CHEMISTRY NERD

ATOMIC STRUCTURE

Detailed JEE Advanced-Level Notes

Complete chapter coverage
Fundamental particles • Atomic models • Electromagnetic radiation • Photoelectric effect • Bohr theory • Hydrogen spectrum • de Broglie waves • Heisenberg uncertainty • Quantum numbers • Orbitals and nodes • Electronic configuration • Spin and magnetic properties • Advanced solved examples and practice set

How to study: Separate classical ideas from quantum-mechanical results. Track units carefully, identify the assumptions behind each formula, and distinguish an orbit (Bohr model) from an orbital (quantum model).

Prepared for JEE Main & JEE Advanced aspirants

1. Fundamental Particles and Atomic Notation

An atom contains a compact, positively charged nucleus and electrons occupying the space around it. The nucleus contains protons and neutrons; electrons are described by quantum states.

For an atom or ion written as $^{A}_{Z}X^{q}$:
Z = atomic number = number of protons; **A** = mass number = protons + neutrons; **N** = A – Z; for charge q in units of e, electrons = Z – q. A positive q means electron loss; a negative q means electron gain.

Fundamental particle properties

Particle	Symbol	Charge	Approx. mass (kg)	Mass (u)
Electron	e■	–1.602×10■¹■ C	9.109×10■³¹	0.0005486
Proton	p■	+1.602×10■¹■ C	1.673×10■²■	1.0073
Neutron	n■	0	1.675×10■²■	1.0087

The proton and neutron masses are approximately 1 u, while electron mass is about 1/1836 of proton mass. Nearly all atomic mass is concentrated in the nucleus.

Isotopes, isobars and isotones

• **Isotopes:** same Z, different A (different neutron number); chemical properties are usually similar.

• **Isobars:** same A, different Z.

• **Isotones:** same neutron number N, different Z.

Average atomic mass is an abundance-weighted average of isotopic masses: average mass = Σ(f■m■), with Σf■ = 1.

2. Discovery of Subatomic Particles and Atomic Models

Thomson's cathode-ray experiment

Cathode rays are streams of negatively charged particles. Their deflection by electric and magnetic fields established the negative charge of electrons. The charge-to-mass ratio e/m was measured; the value is independent of the cathode material and gas used.

Millikan oil-drop experiment

Charged oil drops were suspended between plates. By balancing gravitational and electrical forces, Millikan determined the elementary charge magnitude e. Combining e with e/m gives electron mass.

For a stationary drop: qE = mg (with buoyancy and drag treated appropriately in a full experiment). Charges on drops were integral multiples of e.

Rutherford alpha-particle scattering

Most alpha particles passed through thin gold foil; a small fraction were deflected strongly and a very few rebounded. Conclusions: most of the atom is empty space; positive charge and most mass occupy a tiny, dense nucleus.

The nuclear model could not explain atomic stability or discrete line spectra using classical electrodynamics: an orbiting accelerating electron should radiate energy continuously and spiral into the nucleus.

Limitations of early models

• Thomson's model could not explain large-angle alpha scattering.

• Rutherford's model could not explain stability and line spectra.

• Bohr's model explains hydrogen-like one-electron species well but is inadequate for multi-electron atoms and fine details of spectra.

3. Electromagnetic Radiation and Wave Parameters

Electromagnetic radiation propagates as coupled oscillating electric and magnetic fields. In vacuum, all electromagnetic waves travel at speed c.

$c = \nu\lambda$; $c \approx 3.00 \times 10^{8}$ m s^{-1}
Wavenumber ($\bar{\nu}$) = $1/\lambda$ (commonly in cm^{-1} when λ is in cm)
Period $T = 1/\nu$

Frequency ν is measured in hertz (s^{-1}); wavelength λ is a length. Frequency and wavelength are inversely proportional in a fixed medium. In vacuum, c is constant.

Electromagnetic spectrum

Increasing frequency and energy: radio → microwave → infrared → visible → ultraviolet → X-ray → gamma ray. Wavelength decreases in this direction.

Visible light is approximately 400–700 nm (limits vary by convention). Violet has higher frequency and energy than red.

Energy and momentum of a photon

$E = h\nu = hc/\lambda$; $p = h/\lambda = E/c$
$h = 6.62607015 \times 10^{-34}$ J s

Photon energy is quantized. One mole of photons of frequency ν has energy $N_A h\nu$. For wavelength λ, molar photon energy = $N_A hc/\lambda$.

Useful conversion: $E(eV) = 1240/\lambda(nm)$, approximately.

4. Planck's Quantum Theory and Blackbody Radiation

Classical physics failed to describe the observed spectrum of a hot blackbody at short wavelengths (ultraviolet catastrophe). Planck proposed that oscillators exchange energy in discrete packets.

Allowed oscillator energy: $E_n = nh\nu$, where n = 0, 1, 2, ...
Energy difference between adjacent levels: $\Delta E = h\nu$

The energy of a photon is $h\nu$. Quantization of energy was a conceptual turning point leading to quantum theory.

5. Photoelectric Effect

When light of sufficiently high frequency strikes a metal, electrons are emitted. Key observations: below threshold frequency no emission occurs regardless of intensity; above threshold, maximum kinetic energy depends on frequency, while photocurrent (under suitable conditions) depends on intensity.

Einstein equation: $h\nu = \phi + K_{max}$
$\phi = h\nu_0$ = work function; ν_0 = threshold frequency
$K_{max} = \frac{1}{2} m_e v_{max}^2 = eV_{stop}$

Increasing intensity at fixed ν above threshold increases the number of emitted electrons (photocurrent), not Kmax. Increasing frequency increases Kmax.

Graph interpretations

• Kmax versus ν: straight line of slope h, x-intercept ν_0.

• Stopping potential versus ν: slope h/e, x-intercept ν_0.

• Photocurrent versus applied potential: saturation current rises with intensity; stopping potential is unchanged by intensity at fixed frequency.

Worked example

A metal has work function 2.0 eV and is illuminated with 400 nm light. Photon energy ≈ 1240/400 = 3.10 eV. Kmax = 3.10 − 2.0 = **1.10 eV**; stopping potential magnitude = 1.10 V.

6. Atomic Spectra and Hydrogen Spectrum

An excited atom can emit radiation when an electron moves from a higher energy state to a lower one. The photon energy equals the energy difference: hν = Ehigh – Elow.

Rydberg equation for hydrogen:
$1/\lambda = R_H(1/n_{\blacksquare}^2 - 1/n_{\blacksquare}^2)$, $n_{\blacksquare} > n_{\blacksquare}$
$R_H \approx 1.097 \times 10_{\blacksquare}\ m_{\blacksquare}^{-1}$

For hydrogen-like ions, replace R_H with the appropriate reduced-mass Rydberg constant or use the Bohr energy relation with Z^2.

Spectral series

Series	Final level $n_{\blacksquare}$	Region (approx.)
Lyman	1	Ultraviolet
Balmer	2	Visible / near UV
Paschen	3	Infrared
Brackett	4	Infrared
Pfund	5	Infrared

For a series, the series limit occurs as $n_{\blacksquare} \to \infty$. The shortest wavelength corresponds to maximum photon energy and the series limit.

Number of spectral lines

If an electron is initially at level n and all downward transitions are possible, maximum distinct lines = n(n – 1)/2.

This counts all possible pairs of levels. If only selected transitions are allowed or observed, the actual number may be smaller.

7. Bohr Model for Hydrogen-like Species

A hydrogen-like species contains one electron: H, $He_{\blacksquare}$, $Li^{2}_{\blacksquare}$, $Be^{3}_{\blacksquare}$, etc. Bohr's model assumes circular stationary orbits with quantized angular momentum.

Angular momentum: $mvr = nh/(2\pi) = n_{\blacksquare}$
Radius: $r_{\blacksquare} = a_{\blacksquare}\ n^2/Z$
Energy: $E_{\blacksquare} = -13.6\ Z^2/n^2$ eV per atom
Velocity: $v_{\blacksquare} = 2.18 \times 10_{\blacksquare}\ (Z/n)\ m\ s_{\blacksquare}^{-1}$

$a_{\blacksquare} = 0.529$ Å is the Bohr radius for hydrogen ground state. These expressions use the infinite-nuclear-mass approximation; reduced mass gives a small correction.

Important consequences

- $r_{\blacksquare} \propto n^2/Z$; higher n means a larger orbit, and higher Z contracts the orbit.
- $|E_{\blacksquare}| \propto Z^2/n^2$; more negative energy means a more tightly bound electron.
- Ionization energy from level n = $13.6Z^2/n^2$ eV.
- Energy required for transition $i \to f$ is $E_f - E_i$; absorption requires positive energy.

Worked example: $He_{\blacksquare}$

For $He_{\blacksquare}$ in n = 2: $E_{\blacksquare} = -13.6(4)/4 = -13.6$ eV. Its radius is $r_{\blacksquare} = 0.529 \times 4/2$ Å = 1.058 Å. Ionization from n=2 requires 13.6 eV.

Excitation and ionization

Excitation raises an electron to a higher bound level; ionization takes it to n = ∞ (E = 0). Do not confuse excitation energy with ionization energy.

For an electron initially in level $n_{\blacksquare}$, energy needed to reach $n_{\blacksquare}$ is $13.6Z^2(1/n_{\blacksquare}^2 - 1/n_{\blacksquare}^2)$ eV when $n_{\blacksquare} > n_{\blacksquare}$.

8. de Broglie Matter Waves

De Broglie proposed that moving particles have wave character. The wavelength is inversely proportional to momentum.

$\lambda = h/p = h/mv$ (non-relativistic)
For a particle of kinetic energy K: $\lambda = h/\sqrt{(2mK)}$
For an electron accelerated through potential V: $\lambda = h/\sqrt{(2m_e eV)}$

For an electron, $\lambda(\text{Å}) \approx 12.27/\sqrt{V}$ when V is in volts, under the non-relativistic approximation. At high accelerating voltages, relativistic correction is needed.

Bohr quantization from standing waves

A stable circular matter wave must fit an integer number of wavelengths around the circumference: $2\pi r = n\lambda$. Substituting $\lambda = h/mv$ gives $mvr = nh/2\pi$, Bohr's angular-momentum condition.

Worked example

An electron is accelerated through 150 V. $\lambda \approx 12.27/\sqrt{150}$ Å ≈ **1.00 Å** (non-relativistic estimate).

9. Heisenberg Uncertainty Principle

It is impossible to specify simultaneously and exactly both the position and momentum components of a quantum particle. This is a fundamental property, not merely an instrument defect.

$\Delta x \, \Delta p_{\blacksquare} \geq \blacksquare/2 = h/(4\pi)$
$\Delta E \, \Delta t \geq \blacksquare/2$ (energy-time form; interpretation differs from position-momentum observables)

A more localized wave packet requires a broader momentum distribution. For a particle of mass m, $\Delta p = m\Delta v$ in the non-relativistic case.

Implications for electrons

• An electron cannot have a precise classical trajectory in an atom.

• The idea of fixed Bohr paths is not the modern quantum description.

• Orbitals represent probability distributions, not physical tracks.

Order-of-magnitude estimate: confining an electron to a region of size Δx gives a minimum momentum uncertainty of roughly $\blacksquare/(2\Delta x)$, and hence a nonzero kinetic-energy scale.

10. Quantum Mechanical Model and Orbitals

The electron is described by a wavefunction ψ. The probability density is $|\psi|^2$; the probability of finding the electron in a volume element $d\tau$ is $|\psi|^2 d\tau$. A normalized wavefunction satisfies $\int |\psi|^2 d\tau = 1$.

An orbital is a one-electron spatial wavefunction (with spin treated separately). It is not an orbit. Orbitals are characterized by quantum numbers n, l and m_l; an electron also has spin quantum number m_s.

Four quantum numbers

Quantum number	Allowed values	Meaning
Principal n	1, 2, 3, ...	Shell, energy scale and size
Azimuthal l	0 to n–1	Subshell; orbital angular momentum magnitude
Magnetic m_l	–l to +l	Orientation component; 2l+1 values
Spin m_s	+½ or –½	Electron spin projection

Subshell labels: l = 0,1,2,3 correspond to s,p,d,f. Number of orbitals in a subshell = 2l+1; maximum electrons = 2(2l+1).

For a shell n: number of orbitals = n^2; maximum electrons = $2n^2$. For a subshell l: orbitals = 2l+1; maximum electrons = 2(2l+1).

Allowed combinations: quick checks

• For n = 3, l can be 0, 1 or 2; 3f is not allowed.

• For l = 2, m_l = –2, –1, 0, +1, +2.

• A 4p electron has n=4, l=1, and m_l = –1, 0 or +1; m_s = ±½.

• No two electrons in an atom can have the same set of all four quantum numbers (Pauli principle).

11. Shapes, Nodes and Probability

Orbital shapes

• **s orbitals:** spherical; one orbital per s subshell.

• **p orbitals:** dumbbell-shaped; three orientations p■, p■, p_z.

• **d orbitals:** five orbitals; four are commonly clover-like, while d_z² has two lobes and a toroidal ring.

• **f orbitals:** seven orbitals with more complex angular shapes.

The sign or color convention of orbital lobes represents the phase of the wavefunction, not positive and negative electric charge.

Nodes

Total number of nodes = n – 1
Angular (directional) nodes = l
Radial nodes = n – l – 1

A node is a surface or region where the wavefunction, and therefore probability density, is zero. Radial nodes are spherical surfaces; angular nodes are planes or cones depending on l and m_l.

Examples: 2s has 1 radial node; 2p has 1 angular node and 0 radial nodes; 3p has 1 radial and 1 angular node; 3d has 2 angular and 0 radial nodes.

Radial probability

The probability of finding an electron between r and r+dr is proportional to $4\pi r^2|R(r)|^2dr$ for a spherically symmetric orbital. The radial distribution function can have maxima; the most probable radius is not necessarily the expectation value of r.

12. Energies of Orbitals and Penetration

For a hydrogen-like one-electron species, energy depends only on n in the non-relativistic model. In multi-electron atoms, electron-electron repulsion and shielding make orbital energies depend on both n and l.

Penetration and shielding

Penetration describes how much electron density is found close to the nucleus. For a given shell, s penetrates more than p, p more than d, and d more than f. Greater penetration generally means stronger nuclear attraction and lower energy.

Typical energy order within a shell: ns < np < nd < nf (for multi-electron atoms).

The (n+l) rule is a useful approximate ordering: lower n+l generally fills first; for equal n+l, lower n fills first. It is a guideline, not an absolute law; close energies and electron-electron effects cause exceptions.

Hydrogen-like versus multi-electron

• Hydrogen-like: all orbitals with same n are degenerate in the simple model.

• Multi-electron: subshells of same n generally differ in energy because penetration and shielding differ.

• External fields can split degeneracies (Stark and Zeeman effects).

13. Electronic Configuration and Filling Rules

Aufbau principle

Electrons occupy available orbitals in order of increasing energy, using the approximate (n+l) rule.

Pauli exclusion principle

An orbital can contain at most two electrons, and they must have opposite spins. No two electrons in an atom share all four quantum numbers.

Hund's rule of maximum multiplicity

In degenerate orbitals, electrons occupy separate orbitals with parallel spins before pairing. This reduces electron-electron repulsion and gives a more stable arrangement.

Common filling sequence

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p

Capacities: s^2, p■, d^1■, f^1■. A subshell's superscript is the number of electrons in it.

Important exceptions

Some transition elements show configurations that differ from a naive Aufbau prediction because the relevant subshell energies are close and total energy depends on several effects. Common textbook ground-state configurations include:

• Cr (Z=24): [Ar] 3d■ $4s^1$ (not [Ar] 3d■ $4s^2$).

• Cu (Z=29): [Ar] $3d^1$■ $4s^1$ (not [Ar] 3d■ $4s^2$).

Do not treat 'half-filled and fully-filled subshell stability' as a universal standalone rule that predicts every configuration. Use experimentally established ground-state configurations where required.

Cations of transition metals

When transition-metal cations form, electrons are removed from the orbital with the highest principal quantum number first. Thus 4s electrons are removed before 3d electrons: Fe = [Ar]3d■$4s^2$; Fe^2■ = [Ar]3d■; Fe^3■ = [Ar]3d■.

14. Magnetic Properties and Spin

Paired electrons have opposite spins and their spin magnetic moments cancel approximately. Species with one or more unpaired electrons are paramagnetic; species with all electrons paired are diamagnetic.

For many introductory problems, spin-only magnetic moment is:

$\mu = \sqrt{[n(n+2)]}$ BM, where n = number of unpaired electrons and BM is Bohr magneton.

The formula is a spin-only approximation; orbital contributions and spin-orbit coupling can matter, especially for heavier elements.

Examples

• N atom: $1s^2 2s^2 2p^3$ has 3 unpaired electrons; paramagnetic.

• Ne atom: $1s^2 2s^2 2p$■ has no unpaired electrons; diamagnetic.

• Fe^3■ (free-ion high-spin d■): 5 unpaired electrons; spin-only $\mu = \sqrt{35}$ BM.

15. Solved JEE Advanced Illustrations

Illustration 1: hydrogen-like ion

Find the wavelength for the n=3 → n=2 transition in He■. Energy difference = $13.6 \times 4(1/2^2 - 1/3^2) = 54.4(5/36) = 7.56$ eV. $\lambda \approx 1240/7.56 =$ **164 nm**.

Illustration 2: photoelectric effect

A metal of work function 2.2 eV is illuminated by 300 nm radiation. Photon energy = 1240/300 = 4.13 eV. Kmax = 4.13–2.2 = 1.93 eV; stopping potential = 1.93 V.

Illustration 3: quantum numbers and capacity

For n=4, l=2 is a 4d subshell. It has 2l+1=5 orbitals and maximum capacity 10 electrons. Its radial nodes = 4–2–1=1; angular nodes =2; total nodes =3.

Illustration 4: uncertainty

If $\Delta x = 1.0\times10^{-1}$ m, minimum $\Delta p = \hbar/(2\Delta x) = 5.27\times10^{-2}$ kg m s^{-1}. The corresponding non-relativistic Δv scale is $\Delta p/m \approx 5.79\times10$ m s^{-1}.

Illustration 5: spectral lines

An electron initially at n=5 can undergo transitions among levels 1 through 5. Maximum number of distinct lines = 5×4/2 = **10**.

16. Practice Questions: JEE Advanced Level

1. An ion X^{3} has 23 electrons and mass number 56. Find its atomic number, proton number and neutron number.

2. Calculate the energy (in eV) and wavelength (in nm) of a photon having frequency 6.0×10^{1} Hz.

3. Light of wavelength 248 nm falls on a metal of work function 2.0 eV. Find maximum kinetic energy and stopping potential.

4. Calculate the radius and energy of the n=3 orbit of Li^{2} using Bohr's model.

5. For a hydrogen atom, calculate the wavelength emitted in the transition n=4 to n=2. Identify the spectral series.

6. An electron is accelerated from rest through 100 V. Estimate its de Broglie wavelength in Å.

7. For a 5d orbital, determine n, l, possible m_l values, number of radial nodes and angular nodes.

8. How many orbitals and maximum electrons are present in the shell n=4?

9. An electron in a hydrogen atom is excited to n=6. How many distinct emission lines are possible on complete de-excitation?

10. Write the ground-state configurations of Cr, Cu, Fe^{2} and Fe^{3}. State which are paramagnetic.

11. A hydrogen-like ion has ionization energy 54.4 eV from its ground state. Identify Z and calculate its ground-state radius.

12. An electron's position uncertainty is 2.0×10^{-1} m. Find the minimum uncertainty in its velocity.

13. For a 3p electron, list allowed quantum numbers and calculate radial, angular and total nodes.

14. A photon has energy 10.2 eV. Can it excite ground-state hydrogen? If yes, specify the transition.

15. A hydrogen atom in n=3 absorbs a photon of 1.89 eV. Determine the final principal quantum number, if absorption is possible.

17. Answer Key with Explanations

1. X^{3} has 23 electrons, so neutral Z=26. Protons=26; neutrons=56−26=30.

2. $E=h\nu=6.626\times10^{-3}\times6.0\times10^{1}=3.976\times10^{-1}$ J = 2.48 eV. $\lambda=c/\nu=5.00\times10^{-}$ m = 500 nm.

3. Photon energy=1240/248=5.00 eV. Kmax=5.00−2.00=3.00 eV; stopping potential magnitude=3.00 V.

4. Li^{2} has Z=3. $r=0.529\times9/3$ Å=1.587 Å. $E=-13.6\times9/9=-13.6$ eV.

5. $1/\lambda=R(1/4-1/16)=3R/16$; $\lambda\approx486$ nm. Balmer series.

6. λ(Å)=$12.27/\sqrt{100}$=1.227 Å.

7. n=5, l=2; m_l=−2,−1,0,+1,+2. Radial nodes=5−2−1=2; angular nodes=2; total=4.

8. Orbitals=$n^{2}=16$; maximum electrons=$2n^{2}=32$.

9. Lines=6×5/2=15.

10. Cr=[Ar]$3d^{5}4s^{1}$ (paramagnetic); Cu=[Ar]$3d^{10}4s^{1}$ (paramagnetic); Fe^{2}=[Ar]$3d^{6}$ (paramagnetic); Fe^{3}=[Ar]$3d^{5}$ (paramagnetic).

11. $13.6Z^{2}=54.4$, so $Z^{2}=4$ and Z=2 (He). $r=0.529/2=0.2645$ Å.

12. $\Delta v\geq\hbar/(2m\Delta x)=1.055\times10^{-3}/[2\times9.109\times10^{-31}\times2.0\times10^{-1}]\approx2.90\times10$ m s^{-1}.

13. n=3, l=1; $m_l=-1,0,+1$; $m_s=\pm½$. Radial nodes=1; angular=1; total=2.

14. Yes. 10.2 eV equals the hydrogen n=1 to n=2 energy gap (10.2 eV).

15. For n=3, $E=-13.6/9=-1.511$ eV. Absorption of 1.89 eV gives Efinal≈+0.379 eV, above zero; this is enough to ionize the atom, not reach a bound level. The electron is ionized with ≈0.379 eV kinetic energy.

18. Rapid Revision Sheet

Radiation: $c=\nu\lambda$; $E=h\nu=hc/\lambda$; $p=h/\lambda$.
Photoelectric: $K_{max}=h\nu-\phi=eV_{stop}$.
Hydrogen-like Bohr: $r_n=0.529n^2/Z$ Å; $E_n=-13.6Z^2/n^2$ eV.
Spectrum: $1/\lambda=RZ^2(1/n_f^2-1/n_i^2)$ (hydrogen-like approximation).
Matter waves: $\lambda=h/p$; electron accelerated through V: $\lambda(Å)\approx12.27/\sqrt{V}$.
Uncertainty: $\Delta x\Delta p_x\geq\hbar/2$.
Quantum numbers: $n=1,2,...$; $l=0,...,n-1$; $m_l=-l,...,+l$; $m_s=\pm½$.
Orbitals: shell n has n^2 orbitals and $2n^2$ electron capacity; subshell l has $2l+1$ orbitals.
Nodes: total=$n-1$; angular=l; radial=$n-l-1$.

- Always distinguish photon energy from molar photon energy.
- Use the hydrogen-like Bohr formula only for one-electron species.
- For quantum-number questions, check allowed ranges before counting.
- For configurations, apply Aufbau, Pauli and Hund, then account for known exceptions.
- For photoelectric questions, intensity controls current; frequency controls Kmax.

Constants: $h=6.62607015\times10^{-34}$ J s; $\hbar=h/2\pi$; $c=2.998\times10^{8}$ m s^{-1}; $e=1.602\times10^{-19}$ C; $m_e=9.109\times10^{-31}$ kg; 1 eV=1.602×10^{-19} J; $a_0=0.529$ Å; $R_H\approx1.097\times10^{7}$ m^{-1}.

Chemistry Nerd • Understand the model, master the equations, and practice the reasoning.