atomic absorption and emission of light

1889 Rydberg generalized to other H emission lines:

\[ \frac{mv^2}{r} = \frac{ke^2Z}{r^2} \]

\[ L = mvr = n \hbar \]

\[ E = \frac{1}{2} mv^2 - \frac{ke^2Z}{r} \]

\[ r = 0.53 \frac{n^2}{Z} \text{ Å} \]

\[ E_n = -13.6 \frac{(Z^*)^2}{n^2} \text{ (eV)} \]

\[ p = \frac{\hbar}{\lambda} \]

Mosley's Law

\[ E_f = E_{n=2} - E_{n=1} \]

*
Experimental backdrop to atomic quantum theory development

Spectroscopy (emission)

Developed in 1800’s

Hot dense body

Hot (dilute) gas

Prism

or diffraction grating

Emission or “bright line” spectrum

Black body spectrum

11-1.1
H atom absorbs and emits specific wavelengths (energies) of light.

1885 Balmer: visible light

\[ \lambda = (364.56) \left( \frac{n^2}{n^2 - 2^2} \right) \quad : \quad n=3,4,5,6,\ldots,\infty \]

Absorption spectrum

Emission spectrum

Red Balmer Line in Orion Nebula

Absorption spectrum
Energy (discrete set) levels of H (all atoms) are unique
⇒ photons absorbed / emitted unique finger print of atom

\[
\frac{1}{\lambda} = \mathcal{R}_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) : n_1 < n_2
\]

specifically \( n_2 = n_1 + 1, n_1 + 2, \ldots \)

\( \mathcal{R}_H \) is the **Rydberg constant**

\((\mathcal{R}_H = 10,973,731.534 \, \text{m}^{-1}).\)

Energy discrete set of H emission lines are unique (and incredibly precise) finger print of H- atom
He discovered in solar flash spectrum at solar eclipse ~ 1850 long before identified on Earth

Other unique atomic spectra fingerprints
Spectroscopy (absorption)

Cool gas

Darker features where energy has been absorbed by the cool gas

black body spectrum of bulb

intensity (arbitrary units)

Wavelength (angstroms)

1000 3000 10,000 30,000

1000 3000 10,000 30,000

Wavelength (angstroms)
absorption lines in Sun’s spectrum

11-1.6
absorption lines in spectra of stars with different surface temperatures (mass)
Before 1913 – mountains of incredibly precise atomic spectral data. Atoms interact with light in highly organized *discrete* ways. Only some wavelengths “fit”.

**Totally** un-understandable in classical physics of particles.

1913 Bohr (“something stinks in Denmark”)

11-1.7
1913 Bohr Atom

Classical first step

Circular orbit

\[ F = \frac{k(e)(Ze)}{r^2} \] Coulomb's Law

\[ F = \frac{mv^2}{r} \] circular motion

\[
\therefore \quad \frac{mv^2}{r} = \frac{ke^2Z}{r^2}
\]

\[ mv^2 = \frac{ke^2Z}{r} \quad (1) \]
1913 Bohr Atom

Circular orbit

\[ mv^2 = \frac{ke^2Z}{r} \]  

\[ L = mvr = n \frac{\hbar}{\pi} \]

Angular Momentum conserved in classical problem

Angular Momentum Quantized !!

(Bohr had to assume this!)

\[ \frac{\hbar}{2\pi} \]

2 into 1

\[ m \left( \frac{n \frac{\hbar}{mr}}{r} \right)^2 = \frac{ke^2Z}{r} \]

\[ \frac{n^2 \frac{\hbar^2}{mr}}{mr} = ke^2Z \]

\[ r_n = n^2 \left( \frac{\frac{\hbar^2}{ke^2Zm}}{Z} \right) \]

Only quantized orbits allowed!!

\[ r_n = n^2 \left( \frac{\frac{\hbar^2}{ke^2Zm}}{Z} \right) = \frac{n}{Z} \left[ .53(10)^{-10} \text{m} \right] = \left[ .53 \text{Å} \right] \frac{n^2}{Z} = r_n \]

11-1.8a J. Hand correction

2 Bohr radius \( \Rightarrow \)

1 Å = atomic size
Bohr Atom (continued: Energy)

\[
E = KE + PE = \frac{1}{2} mv^2 - \frac{ke^2Z}{r}
\]

\[
E = \frac{1}{2} \left( \frac{Ke^2Z}{r} \right) - \frac{Ke^2Z}{r} = -\frac{1}{2} \frac{Ke^2Z}{r}
\]

\[
\therefore E = -\frac{1}{2} \frac{ke^2Z}{n^2 \frac{\hbar^2}{ke^2Zm}}
\]

\[
E_n = -\left( \frac{k^2e^4Z^2m}{2\hbar^2} \right) \frac{1}{n^2} = -(13.6 \text{ eV}) \frac{Z^2}{n^2}
\]

quantized orbits \(\Rightarrow\) quantized energy!

for \(Z=1\) H \[E_1 = -2.17(10)^{-18} \text{ J} = -13.6 \text{ eV}\]
Planck’s law + Einstein photons = light has some “particle like” properties
1901
1905 PE effect

GP Thompson -1930 – electron has some wave properties

Point source
coherent light
0.2 mm
aperture

De Broglie (1924) matter waves

$\frac{h}{\lambda}$

$p = \frac{h}{\lambda}$
De Broglie (1924) matter waves

\[ \lambda = \frac{h}{p} \]

Recall Bohr said for e⁻ in atomic orbit:

\[ L = mvr = pr = n \frac{h}{2\pi} \]

\[ \therefore \text{ if } p = \frac{h}{\lambda} \]

\[ \text{then } \frac{h}{\lambda} = n \frac{h}{2\pi} \]

\[ 2\pi r = n\lambda \]

Like standing waves on a circular orbit.
Bohr Theory – atomic emission spectra

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

\( Z = \) atomic #  \( Z=1 \) hydrogen

\[ hf = E_{n_2} - E_{n_1} \]

Electron drops down \( \Rightarrow \) photon emitted

\[ E_{n_2} - E_{n_1} = (13.6)\left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = fh \]

\[ c = \lambda f \quad : \quad f = h \frac{c}{\lambda} \]

\[ h \frac{c}{\lambda} = (13.6)\left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \]

\[ \frac{1}{\lambda} = \{ (13.6) \} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \]

Rydberg formula from Bohr!!!

\( \mathcal{R}_H = 10,973,731.534 \text{ m}^{-1} \).

Precision of R unparalleled in history of physics !!!
$h\nu = \Delta E$

$E = h\nu$ of photon used to kick electron up energy ladder

Absorption of photon

$\leftarrow$ emission of photon

electron drops down energy ladder and photon with $E = h\nu$ emitted

$h\nu = \Delta E$
Ionization

Electron kicked out of atom

[any energy above ionization energy possible]

Recombination

Electron drops in
Energy (discrete set) levels of H (all atoms) are **unique**
⇒ photons absorbed / emitted unique fingerprint of atom

1889 Rydberg generalized to other H emission lines:

\[ \frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) : n_1 < n_2 \]

specifically \( n_2 = n_1 + 1, n_1 + 2, \ldots \)

\( R_H \) is the **Rydberg constant**

(\( R_H = 10,973,731.534 \, \text{m}^{-1} \)).

**Orion**
$r_n = [0.53 \, \text{Å}] \, n^2$

$E_n = -(13.6 \, \text{eV}) \frac{1^2}{n^2}$

First step in energy the biggest in UV

Balmer

Lyman

Paschen

11-9
**X-Rays and X-Ray Emission**

Roentgen 1895 X-rays (X-Strallung)

Max von Laue diffraction 1912-1913 (diffraction from planes of atoms in crystal)

Barkla 1911 x-ray emission – “hardness” = penetrating power hard & soft x-rays different targets – differing x-ray hardness emitted (gave us K, L, M, N x-ray emission lines)

Bragg 1912/13 x-ray diffraction \( n\lambda=2dsin(\theta) \)

[can use \( \theta \) to measure interatomic distances \( d \) in solids !!!!]

Mosely (demonstrator in Rutherford’s lab at Manchester)
- Bohr visits Rutherford – Mosely told of new Atomic theory

1913- Mosely used Bragg reflection to determine \( \lambda \) of x-ray emission of various elements \( n\lambda=2dsin(\theta) \)--- know \( d \) of crystal – measure \( \theta \) to determine \( \lambda \)

1913- Mosely’s Law \( 1/\lambda= K [Z-\sigma]^2 \quad \sigma_K=1 \ \sigma_L=1 \)

Z=atomic number !!!!!

“Mosely and the Numbering of the Elements”- by Jaffe – Doubleday NY 1971

1915 - Mosely- killed in WWI – Dardanelles Campaign- (against Turkey)
{Winston Churchhill’s idea (1’st Lord of the Admiralty)
- blood bath and WC didn’t come back till WWII}
X-ray in

\[ n=2 \quad \text{e}^- \quad \text{out} \quad \text{to} \quad n=1 \]

photo-ejected

\[ n=2 \text{ hole} \]

n=1 hole

“K” X-ray out

\[ \text{photon energy} = E_f = hf = h \frac{c}{\lambda} \]

\[ E_f = E_{n=2} - E_{n=1} \]

Z* = effective charge including screening = Atomic No. - 1

\[ E_f = \frac{-13.6 Z^*^2}{2^2} - \frac{-13.6 Z^*^2}{1^2} \{ \text{eV} \} \]

\[ E_f = 10.2 Z^*^2 \{ \text{eV} \} \quad Z^* = (Z-1) \]

\[ E_f (\text{K-edge}) = 10.2 (Z-1)^2 \{ \text{eV} \} . \]

Z = Atomic No.

\[ E_f (\text{K-edge}) = 0.102 (Z-1)^2 \{ \text{keV} \} \]

\[ E = 0.102 (Z-1)^2 \text{ keV} \]
Actual data from previous page taken in Rutgers senior undergrad lab.
\[ \sum_{\text{surf}} E_{\perp} \Delta A = \frac{Q_{\text{inside}}}{\varepsilon_0} \]

Gaussian surf.

\[ Q_{\text{inside}} = +Ze - 1e \]

\[ Q_{\text{inside}} = (Z - 1)e \]

\[ E \frac{4\pi r^2}{\varepsilon_0} = \frac{(Z - 1)e}{\varepsilon_0} \]

\[ E = \frac{(Z - 1)e}{4\pi\varepsilon_0 r^2} \]

This is why Mosley’s Law worked with \((Z-1)!!\)

~ charge distribution in atom interior

n=1 shell electron

n=2 shell 2 electrons

11-14