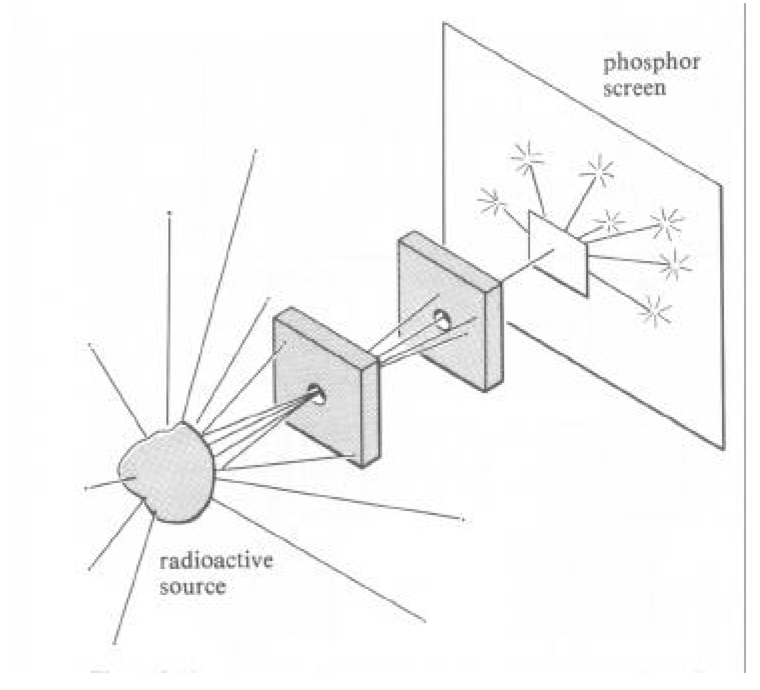
Atoms and Molecules

Rutherford (1910): scattering of charged particles by matter (gold foil).



Conclusion: Atoms consist of mostly empty space. Positively charged nucleus occupies very small volume in each atom.

Atomic Structure

Atoms: nucleus ~ 10^{-14} m *Z* protons, charge $+e$

N neutrons, charge 0

electron cloud ~ 10^{-10} m *Z* electrons, charge $-e$

Atomic number *Z:* 1 to 92 for naturally occurring elements

Atomic mass $A = Z + N$

$e = 1.602 \times 10^{-19}$ C

Z determines the element, *A* the isotope. Elements identified as ^{A}X,

e.g., ^{1}H, hydrogen; ^{12}C, carbon; ^{16}O, oxygen.

Atomic Structure - Classical Theory

Electric (Coulomb) force $$F_e = \frac{kq_1q_2}{r^2} = -\frac{k(Ze)e}{r^2}.$$

Energy *(KE + PE)* $$E = \frac{mv^2}{2} - \frac{kZe^2}{r}.$$

But, classical picture of orbiting electron means it accelerates. Acceleration => radiation of EM waves => loss of energy => collapse of orbit!

Wave-Particle Duality

de Broglie (1910’s): proposes particles have wave-like properties.

$p = h/\lambda$, where p is the momentum of a particle.

Bohr (1913): a semi-classical model for the atom.

Only discrete electron orbit radii are allowed, and when in those orbits, the electron cannot radiate.

Allowed orbits for $mvr = n(h/2p)$ $\quad n = 1,2,3,\ldots$

Note: along with deBroglie’s hypothesis, implies orbit circumference must equal an integer # of wavelengths.

Combine with

$$\frac{mv^2}{r} = \frac{kZe^2}{r^2}.$$

Bohr Model

Permitted levels $r = n^2 (h^2 / 4p^2 me^2 kZ).$

Energy $E = \dfrac{mv^2}{2} - \dfrac{kZe^2}{r} \Rightarrow E(n) = -(2p^2 me^4 k^2 Z^2) / n^2 h^2.$

Orbits are bound until $n \to \infty$. Ground state $n = 1$.

Electrons can make a transition from one bound level to another. A photon is emitted or absorbed.

$E(n_a) = E(n_b) + hn$ (emission)

$E(n_b) + hn = E(n_a)$ (absorption)

where $n_a > n_b$.

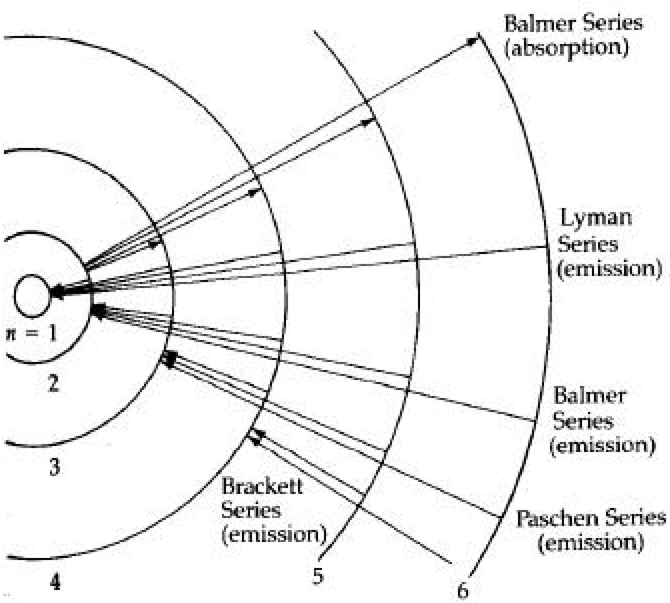
Bohr Model of the Hydrogen Atom

$$Z = 1 \quad \Rightarrow \quad E(n) = -(2p^2 m e^4 k^2)/n^2 h^2 .$$

For a transition between level n_a and n_b:

$1/l_{ab} = R(1/n_b^2 - 1/n_a^2)$, where λ_{ab} = photon wavelength and

R = Rydberg constant = 10.96776 μm^{-1}.



Note Lyman, Balmer, Paschen, Brackett, Pfund series for n_b=1,2,3,4,5.

Only Balmer series falls in visible light range, e.g., H α (Balmer α) line

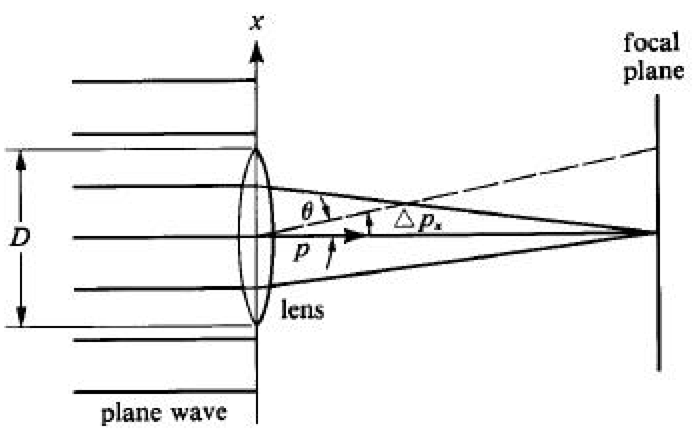
λ_{32} = 653.6 nm.

Back to Wave-Particle Duality

No well-defined orbit radii. Logical conclusion of wave-particle duality => electrons do not have any definite position.

Heisenberg uncertainty principle: $\Delta x \, \Delta p > h.$

Applies to particles and waves. Explains diffraction and interference of particles.

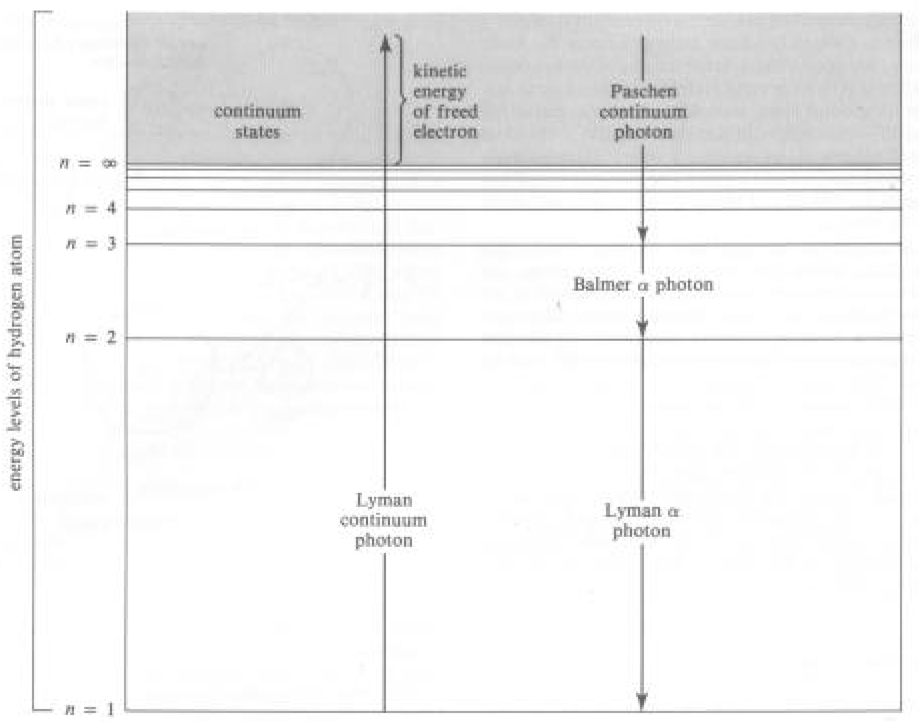


$$\Delta p > \frac{h}{D} \text{ and } p = \frac{h}{l} \quad \Rightarrow \frac{\Delta p}{p} > \frac{l}{D}.$$

$$\text{For } \Delta p << p, \;\; q \cong \frac{\Delta p}{p} = \frac{l}{D}.$$

A Modern View of the Hydrogen Atom

Modern calculations of atomic structure still have discrete energy levels, if not well-defined electron radii. Electron radii described by a “wave” of probability around proton. Bohr orbits are most probable electron positions.



$$E_n = -\frac{13.6\ \mathrm{eV}}{n^2}.$$

A Modern View of the Hydrogen Atom

In general, the energy of an electron depends on a host of quantum numbers:

Principal quantum number $n = 1,2,3,\ldots.$

Angular momentum quantum number $l = 0,1,2,\ldots n\text{-}1$

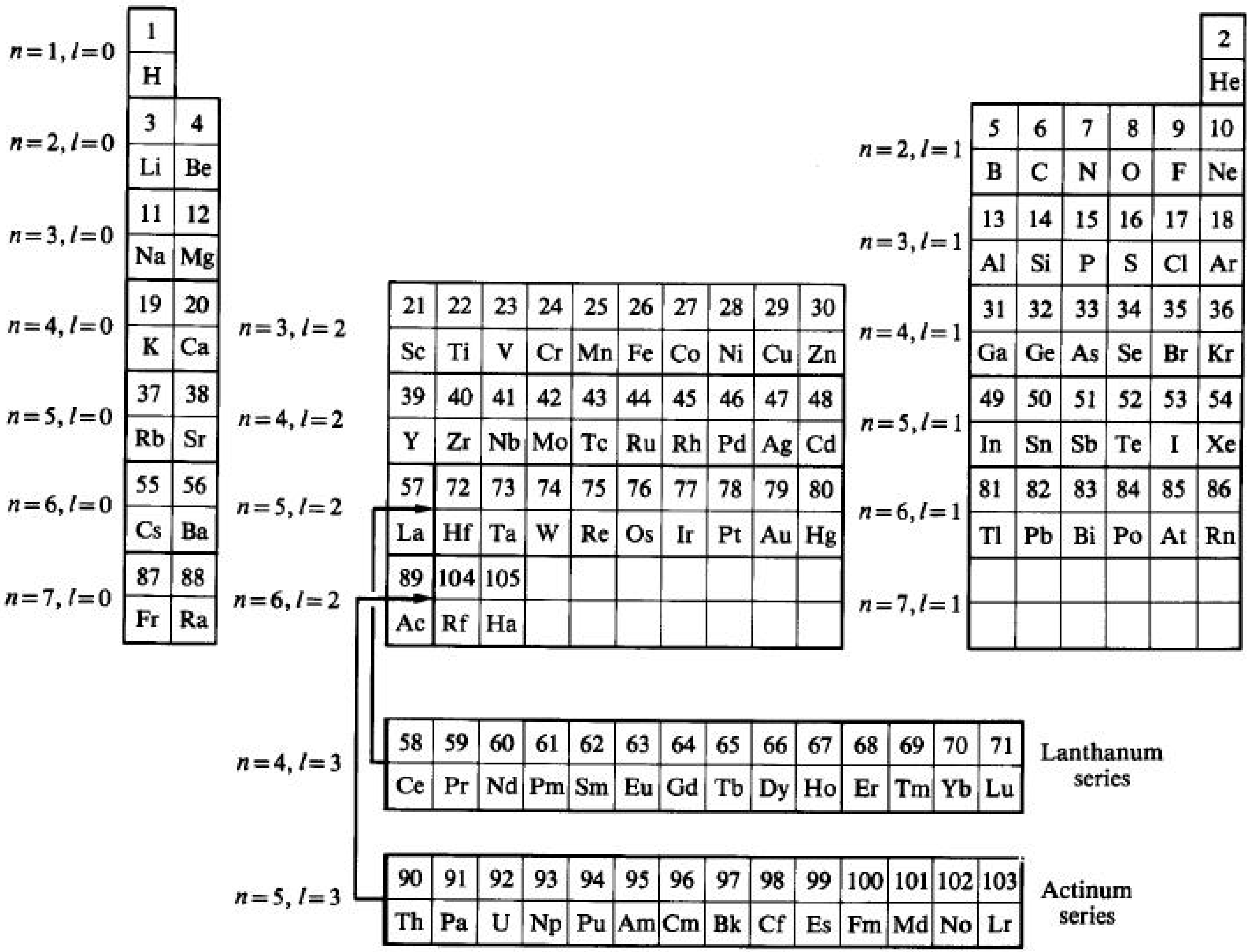
Angular momentum orientation $m_l = -l,-l+1,\ldots0,\ldots l-1, l$

Spin $s = 1/2$

Spin orientation $m_s = -1/2$ or $1/2$.

Pauli Exclusion Principle: No two electrons may have an identical set of quantum numbers => all electrons cannot occupy the lowest energy state.

The Periodic Table



Multi-Electron Atoms

Transitions more complex than for hydrogen atom.

Electrons grouped into “shells”. If outermost shell is not full, electrons there easily excited and/or ionized. If only one electron in outermost shell, transitions similar to H.

Ions: when one or more electrons escape to the continuum. If one electron remaining, energy levels similar to H.

$$E_n = -\frac{13.6\ \mathrm{eV}\ Z^2}{n^2},$$ e.g., He II, Li III, O VIII, Fe XXVI.

Nomenclature: He^+=He II, Ca = Ca I, Ca^+=Ca II, Ca^{++}=Ca III

Molecules

Complex states.

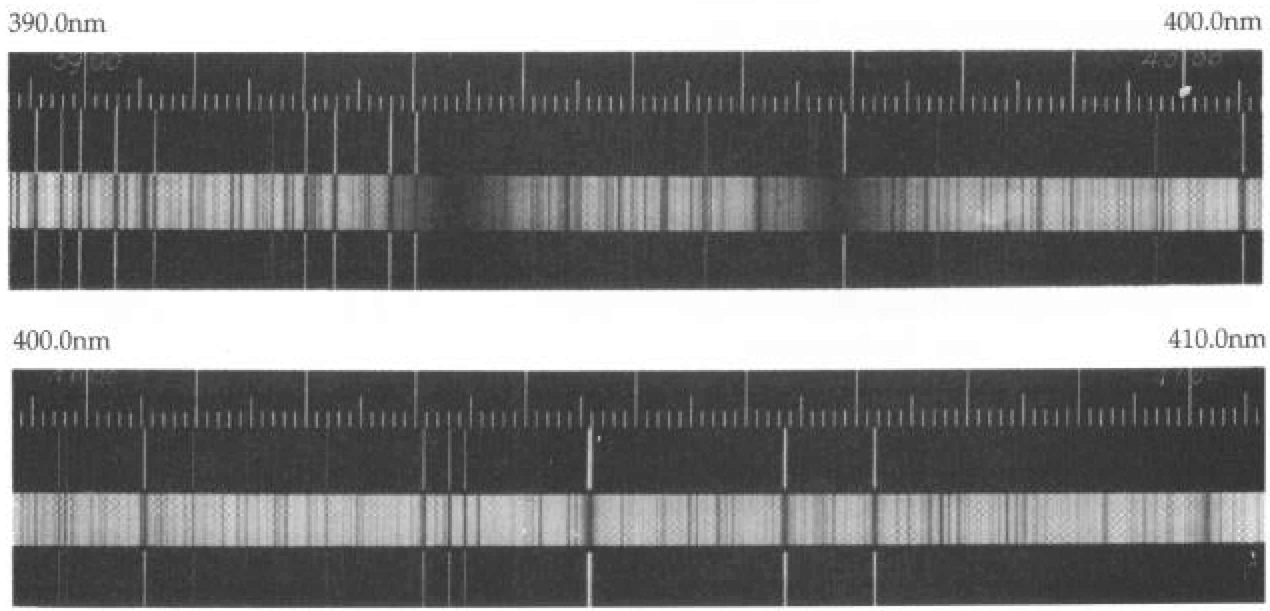
Transitions: electronic, rotational, vibrational.

For example, CO rotational levels

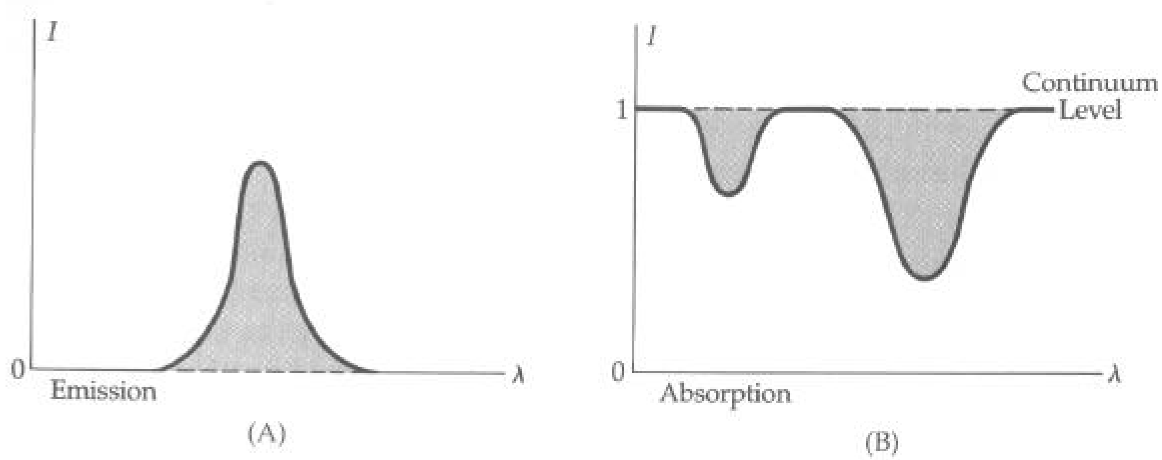
$$E = \left(\frac{h}{2p} \right)^2 \frac{J(J+1)}{2mr^2}, \quad J = 0,1,2,\ldots$$

$$J:1 \rightarrow 0 \quad n = 115.3\,\text{GHz}, \ l = 2.6\,\text{mm}.$$

Spectral Lines



Solar spectrum



Emission and absorption lines

Spectral Lines

Absorption line: excitation to higher energy level by absorbing photon from background continuum with energy $\Delta E = h\nu$. Subsequently, have

(1) de-excitation by collision, so no photon produced

(2) de-excitation to a different level, so photon of different energy (and ν) produced

(3) de-excitation to original level, but photon (of same energy as original photon) may be emitted in any direction.

Emission line: Collisional excitation to higher level, followed by radiative decay so that a photon of energy $\Delta E = h\nu$ produced.

Forbidden emission line: Transition would be collisionally de-excited in laboratory, but de-excitation occurs radiatively in rarified interstellar gas.

Spectral Line Broadening

(1) natural broadening

$\Delta E\,\Delta t > \dfrac{h}{2p}$ => a natural width to energy levels

Lifetime of excited level $\Delta t \sim 10^{-8}$ s $\Rightarrow$ $\Delta n = \dfrac{\Delta E}{h} = \dfrac{1}{2p\Delta t}$.

$c = n\,l \quad \Rightarrow \quad \Delta l = \dfrac{l^2}{c}\Delta n = 1.3\times10^{-5}$ nm for $l = 500$ nm.

(2) collisional broadening

– energy levels shifted by electrostatic interaction with neighboring atoms

– a direct dependence on particle density

– in a gas of sufficient density, characteristic spectral features disappear; gas emits a continuum of wavelengths.

Spectral Line Broadening

(3) Zeeman effect

A splitting of energy levels due to magnetic (**B**) field.

If splitting resolved, measure **B** strength.

If splitting unresolved, see broadened line.

(4) thermal Doppler broadening

Atomic motions along line-of-sight => Doppler shifts

$$\frac{\Delta l}{l} = \frac{v}{c},$$ e.g., for H at T = 6000 K,

$$< v > \approx 12\,\text{km/s} \quad \Rightarrow \quad \Delta l \approx 0.025\,\text{nm}$$

for $l = 653.6\,\text{nm}$ Ha line.

Spectral Line Broadening

(5) macroscopic broadening

Due to Doppler shifts from large-scale unresolved motions

– turbulence

– expansion or contraction

– rotation

Kirchoff's Rules

Relate appearance of spectra to the composition and physical state of an object.

(1) A hot and opaque solid, liquid, or highly compressed gas emits a continuous spectrum.

(2) A hot, transparent gas produces a spectrum of emission lines. Specific lines depend on which elements present in gas.

(3) Relatively cool, transparent gas in front of a continuum source produces absorption lines. Specific lines depend on which elements present in gas.