s repel each other, altering the shape of the Coulomb potential. Figure shows orbitals in order of increasing energy.
- Orbitals can only accommodate 2 states, e⁻'s spin up & spin down.
- e⁻'s cannot share states (Pauli Exclusion principle) - only two electrons can fill each orbital.
- To construct an atom in the ground state from scratch ("aufbau principle"), place e⁻ one at a time into the lowest empty energy state (see figure). In a sub-shell, electrons "prefer" not to pair up until there are no empty orbitals left (Hund's rule)
Fine-structure in Hydrogen

- Last lecture it was stated: In hydrogen, all orbitals in the same shell (n) have same energies but only differ in angular momentum vectors. Not strictly true.

In high precision spectrometry, hydrogen spectral lines (e.g. Balmer lines) exhibit "fine structure" actually dividing into very several closely spaced spectral lines of slightly different photon wavelength. (Splitting shown is exaggerated)

- In hydrogen, sub-shells (s, p, d, f etc.) and the orbitals within them have very slightly different energies.
- In "multi-electron" atoms these differences in energy are much larger so spectra are more complicated.

Zeeman Effect

In emission spectra of atoms in a strong magnetic field (B), some normally single lines split up

Why?

Consider Orbitals in Magnetic fields

- Orbit of e- has angular momentum L. The vector for L is an arrow which is the axis of orbital rotation.
- Orbit of an e- is like a little magnetic compass needle (magnetic dipole); south pole @ arrow end of the L vector
  - If dipole aligned to field: U is low →
  - If dipole perpendicular to B, U is zero →
  - If dipole opposite to field: U is high →
- Classical Physics: magnetic dipoles tend to align with magnetic fields to minimise U
- Quantum mechanics: orbital magnetic dipoles cannot align completely with B field (Uncertainty principle)
- L points only in quantised directions indicated by magnetic quantum number m_{L}

Stern-Gerlach Experiment

- Schrödinger's equation does not predict electron spin; Added in later.
- Stern-Gerlach experiment proved electron has spin - behaves like small magnet & direction that spin points in magnetic field is quantised; Spin "up" or "down only.
- Beam of atoms with a single unpaired s-electron (e.g. H or Ag) passed through non-uniform magnetic field B is split in two due to interaction of B with 2 orientations of unpaired e- spin.

X-rays again

- e- accelerated through ~20kV give off continuum background spectrum of X-rays when stopped by target e.g. W, Mo.
- Maximum possible photon energy is the incident e- energy eV_{acc}
  \[ h \nu_{max} = hc/\lambda_{max} = eV_{acc} \]
- Sharp peaks of "characteristic X-rays" (CX) also produced when incident e- knock out deep inner shell e- (n = 1, 2, & 3) allowing higher e- to drop down & emit X-ray peaks.
- Moseley showed CX are produced in all atoms by transitions similar to the first two Lyman & Balmer lines in hydrogen: for larger atoms these photons are in X-ray range.
Moseley & X-rays

- Moseley (1913) plotted $f$ for CX of elements versus atomic number on periodic table - Straight line graph
- Simple relationship between place on periodic table (atomic number) and a physical quantity - photon frequency.
- Moseley's analysis of his data proved atomic number = nuclear charge
- CX frequency insensitive to chemical environment of atom because deep shells not involved in chemical bonds.
- Method now used to identify atoms in electron microscope (EDS or "EDAX" Energy Dispersive Analysis of X-Rays).
- Moseley was a very young & promising physicist but died fighting in WW1

Chemistry IS Physics!