III. Atomic Spectroscopy

Spectrum of atomic hydrogen

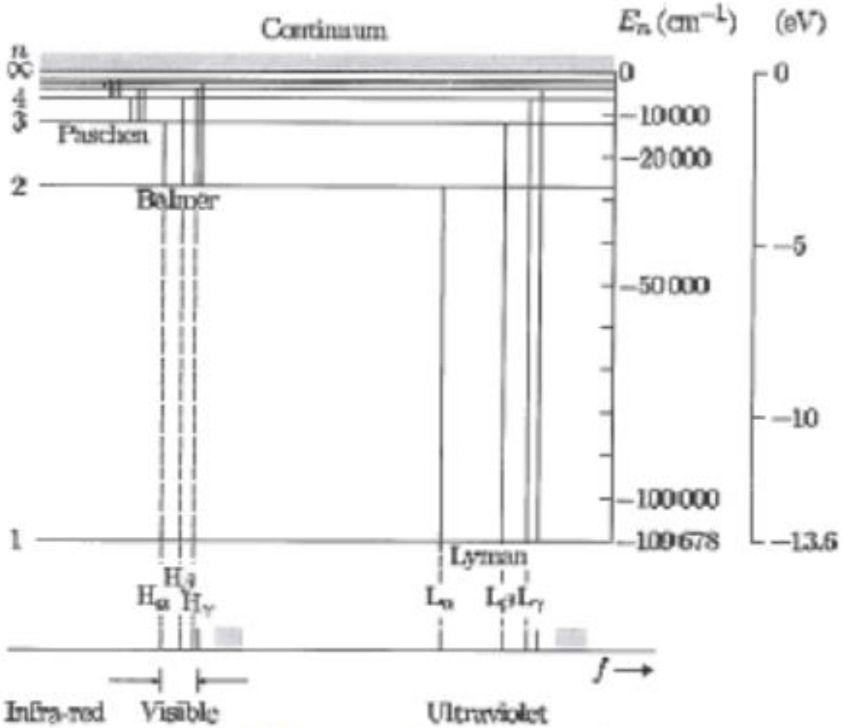


Fig. 1.1 The energy levels of the hydrogen atom. The transitions from higher shells $n' = 2, 3, 4, \ldots$ down to the $n = 1$ shell give the Lyman series of spectral lines. The series of lines formed by transitions to other shells are: Balmer ($n = 2$), Paschen ($n = 3$), Brackett ($n = 4$) and Pfund ($n = 5$) (the last two are not labelled in the figure). Within each series the lines are denoted by Greek letters, e.g. L_α for $n = 2$ to $n = 1$ and H_β for $n = 4$ to $n = 2$.

· Rydberg experimentally found

$$\frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$$

$$\boxed{R = \text{Rydberg constant} = 1.09 \times 10^7\ \text{m}^{-1} = \frac{\alpha^2 m_e c}{2h}}$$

Balmer $\frac{1}{\lambda} = 1.09 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \cancel{1.09 \times 10^7}$

$H_\alpha = \lambda \simeq 600$ nm

Bohr's theory: $\frac{m_e v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}$

equivalent to Kepler's law

$$\omega = \frac{v}{r} \qquad \omega^2 = \frac{e^2/4\pi\varepsilon_0}{m_e r^3}$$

$$T = \frac{2\pi}{\omega} \qquad \boxed{T^2 \propto r^3}$$

Total electron energy $E = \frac{1}{2} m_e v^2 - \frac{e^2/4\pi\varepsilon_0}{r}$

$$\frac{1}{2}\frac{e^2/4\pi\varepsilon_0}{r} - \frac{e^2/4\pi\varepsilon_0}{r}$$

$$= -\frac{e^2/4\pi r}{2r}$$

$E_{kin} = \frac{1}{2} E_{pot}$

Bohr's assumptions..

(a) There are certain allowed orbits where the electron has a fixed energy

(b) The electron looses energy only when it jumbs between those levels

(c) The electron angular moment is quantized

$$m_e v \cdot r = n \hbar$$

$$\left.\begin{aligned} m_e^2 v^2 r^2 &= \hbar^2 n^2 \\ \frac{m_e v^2}{r} &= \frac{e^2}{4\pi\varepsilon_0 r^2} \end{aligned}\right\} \qquad r = \underbrace{\frac{\hbar^2}{(e^2/4\pi\varepsilon_0) m_e}}_{a_0 = \text{Bohr radius}} n^2$$

$$E = -\frac{\frac{e^2}{4\pi\varepsilon_0}}{2a_0} \frac{1}{n^2} \qquad \bar{\nu} = R_\infty \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$$

$$hc R_\infty = \frac{(e^2/4\pi\varepsilon_0) m_e}{2\hbar^2}$$

$$\boxed{R_\infty = 10\,979\,731.568\,525 \text{ m}^{-1}}$$

note: hc is conversion factor between energy and wavenumbers

For a nucleus with finite mass the electron mass should be replaced by the reduced mass

$$\boxed{m = \frac{m_e M}{m_e + M} \quad \text{reduced mass}}$$

For hydrogen we get

$$R_H = R_\infty \frac{M_p}{m_e + M_p} \simeq R_\infty \left(1 - \underbrace{\frac{m_e}{m_p}}_{\frac{1}{1836}}\right)$$

This leads to an observable difference in spectral lines = Isotope shift (only part of it)

For deuterium

$$R_D = R_\infty \left(1 - \frac{m_e}{2m_p}\right)$$

$$\boxed{\left.\begin{aligned} n &= 1 \\ v &= \alpha c \end{aligned}\right\} \text{velocity of electron in H - groundstate}}$$

Sommerfeld introduced elliptical orbits and relativistic effects finding $\boxed{\frac{v}{c} = \frac{\alpha}{n}}$ $\alpha = \frac{e^2/4\pi\epsilon_0}{\hbar c} \simeq 1/137$ = fine structure constant

Moseley plot

Mosely measured x-ray spectra of many atoms versus Z

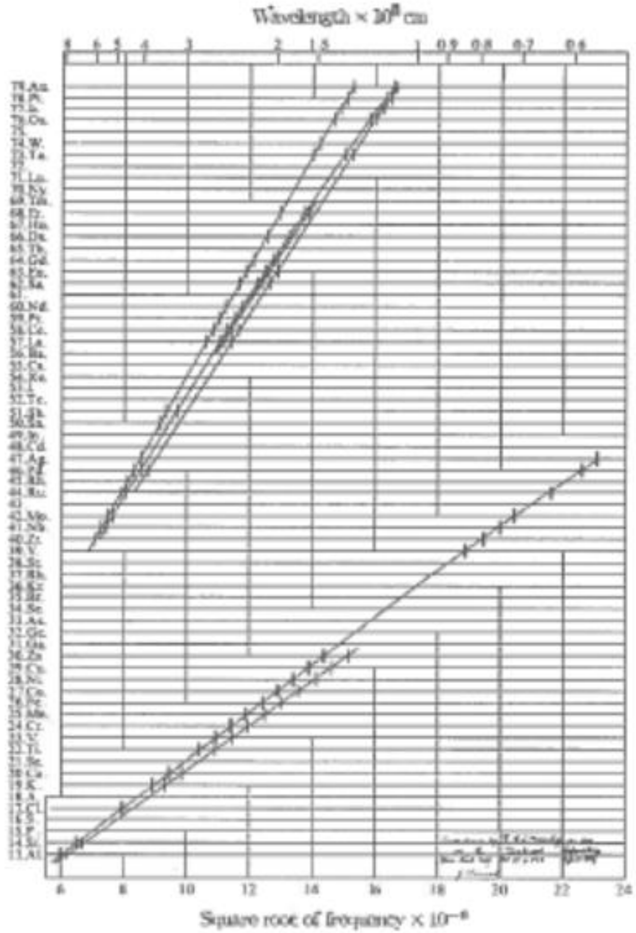


Fig. 1.2 Moseley's plot of the square root of the frequency of X-ray lines of elements against their atomic number. Moseley's work established the atomic number Z as a more fundamental quantity than the 'atomic weight' (now called relative atomic mass). Following modern convention the units of the horizontal scales would be ($10^8 \sqrt{\text{Hz}}$) at the bottom and (10^{-10} m) for the log scale at the top. (Archives of the Clarendon Laboratory, Oxford; also shown on the Oxford physics web site.)[13]

[13] The handwriting in the bottom right corner states that this diagram is the original for Moseley's famous paper in *Phil. Mag.*, 27, 703 (1914).

shell structure of atoms due to Pauli principle:

each shell contains only electrons with different quantum numbers

shell		
K:	$n=1$ shell	2 electrons
L:	$n=2$ shell	8 electrons
M:	$n=3$ shell	18 electrons

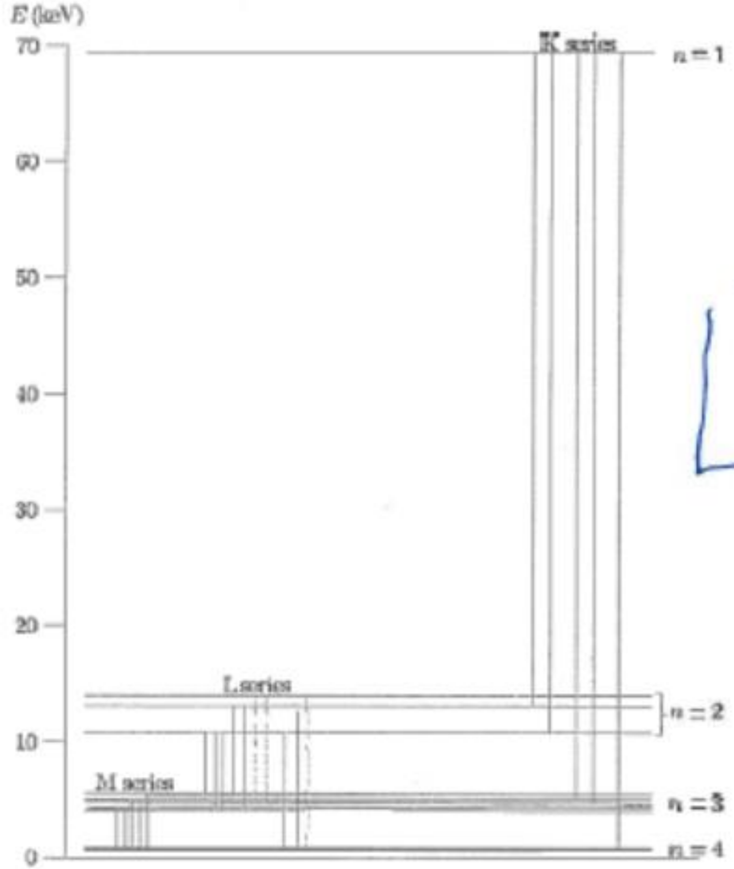
x-ray production:

fast electrons accelerated by a high voltage knock an inner electron out, leaving a vacancy

This vacancy fills when an out electron falls down into the hole

Energy levels of inner shells of tungsten atom

Fig. 1.3 The energy levels of the inner shells of the tungsten atom ($Z = 74$) and the transitions between them that give rise to X-rays. The level scheme has several important differences from that for the hydrogen atom (Fig. 1.1). Firstly, the energies are tens of keV, as compared to eV for $Z = 1$, because they scale as Z^2 (approximately). Secondly, the energy levels are plotted with $n = 1$ at the top because when an electron is removed from the K-shell the system has more energy than the neutral atom; energies are shown for an atom with a vacancy (missing electron) in the K-, L-, M- and N-shells. The atom emits X-ray radiation when an electron drops down from a higher shell to fill a vacancy in a lower shell—this process is equivalent to the vacancy, or hole, working its way outwards. This way of plotting the energies of the system shows clearly that the removal of an electron from the K-shell leads to a cascade of X-ray transitions, e.g. a transition between the $n = 1$ and 2 shells gives a line in the K-series which is followed by a line in another series (L-, M-, etc.). When the vacancy reaches the outermost shells of electrons that are only partially filled with valence electrons with binding energies of a few eV (the O- and P-shells in the case of tungsten), the transition energies become negligible compared to those between the inner shells. This level scheme is typical for electrons in a moderately heavy atom, i.e. one with filled K-, L-, M- and N-shells. (The lines of the L-series shown dotted are allowed X-ray transitions, but they do not occur following K_α emission.)



to account for the higher charge of other atoms (other than H-atom) replace

$e^2/4\pi\varepsilon_0$ by $Ze^2/4\pi\varepsilon_0$

$$\boxed{\frac{1}{\lambda} = R_\infty \left\{ \frac{(Z-\delta_K)^2}{1^2} - \frac{Z-\delta_L}{2^2} \right\}}$$

δ_K and δ_L are screening factors

When an electron is removed from an inner shell the system has more energy than the neutral atom! The atom emits this radiation in an X-ray

Radiative decay

An electric dipole moment $-ex_0$ oscillating at the angular frequency ω radiates power P according to

$$P = \frac{e^2 x_0^2 \omega^4}{12\pi \epsilon_0 c^3}$$

the harmonicall oscillating electron has a total energy of $E = m\omega^2 x_0^2/2$

Rate of energy decrease = power

$$\frac{dE}{dt} = \frac{e^2 x_0^2 \omega^4}{12\pi \epsilon_0 c^3} = -\frac{e^2\omega^2}{6\pi\epsilon_0 m c^3} = -\frac{E}{\tau}$$

$$\boxed{\frac{1}{\tau} = \frac{e^2\omega^2}{6\pi\epsilon_0 m c^3}}$$

classical value of is the fastest time an atom electron can decay for a certain transition

for $\lambda = 589$ $\tau = 16\,ns \approx 10^{-8}\,s$

very close to the actual value

Life times vary over a wide range

quantum jumps of ions in ion traps can be observed

Einstein A and B coefficients

What happens to an atom interacting with radiation of energy density $\rho(\omega)$?
It interacts strongly with that frequency close to a transition

$$\omega_{12} = (E_2 - E_1)/\hbar$$

$$\frac{dN_2}{dt} = N_1 B_{12}\,\rho(\omega_{12}) - N_2 B_{21}\,\rho(\omega_{12}) - N_2 A_{21}$$

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt} \qquad \frac{d}{dt}(N_1+N_2) = c$$

$$N_1 + N_2 = \text{constant}$$

some atom $N_2(t) = N_2(0)\exp(-A_{21}t)$

$$1/\tau = A_{21} = \text{mean lifetime}$$

assume two level scheme

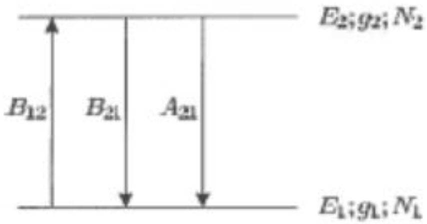


Fig. 1.4 The interaction of a two-level atom with radiation leads to stimulated transitions, in addition to the spontaneous decay of the upper level.

Einstein imagined what would happen if an atom where interacting with black body radiation. At equilibrium $dN/dt = 0$

$$\rho(\omega_{12}) = \frac{A_{21}}{B_{21}}\,\frac{1}{(N_1/N_2)(B_{12}/B_{21}) - 1}$$

$$= \frac{\hbar\omega^3}{\pi c^3}\,\frac{1}{\exp(\hbar\omega/k_BT) - 1}$$

$$\frac{N_2}{g_2} = \frac{N_1}{g_1}\exp\left(-\frac{\hbar\omega}{k_BT}\right)$$

These equations hold for all T so we can equate the parts $\exp(\hbar\omega/k_BT)$ and the temperature containing part separately

$$\boxed{A_{21} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{21} \qquad B_{12} = \frac{g_2}{g_1} B_{21}.}$$

strong absorption is associated with strong emission

Atomic units

$2\pi a_0^2 \simeq 1.5 \times 10^{-16}\, m^2$

important scales
in atomic physics:

length: Bohr radius $a_0 = \frac{\hbar^2}{(e^2/4\pi\varepsilon_0) m_e} = 5\times10^{-11}\, m = 0.05\, nm$

energy: $hc R_\infty = \frac{m_e (e^2/4\pi\varepsilon_0)^2}{2\hbar} = 13.6\, eV$

$P = \frac{e^2}{4\pi\varepsilon_0 a_0}$ = potential energy of electron in 1st Bohr radius = 27.2 eV

$E = \frac{\Delta P}{a_0} = \frac{27.2\, eV}{5\times10^{-11}\, m} \cong 5\times10^{11}\, \frac{V}{m}$

Relativistic effect depend on
fine structure constant $\alpha = \frac{e^2/4\pi\varepsilon_0}{\hbar c} \simeq \frac{1}{137}$

$\frac{v}{c} = \frac{\alpha}{n}$

magnetic moment: $\boxed{\text{Bohr magneton } \mu_B = \frac{e\hbar}{2m_e} = 9\times10^{-24}\, J/T}$

This depends on the unpaired electrons
properties of the in an atom and has similar a value for all atoms

In contrast other properties scale with various powers of Z (example U^{+91})

Energies $\sim Z^2$ size $\sim \frac{1}{Z}$ | $E(U^{+91}) = 92^2 \times 13.6 = 115\, keV$
$r(U^{+91}) = \frac{a_0}{92} = 5\times10^{-13}\, m$

Note on laser cooling (to Carlos presentation)

The scattering force = rate of change of momentum when an atom absorbs radiation

= rate at which light delivers energy divided by c

$$\boxed{F_{rad} = \frac{\overbrace{IA}^{\text{power absorbed}}}{c} \Rightarrow \frac{F_{rad}}{A} = \frac{I}{c} = \text{radiation pressure}}$$

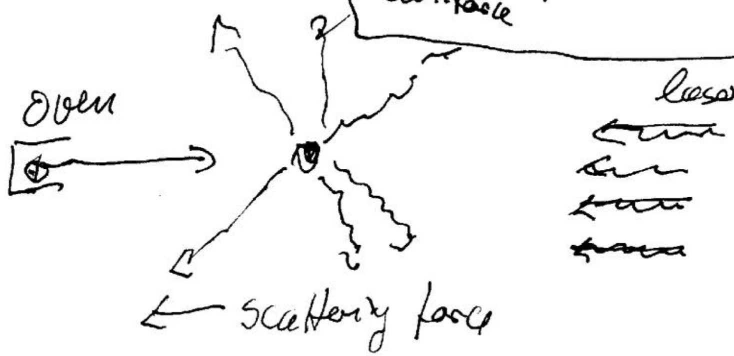
example $IA = 1\,W \Rightarrow F = \dfrac{1\,W}{3\times10^8\,m/s} = \dfrac{1\ \text{Joule}/s}{3\times10^8\,m/s} = \dfrac{1\,Nm/s}{3\times10^8\,m/s} = 3\times10^{-9}\,N$

A counter propagating laser beam exerts a force

$$F = -\sigma_{abs}\frac{I}{c} \qquad \sigma_{abs} \propto \lambda_{res}^2$$

much larger than geometrical cross section of atom ($\approx 10^4$)

$$\boxed{F_{\text{Scatt force}} = \text{photon momentum} \times \text{scattering rate}}$$



scattering rate $R_{scatt} = \Gamma \rho_{22}$

life time and population of excited state