The power of analytical spectroscopy


Byzantine Icon (AD 1534), “Our Lady, the Life-giving Spring”
1.2. Basic Principles of Atomic Physics

Extremely simplified quantum mechanical model of the atom is the Bohr model based on Rutherford scattering experiments. Negative electrons are ‘bound’ by electric (Coulomb) attraction to positive nucleus.

The atomic nucleus:
- positive charge: \(+1.6 \cdot 10^{-19}\) C
- atomic mass: \(\sim A \cdot 1.66 \cdot 10^{-24}\) g
- miniscule size: \(\sim 5 \cdot 10^{-13}\) cm

The electron orbits:
- negative charge: \(-1.6 \cdot 10^{-19}\) C
- negligible mass: \(\sim 9 \cdot 10^{-28}\) g
- fair size: \(\sim 1-5 \cdot 10^{-10}\) cm

Only certain orbits for electrons are allowed: quantum states are characterized by certain radius and energy state, only limited number of electrons allowed per quantum state.
The Hydrogen Atom

\[ E_n = -Z^2 \frac{E_0}{n^2} \quad E_0 = 13.6 \text{ eV} \]

\( E_0 \) is energy necessary to ionize atom
\( Z \) is charge of nucleus, \( Z = 1 \)

\( n = \) main quantum number
\( \ell = n-1 \) orbital momentum quantum number

http://www.walter-fendt.de/ph14e/bohrh.htm
http://www.falstad.com/qmatom/
Mathematics of Quantum Transitions

Hydrogen atom: single proton in nucleus, single electron in orbit

\[
r_n = n^2 \cdot 0.529 \cdot 10^{-9} [m]\]

Electron orbit radius

\[
E_n = - \frac{13.606}{n^2} [eV]
\]

Electron orbit energy

Electron transition between orbits requires or releases energy:

Energy comes quantized as light particles: photons

\[
1 \text{ eV} = 1.6 \cdot 10^{-19} \text{ J}
\]
Transition between Energy Orbitals

Possible emission or absorption of light with fixed wavelengths by transitions of electrons between orbits! Wavelength depends on energy difference between orbits!

\[ E_n = -\frac{13.6}{n^2} \]

Hydrogen emission spectrum

Balmer Series
Energy and wavelength of emitted or absorbed light photons

\[
E_v = E_{n_i} - E_{n_f} = 13.6 \cdot \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) [eV]
\]

\[
E_v = h \cdot \nu = \frac{h \cdot c}{\lambda} \quad \frac{1}{\lambda} = \frac{13.6}{h \cdot c} \cdot \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) [eV]
\]

\[
h \equiv \text{Planck Constant:} \quad 6.626 \cdot 10^{-34} [J \cdot s]
\]

\[
c \equiv \text{Speed of Light:} \quad 2.987 \cdot 10^8 [m/s]
\]

\[
\frac{13.6 [eV]}{c \cdot h} = 1.097 \cdot 10^7 \left[ \frac{1}{m} \right] = R_H
\]
Examples

Calculate the wavelength of a photon emitted by an electron transition in the hydrogen atom from the $L$-shell ($n = 2$) to the $K$-shell ($n = 1$) (Lyman-series $L_\alpha$!)

$$\frac{1}{\lambda} = R_H \cdot \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_H \cdot \left( \frac{1}{2^2} - \frac{1}{1^2} \right) = 1.097 \cdot 10^7 [1/m] \cdot 0.75$$

$$\lambda = 121.5 \cdot 10^{-9} m = 121.5 \text{ nm} : \text{wavelength}$$

In interstellar space you find highly excited hydrogen atoms which emit radio waves. The wavelength corresponds transition from $n = 273$ to $n = 272$. Calculate the wavelength!

$$\frac{1}{\lambda} = R_H \cdot \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_H \cdot \left( \frac{1}{272^2} - \frac{1}{273^2} \right) = 1.097 \cdot 10^7 [1/m] \cdot 9.88 \cdot 10^{-8}$$

$$\lambda = 0.923 m : \text{radio wavelength}$$
The wavelength range extends from $10^{-15}$ m (γ-radiation) or $10^{-9}$ m (X-ray radiation) through $10^{-6}$ m (visible light) to radio wave lengths 1 m.
Each element has its own characteristic transitions depending on the orbit quantum numbers and the charge $Z$ (number of electrons, protons). These transitions can be analyzed by so-called spectroscopy of light to determine the elemental abundance!
Multi-Electron Atoms

Z is the charge and determines the chemical characteristics of the element, e.g. $Z=1$ (Hydrogen) $Z=47$ (Silver). Electron transitions and photon emission is more complex and depends on $Z$ and the shielding $S_n$ by inner electron shells.

\[ E_n = -\left( Z - S_n \right)^2 \cdot \frac{13.6}{n^2} \approx -\left( Z - 1 \right)^2 \cdot \frac{13.6}{n^2} \]

\[ E_K = E_n - E_1 = -\left( Z - 1 \right)^2 \cdot \frac{13.6}{n^2} + \left( Z - 1 \right)^2 \cdot \frac{13.6}{1^2} \]

\[ E_K = (Z - 1)^2 \cdot 13.6 \cdot \left( 1 - \frac{1}{n^2} \right) = \frac{hc}{\lambda_K} \]

\[ \lambda_K = \frac{hc}{E_\gamma} = \frac{hc}{E_n - E_1} \]
X-ray transitions in high Z atoms

Ag analysis

Tungsten $Z = 74$

- $K_{\alpha} (22.6$ keV$)$
- $K_{\beta} (24.9$ keV$)$
- $L_{\alpha\beta\gamma} (2.9$ keV$)$
Example: Calculate the K and L x-ray lines for Ag

\[ E_K = (Z-1)^2 \cdot 13.6 \text{[eV]} \cdot \left(1 - \frac{1}{n_i^2}\right) \]

Ag: \( Z = 47 \)

\[ E_{K\alpha} = 46^2 \cdot 13.6 \text{[eV]} \cdot \left(1 - \frac{1}{4}\right) = 21583 \text{[eV]} \]

\[ E_{K\beta} = 46^2 \cdot 13.6 \text{[eV]} \cdot \left(1 - \frac{1}{9}\right) = 25580 \text{[eV]} \]

\[ E_L = (Z-1)^2 \cdot 13.6 \text{[eV]} \cdot \left(\frac{1}{2^2} - \frac{1}{n_i^2}\right) \]

\[ E_{L\alpha} = (46)^2 \cdot 13.6 \text{[eV]} \cdot \left(\frac{1}{4} - \frac{1}{9}\right) = 3997 \text{[eV]} \]
transition scheme with orbital momentum quantum number

Level splitting occurs due to elliptic orbitals. This introduces fine structure in the atomic light spectrum.
higher accuracy x-ray energies

<table>
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<th>Z</th>
<th>Element</th>
<th>Kα₁</th>
<th>Kα₂</th>
<th>Kβ₁</th>
<th>Lα₁</th>
<th>Lα₂</th>
<th>Lβ₁</th>
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<td>47</td>
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<td>2.978</td>
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Easy to obtain:  
http://xray.uu.se/hypertext/XREmission.html  
http://www.csrrri.iit.edu/mucal.html  
http://ie.lbl.gov/xray/

Typical spectra:  
http://ie.lbl.gov/xray/ag.htm
Summary

For using atomic spectroscopy methods we need to excite the atoms of the material that should be analyzed. The decay back to the atomic ground state configuration causes the emission of photons with characteristic energies which can be observed by spectroscopy methods!