Unit 3 · Atomic Structure

STUDY NOTES

WHAT NEB'S GRADE 11 EXAM ASKS

- **CDC's grid (2077):** Physical Chemistry (Units 1–8 together): 28 of 75 marks
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** short question (with Unit 4): X with 2, 8, 5 electrons: identify it, protons and electrons (P, 15); why X^{3-} is larger than X; a compound with X at −3
- **MCQ (1 mark)**
  - Pauli's principle; species with the same configuration
  - what Bohr's model used; longest de Broglie wavelength at one speed
  - why half-filled and filled are stable (symmetry, exchange energy)
  - orbital filled last; an excited-state configuration
  - the d-block metal from its valence shell
  - region of the $3 \rightarrow 2$ line; what m gives
  - $n = 3, l = 2, m = -1$ is 3d; electrons with $l = 0$
- **Short (5 marks, in parts)**
  - scattering experiment: why the name, observations, three conclusions; Rutherford's limitation
  - three Bohr postulates; how he explained stability; orbit, its energy, stationary states
  - Rutherford vs Bohr: two likenesses, two differences; the postulate behind the spectrum; why an emission spectrum; the series and regions
  - reasons: electrons don't fall in; 4p above 3s; Bohr against uncertainty; duality only for small things; N has 3 unpaired
  - state: Hund, Heisenberg, de Broglie, duality; differences: orbit/orbital, n/l, Lyman/Balmer, s/p
  - [Ar] $3d^{10}\ 4s^2$: p and e, group, block, period, X^{2+} and its size; three models, which is Rutherford's
  - what n tells; quantum numbers of a 3p electron; l and m of p; **draw the three p orbitals**
  - $\Delta x \Delta p \geq h/4\pi$: name, terms, big objects; degenerate orbitals; which of four box diagrams obeys Hund
- **Long (8 marks)**: Aufbau and (n + l); Cr's configuration, 4s below 3d, the 15th electron's quantum numbers, Cr^{3+} and its unpaired electrons; Bohr orbits and the $3 \rightarrow 2$ series; the spectrum's series x, y and regions; Cu and Cr configurations justified, Cu^{2+}; Hund's rule from boxes

Key terms

Nucleus: tiny, dense, positive center with nearly all the mass (about 10^{-14} m; atom 10^{-10} m).

Orbit (shell): Bohr's fixed circular path of fixed energy (K, L, M, N; n = 1, 2, 3, 4).

Stationary state: an orbit in which the electron neither gives out nor takes in energy.

Ground state: lowest level, n = 1; **excited states**: those above it.

Emission spectrum: bright lines of light given out as electrons fall; **absorption spectrum**: dark lines where light is taken in.

Continuous spectrum: every wavelength (rainbow, hot filament); **line spectrum**: sharp lines only (atoms of a gas).

Wave number $\bar{\nu}$: $1/\lambda$, waves per meter.

Zeeman effect: lines split in a magnetic field; **Stark effect**: in an electric field.

Wave–particle duality (de Broglie): every moving particle has a wave.

Orbital: 3D region round the nucleus where an electron is most likely (90%) to be found.

Node: place where the chance of finding the electron is zero (ns has n − 1 spherical nodes; a p orbital a nodal plane).

Quantum numbers: n, l, m, s, describing an electron's state.

Degenerate orbitals: same energy (three 2p, five 3d).

Paramagnetic: unpaired electrons, drawn into a magnet; **diamagnetic**: all paired, weakly repelled.

Multiplicity: number of unpaired electrons.

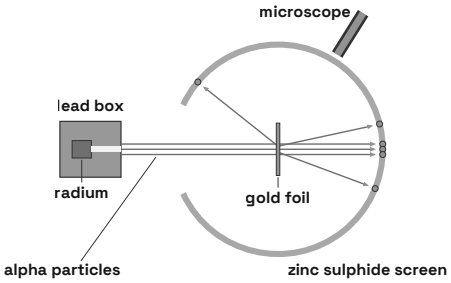
Electronic configuration: arrangement of an atom's electrons in shells, subshells and orbitals.

Formulas

$\Delta E = E_2 - E_1 = h\nu$	$h = 6.626 \times 10^{-34}$ J s **Use:** energy of the photon of a jump
$mvr = \dfrac{nh}{2\pi}$	$n = 1, 2, 3 \ldots$ **Use:** allowed orbits
$E_n = -\dfrac{13.6}{n^2}$ eV, $r_n = 0.0529\, n^2$ nm	$= -2.18 \times 10^{-18}/\mathrm{n}^2$ J **Use:** hydrogen's levels, radii
$\dfrac{1}{\lambda} = R_H \left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} \right)$	$R_H = 1.097 \times 10^7$ m^{-1}; n_1 lower **Use:** hydrogen's lines
$\lambda = \dfrac{h}{mv} = \dfrac{h}{p}$	de Broglie **Use:** wavelength of a particle
$\Delta x \cdot \Delta p \geq \dfrac{h}{4\pi}$	$\Delta p = m\Delta v$; $\hbar = h/2\pi$ **Use:** uncertainty
$2n^2$, $2(2l + 1)$, $2l + 1$	**Use:** electrons per shell, per subshell; orbitals per subshell

Rutherford's atom

- particles: electron (Thomson, 1897), nucleus (Rutherford, 1911), proton (1919), neutron (Chadwick, 1932; mass a little more than a proton's, ~1840 electrons)



Alpha particles (He^{2+}) from radium in a lead box, gold foil about 0.4 μm thick, a zinc sulphide screen round it, watched through a microscope.

Observations → conclusions

1. most (over 99%) straight through → atom mostly **empty space**
2. a few turned a little → positive charge **concentrated**
3. about 1 in 20,000 turned over 90°, some straight back → mass and positive charge in a tiny **nucleus**

Nuclear (planetary) model: dense positive nucleus; electrons circling fast, held by attraction; atom neutral; mostly empty

Limitation: an orbiting electron accelerates, so (Maxwell) radiates energy and should **spiral into the nucleus** in about 10^{-11} s; atoms would be unstable; it would give a continuous spectrum, not lines

Bohr's model (1913)

1. electrons only in certain orbits (shells, energy levels), K, L, M, N
2. energy rises outward, $E_1 < E_2 < E_3$; in an orbit no energy lost → **stationary states** (stability)
3. a jump takes in or gives out exactly $\Delta E = h\nu$
4. allowed orbits: $mvr = nh/2\pi$ (quantized angular momentum)

- energies negative: a free electron is zero
- **likeness** to Rutherford: nucleus at the center with nearly all the mass; electrons round it
- **difference**: Bohr's orbits are fixed, of fixed energy, no radiation; Rutherford's electrons radiate and can be anywhere

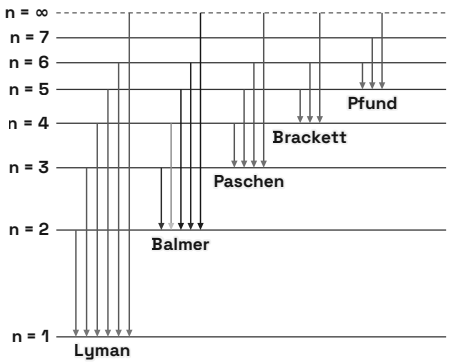
Defects

- only one-electron species (H, He^+, Li^{2+})
- no Zeeman or Stark splitting, no fine structure
- electron only a particle (no duality)
- no reason for $mvr = nh/2\pi$
- fixed path breaks the uncertainty principle

Hydrogen's spectrum

- spark → electrons excited to many levels → each falls by its own route; **every jump down is one line** (fixed levels, fixed wavelengths): many lines from one electron
- emission spectrum, since the light is given out as electrons fall; every element its own lines, like a bar code (helium found in the Sun, 1868)

Series	Falls to	Region
Lyman	$n_1 = 1$	ultraviolet
Balmer	$n_1 = 2$	visible
Paschen	$n_1 = 3$	infrared
Brackett	$n_1 = 4$	infrared
Pfund	$n_1 = 5$	infrared



Each arrow a jump down, one line; a series ends on one level.

- 3 → 2 gives 1.89 eV, red, 656 nm (Balmer); 1 → 2 needs energy taken in (absorption)
- shortest line of a series: $n_2 = \infty$
- flame test: Na yellow-orange, K lilac, Li crimson, Ca brick red, Sr crimson red, Ba apple green, Cu blue-green

Quantum mechanical model

de Broglie (1924)

1. $E = h\nu$ (Planck) and $E = mc^2$ (Einstein)
2. $mc^2 = hc/\lambda$
3. $\lambda = h/mc$; for any particle $\lambda = h/mv$

- electron: λ about an atom's size; a ball: far too small to detect

- a whole number of waves round an orbit: $2\pi r = n\lambda \rightarrow mvr = nh/2\pi$, Bohr's rule explained

Heisenberg (1927): position and momentum can't both be known exactly at once

- the short-wave photon that finds an electron kicks it ($p = h/\lambda$); not a fault of instruments
- matters only for microscopic particles
- so no orbits: only a **probability** of finding the electron; ψ^2 = probability density (Schrödinger, 1926); its cloud = orbital
- 1s most likely at 0.0529 nm (Bohr's radius); 2s, 3s larger, with 1 and 2 nodes

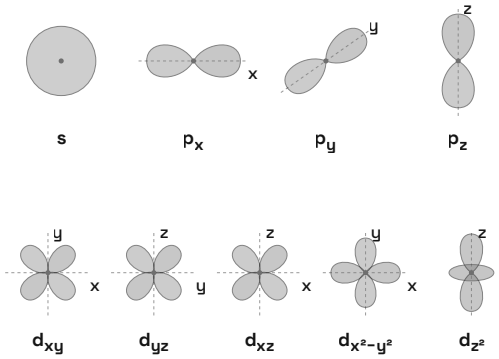
Orbit vs orbital

- orbit: circular path, fixed distance, 2D, definite position (against uncertainty), holds $2n^2$
- orbital: 3D region of probability, a shape (sphere, dumbbell), holds at most 2

Quantum numbers

	Gives	Values
n principal (Bohr)	shell, size, energy; $2n^2$	1, 2, 3 …
l azimuthal (Sommerfeld)	subshell, shape	0 … n − 1 (s, p, d, f)
m magnetic	orientation, number of orbitals	−l … +l
s spin (Uhlenbeck, Goudsmit, 1925)	spin	+½, −½

- l = 0 s sphere; 1 p dumbbell; 2 d mostly four lobes
- no 1p, 2d, 3f (l < n)
- p: m = −1, 0, +1 → p_x, p_y, p_z
- 3p electron: n = 3, l = 1, m = −1, 0 or +1, s = ±½
- n = 3, l = 2 is 3d
- 4p above 3s: higher n + l (5 > 3)



s a sphere; p_x, p_y, p_z two lobes along each axis, a nodal plane at the nucleus; five d orbitals.

- the three p orbitals of one shell have the **same energy** (degenerate)

Filling rules

Pauli's exclusion principle (1925): no two electrons in an atom have the same four quantum numbers → an orbital holds at most **2, with opposite spins**

- helium: (1, 0, 0, +½) and (1, 0, 0, −½)

Aufbau: orbitals fill in increasing energy

- lower **n + l** first; equal n + l → lower **n** first
- 1s 2s 2p 3s 3p **4s 3d** 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p

Hund (1925): degenerate orbitals fill **singly, parallel spins**, before pairing (less repulsion, more stable; maximum multiplicity)

- N $1s^2\ 2s^2\ 2p^3$: three unpaired (↑ ↑ ↑)
- unpaired: B 1, C 2, N 3, O 2, F 1, Ne 0
- C's 2p as ↑↓ in one box breaks Hund; ↑↑ in one box breaks Pauli

Configurations

- noble gas core: Na [Ne] $3s^1$
- Sc [Ar] $4s^2\ 3d^1$ … Zn [Ar] $4s^2\ 3d^{10}$; writing 3d before 4s is also right
- **Cr [Ar] $4s^1\ 3d^5$, Cu [Ar] $4s^1\ 3d^{10}$**: half-filled and filled d are extra stable (symmetry; exchange energy: 5 parallel spins give 10 pairs)
- Cr's 15th electron: third in 3p, n = 3, l = 1, m = +1, s = +½ (filling m = −1, 0, +1 in turn)
- ions: lose from the **outermost shell** (4s before 3d); gain into the next vacancy
- Na^+ = [Ne], Cl^- = [Ar]; Ti^{2+} [Ar] $3d^2$, Ti^{4+} [Ar]
- Fe^{2+} [Ar] $3d^6$; Fe^{3+} [Ar] $3d^5$ (half-filled, more stable)
- Cr^{3+} [Ar] $3d^3$: 3 unpaired; Cu^{2+} [Ar] $3d^9$: 1 unpaired
- [Ar] $3d^{10}\ 4s^2$ is zinc: 30 p, 30 e; group 12, d block, period 4; Zn^{2+} smaller
- block = subshell of the last electron: s (groups 1–2), p (13–18), d, f

COMMON MISTAKES

✗ Fe^{2+} = [Ar] $4s^2\ 3d^4$
✓ 4s goes first: [Ar] $3d^6$.

✗ Cr = [Ar] $4s^2\ 3d^4$, Cu = [Ar] $4s^2\ 3d^9$
✓ $4s^1\ 3d^5$ and $4s^1\ 3d^{10}$.

✗ Pauli: two electrons can't be in the same space
✓ no two have the same four quantum numbers.

✗ the principal quantum number came from Pauli
✓ from Bohr (1913).

✗ Bohr's model, 1931; “Panchen” series
✓ 1913; Paschen.

✗ Rutherford discovered the proton in 1911
✓ 1911 the nucleus; the proton 1917–19.

✗ Planck: light is wave and particle
✓ Planck: energy in quanta, $E = h\nu$; photons are Einstein's (1905).

✗ orbit and orbital are the same
✓ an orbital is a 3D region of probability, not a path.

✗ 4s fills first so it empties last
✓ 4s empties first.