GATE Chemistry Revision Notes

Quantum Chemistry and Atomic Structure

WHY QUANTUM CHEMISTRY ?

Microscopic particles do not follow classical paths. Their state is described by a wavefunction, and measurement gives probabilities.

Core idea :-

A quantum state contains all available information. An operator extracts a measurable value from that state.

> state psi + operator A = measurable result

This volume builds four exam skills :

- → translate words into operators and equations
- → recognize standard model energies quickly
- → count nodes, degeneracy and allowed states
- → use approximation methods with clear logic

GATE route :-

First identify the model. Then write the eigenvalue, check quantum numbers, and only then substitute values.

Bottom recall :-

Choose the quantum model before selecting any equation or quantum number.

→ Choose the quantum model before selectin...

POSTULATES : THE MAP

1. State postulate :-

A normalized wavefunction or ket represents the state of a system. A global phase does not change the physical state.

2. Observable postulate :-

Every measurable quantity has a linear Hermitian operator. Its eigenvalues are real and are possible measurement outcomes.

3. Measurement postulate :-

Measuring A gives one eigenvalue. The probability equals the squared overlap with that eigenstate.

4. Average value :-

Repeated measurements give the expectation value, not necessarily one allowed result from a single trial.

$$\langle A \rangle = \langle \psi | A | \psi \rangle$$

5. Time evolution :-

An isolated state evolves through the time-dependent Schrodinger equation under its Hamiltonian.

Bottom recall :-

A valid postulate links states, observables, measurement probability and time evolution.

→ A valid postulate links states, observab...

WAVEFUNCTION & BORN RULE

Wavefunction psi :-

The wavefunction is a probability amplitude. It may be positive, negative or complex, but it is not directly observable.

Born interpretation :-

The quantity psi squared is probability density. A small interval dx contains probability psi(x) squared dx.

$$P(a \text{ to } b) = \int_a^b |\psi(x)|^2 \, dx$$

Normalization :-

The particle must exist somewhere in the allowed space, so total probability is one.

$$\int_{\text{all space}} |\psi|^2 \, d\tau = 1$$

Acceptable wavefunctions are :

→ single-valued and finite

→ continuous where the potential is finite

→ square-integrable and normalizable

Mistake : psi may change sign. Probability density never becomes negative.

Bottom recall :-

Probability density is nonnegative, normalized and obtained from the squared amplitude.

DIRAC BRA-KET NOTATION

Ket and bra :-

A ket |psi⟩ is a state vector. Its complex-conjugate transpose is the bra ⟨psi| .

inner product : ⟨phi | psi⟩

outer product : |psi⟩⟨phi|

Orthogonality :-

Two different eigenstates of a Hermitian operator are orthogonal when their eigenvalues are nondegenerate.

$\langle m \mid n \rangle = \delta_{mn}$

Completeness :-

A complete orthonormal set can expand any allowed state. The coefficients are probability amplitudes.

$\lvert psi \rangle = \sum_n c_n \lvert n \rangle$

$c_n = \langle n \mid psi \rangle$, $\sum c_n^2 = 1$

GATE check : if the state is already normalized, squared coefficients must add to one.

Bottom recall :-

Expansion coefficients are overlaps; their squared magnitudes add to one.

→ Expansion coefficients are overlaps; the...

OPERATORS & EIGENVALUES

Operator action :-

An operator changes a function. An eigenfunction keeps its shape and gains only a constant eigenvalue.

$$\hat{A}\,\psi_a = a\,\psi_a$$

Common one-dimensional operators :

$$\text{position } \hat{x} = x$$

$$\text{momentum } \hat{p}_x = -i\hbar\, d/dx$$

$$\text{Hamiltonian } \hat{H} = -(\hbar^2/2m)\,d^2/dx^2 + V$$

Hermitian property :-

Hermitian operators have real eigenvalues. Their eigenfunctions provide orthogonal states, so observables use Hermitian operators.

Linearity :-

$\hat{A}$ acting on a sum equals the same sum of separate actions. This allows superposition.

Mistake : an arbitrary wavefunction need not be an eigenfunction of the chosen operator.

Bottom recall :-

An eigenfunction keeps its form after the matching operator acts on it.

→ An eigenfunction keeps its form after th...

COMMUTATORS & UNCERTAINTY

Commutator :-

The commutator tests whether two operations can be performed in either order with the same result.

$$[A,B] = AB - BA$$

Compatible observables :-

If two operators commute, they can share simultaneous eigenfunctions and both values may be sharp together.

$$[x,p_x] = i\,\hbar$$

Uncertainty principle :-

Noncommuting observables cannot both have arbitrarily small spreads in the same state.

$$\delta x\ \delta p_x \geq \hbar/2$$

$$\delta A\ \delta B \geq \langle [A,B] \rangle / 2$$

This is not instrument error. It is an intrinsic spread of outcomes in a quantum state.

GATE cue :-

A Hamiltonian commuting with an operator means that observable is conserved in time.

Bottom recall :-

Commuting observables can share exact values; noncommuting pairs have intrinsic spread.

SCHRODINGER EQUATIONS

Time-dependent equation :-

This is the general equation of motion for a nonrelativistic quantum state.

$$i\,\hbar\,\frac{d\Psi}{dt} = \hat{H}\,\Psi$$

Stationary potential :-

When the potential has no time dependence, separate space and time. The spatial part satisfies an eigenvalue equation.

$$\hat{H}\,\psi = E\,\psi$$

$$\Psi(x,t) = \psi(x)\,\exp(-iEt/\hbar)$$

Stationary state :-

The phase changes with time, but Ψ squared stays constant. Therefore the probability density is time independent.

Boundary conditions :-

The wavefunction and its first derivative are continuous at a finite potential step. Infinite walls force psi to zero.

Exam route : write the potential region by region, solve, then match boundary conditions.

Bottom recall :-

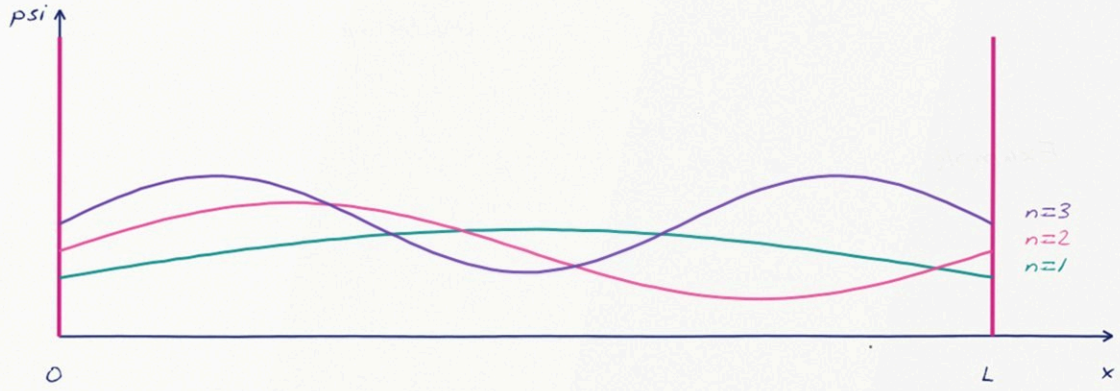
A stationary state changes phase with time while its probability density stays fixed.

→ A stationary state changes phase with ti...

INFINITE 1D BOX

Model :-

A particle moves freely between x = 0 and L. Infinite walls prevent escape and force nodes at both ends.



$$psi_n = root(2/L)\ sin(n\pi x/L)$$

$$E_n = n^2\pi^2 hbar^2/(2mL^2)$$

→ n = 1, 2, 3, ... ; zero is not allowed

→ number of internal nodes = n - 1

→ energy grows as n squared and 1/L squared

Zero-point energy is nonzero because a constant wavefunction cannot satisfy both infinite-wall boundaries.

Probability pattern :-

State n has n probability lobes. Each internal node has zero probability, while the antinodes are the most likely positions.

Bottom recall :-

Box energy grows with n squared and falls with the square of box length.

BOX : EXPECTATION VALUES

Symmetry first :-

The probability density of every stationary box state is symmetric about L/2. Therefore the mean position is L/2.

$$\langle x \rangle = L/2$$

$$\langle p_x \rangle = 0$$

Momentum spread :-

The standing wave contains equal positive and negative momentum components. Mean momentum vanishes, but its square does not.

$$\langle p_x^2 \rangle = n^2 \pi^2 \text{hbar}^2 / L^2 .$$

Useful result :-

$$\langle x^2 \rangle = L^2 (1/3 - 1/(2n^2 \pi^2))$$

A stationary box state has definite energy but not definite position or momentum.

Fast check : doubling L divides every energy by four and doubles all spatial scales.

Bottom recall :-

Symmetry gives mean position L over 2 and zero mean momentum in the box.

→ Symmetry gives mean position L over 2 an...

2D & 3D BOXES

Separable motion :-

For rectangular boundaries, the total wavefunction is a product of one-dimensional functions. Total energy is the sum of directional energies.

$$E = (\pi^2 \hbar^2/2m)(n_x^2/L_x^2 + n_y^2/L_y^2 + n_z^2/L_z^2)$$

Cubic box :-

Equal side lengths make energy depend only on the sum of three squared quantum numbers.

$$E \text{ proportional to } n_x^2 + n_y^2 + n_z^2$$

Degeneracy :-

Different quantum-number triples may have the same energy. Permuting unequal numbers gives distinct spatial states.

→ (1,1,2) has three spatial permutations

→ (1,2,3) has six spatial permutations

→ include spin only when the question asks

A rectangular distortion usually removes permutation degeneracy because the three length denominators differ.

Fast example :-

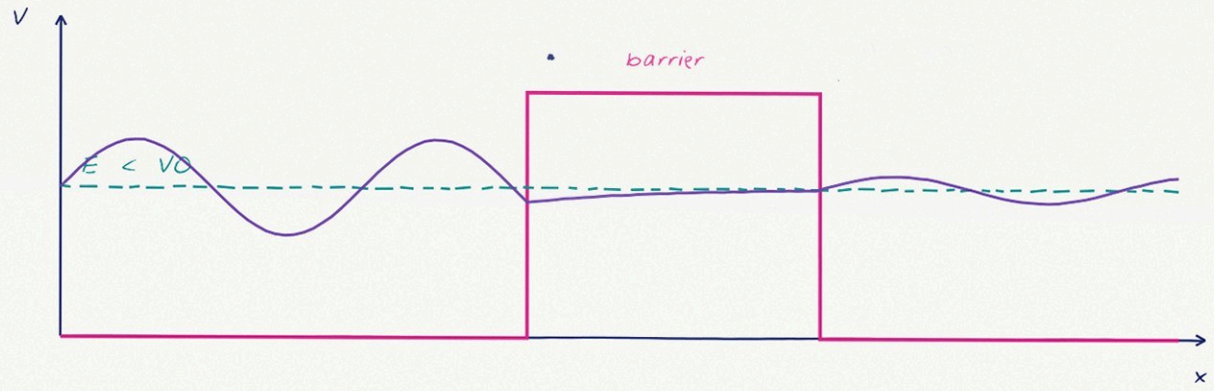
In a cube, (1,1,3) and (1,3,1) are degenerate. In a box with unequal sides, compare the full weighted sums.

→ Count every distinct permutation before...

FINITE WELL & TUNNELLING

Finite well :-

A finite wall does not force the wavefunction to zero. Bound-state tails penetrate into the classically forbidden region.



Tunnelling :-

A particle may cross a barrier even when its energy is below the barrier height. The wave decays inside but remains nonzero beyond it.

$$T \approx \exp(-2\kappa a)$$

$$\kappa = \sqrt{2m(V_0 - E)}/\hbar$$

→ wider barrier gives smaller transmission

→ higher barrier gives smaller transmission

→ lighter particle tunnels more easily

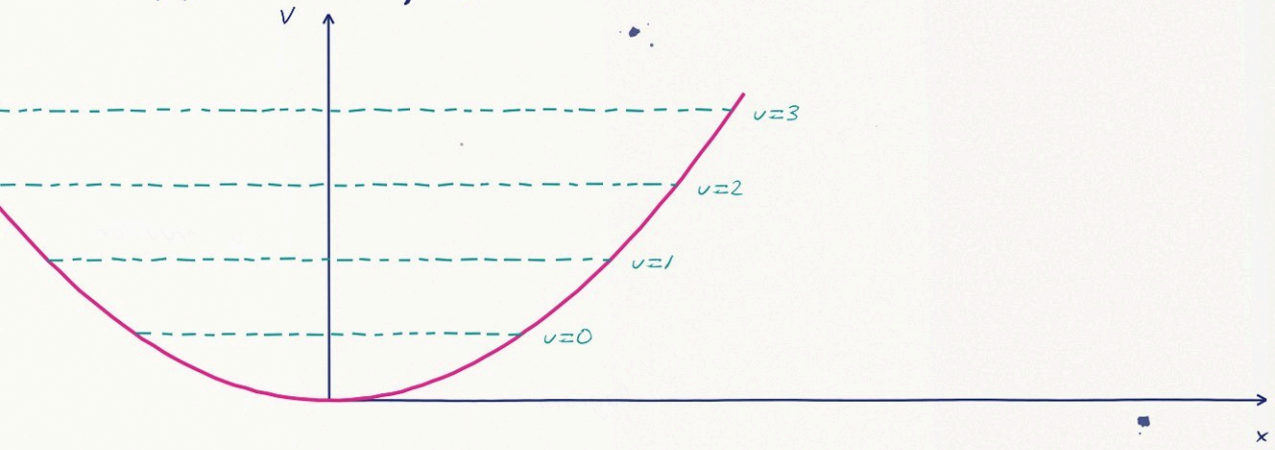
Applications include alpha decay, scanning tunnelling microscopy and proton transfer.

→ Tunnelling increases for a thinner, lowe...

HARMONIC OSCILLATOR

Model :-

Near a stable equilibrium, a smooth molecular potential is approximately parabolic. This models small bond vibrations.



$$V(x) = (1/2)\kappa x^2$$

$$E_v = (v+1/2)\hbar\omega$$

$$\omega = \sqrt{\kappa/\mu}$$

→ $v = 0, 1, 2, \ldots$

→ adjacent levels are equally spaced

→ zero-point energy = $\hbar\omega / 2$

A heavier reduced mass lowers the frequency and compresses the vibrational energy spacing.

Classical turning points :-

At $V = E$, classical speed is zero; quantum probability still extends beyond the turning point.

A stronger bond has larger κ, so it gives a higher vibrational frequency when reduced mass is unchanged.

OSCILLATOR WAVEFUNCTIONS

Hermite form :-

Each eigenfunction is a Gaussian envelope multiplied by a Hermite polynomial. Higher states oscillate more often.

$$\psi_v(x) = N_v H_v(\alpha x) \exp(-\alpha^2 x^2/2)$$

$$H_0 = 1, \quad H_1 = 2q, \quad H_2 = 4q^2 - 2$$

Node rule :-

The v-th harmonic-oscillator state has v nodes. Its parity alternates: even v gives even parity.

Selection rule :-

$$\delta v = \pm 1 \quad \text{for harmonic IR transitions}$$

Anharmonic reality :-

Real bonds dissociate, so level spacing decreases at high v. Weak overtone transitions and Delta v above one become possible.

Parity shortcut :-

The expectation value of any odd operator vanishes in a state of definite parity over symmetric limits.

This shortcut removes many oscillator integrals before any algebra begins.

Bottom recall :-

The oscillator state v has v nodes and parity that alternates with v.

ANGULAR MOMENTUM

Quantum vector :-

Angular momentum has a definite total magnitude and one definite laboratory component, usually chosen as z.

$$L^2 \; |l,m\rangle = l(l+1)\hbar^2 \; |l,m\rangle$$

$$L_z \; |l,m\rangle = m\hbar \; |l,m\rangle$$

→ $l = 0, 1, 2, \ldots$

→ $m = -l, \ldots, 0, \ldots, +l$

→ one l value contains $2l+1$ orientations

Commutators :-

$$[L_x, L_y] = i\hbar L_z$$

The three Cartesian components cannot be simultaneously exact, but L squared commutes with every component.

Ladder operators :-

L-plus raises m by one and L-minus lowers m by one without changing l.

Magnitude and direction :-

$$L = \hbar \sqrt{l(l+1)}$$

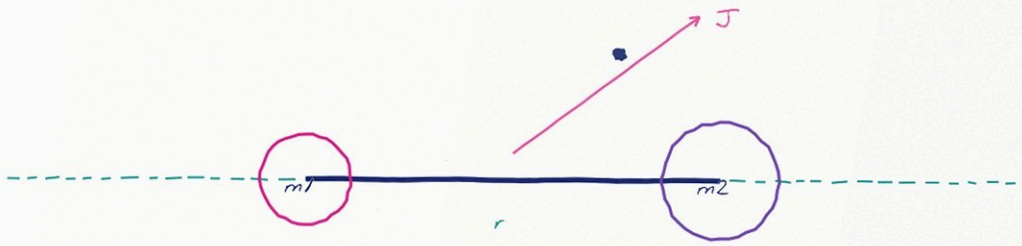
The angular functions are spherical harmonics Y-lm. Their angular nodes and orientations follow l and m.

→ For angular momentum, magnitude uses l w...

RIGID ROTOR

Model :-

A rigid diatomic molecule rotates with a fixed bond length. Its moment of inertia controls the rotational spacing.



$$I = \mu r_e^2$$

$$E_J = \text{hbar}^2 J(J+1)/(2I)$$

→ $J = 0, 1, 2, \ldots$

→ degeneracy of level $J = 2J+1$

→ spacing $E(J+1)-E(J)$ grows with J

Microwave selection rule :-

$$\delta J = +-1$$

Only molecules with a permanent dipole show a pure rotational absorption spectrum.

Rotational constant :-

$$\tilde{B} = h/(8\pi^2 I c)$$

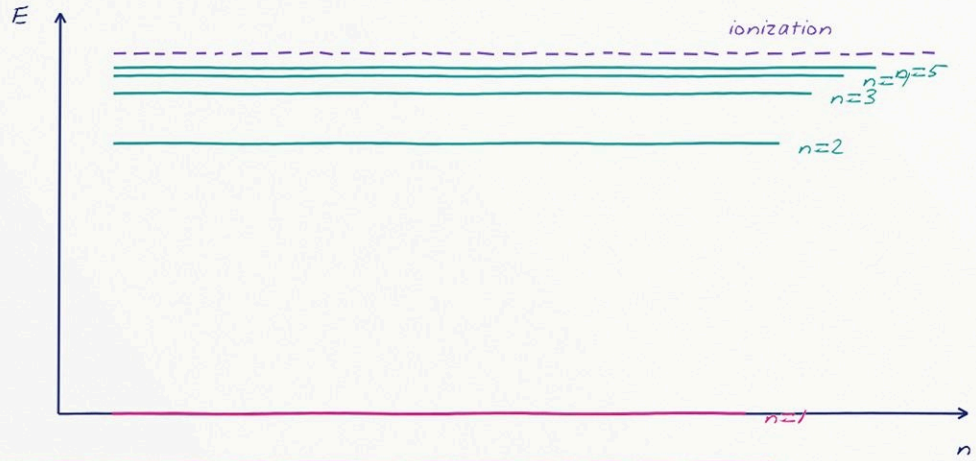
Adjacent absorption lines are separated by $2\tilde{B}$. A heavier isotopologue has larger I and smaller spacing.

→ A heavier isotopologue has larger moment...

HYDROGEN-LIKE ATOM

Coulomb problem :-

An electron moves in the spherical Coulomb field of a nucleus with charge +Ze. Separation gives radial and angular equations.



$$E_n = -13.6\ Z^2/n^2\ \text{eV}$$

→ n = 1, 2, 3,... controls energy and size

→ energy depends only on n in Coulomb field

→ ionization limit is E = 0

Increasing Z makes the state more tightly bound and contracts the typical orbital size by roughly 1/Z.

Degeneracy :-

For a fixed n, hydrogen has n^2 spatial states. Including the two spin projections gives $2n^2$ states.

Radius scale :-

$$\text{typical } r \text{ proportional to } n^2 a_0/Z$$

→ Hydrogenic binding grows as Z squared an...

ATOMIC QUANTUM NUMBERS

The four labels :-

→ n : shell, energy and radial scale

→ l : subshell and orbital angular momentum

→ m_l : spatial orientation

→ m_s : spin projection, $+1/2$ or $-1/2$

Allowed ranges :-

$l = 0$ to $n-1$; $m_l = -l$ to $+l$

Node counting :-

total nodes $= n-1$

angular nodes $= l$

radial nodes $= n-l-1$

Orbital capacity :-

A subshell contains $2l+1$ orbitals and holds $2(2l+1)$ electrons after spin is included.

Mistake : a 2d or 3f orbital is impossible because l cannot reach n.

Bottom recall :-

Total, angular and radial nodes are $n-1$, l and $n-l-1$ respectively.

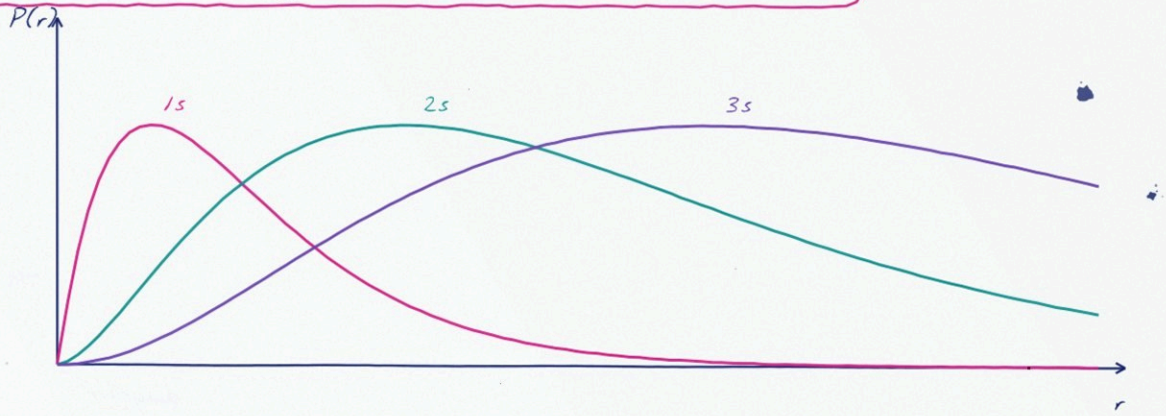
→ Total, angular and radial nodes are $n-1$,...

RADIAL DISTRIBUTION

What is plotted ?

The radial probability $P(r)dr$ gives the chance of finding the electron within a spherical shell of thickness dr.

$$P(r) = r^2 \; R_{n,l}(r)^2$$



Most probable radius :-

It is the r value at a peak of $P(r)$, not necessarily the mean radius.

hydrogen 1s peak : $r = a_0$

Penetration :-

For the same n, lower l orbitals penetrate closer to the nucleus. Thus s penetrates more than p, then d, then f.

Greater penetration usually means lower energy in multi-electron atoms because nuclear attraction is less screened.

Bottom recall :-

Greater penetration lowers orbital energy in a multi-electron atom.

→ Greater penetration lowers orbital energ...

SPIN, PAULI & DETERMINANTS

Electron spin :-

Spin is intrinsic angular momentum. An electron has s = 1/2 and two allowed projections.

$$S^2 = s(s+1)\hbar^2; \quad S_z = m_s\hbar$$

Pauli exclusion principle :-

No two electrons in one atom may share all four quantum numbers. A spatial orbital holds at most two opposite spins.

Antisymmetry :-

Exchanging two electrons changes the sign of the total electronic wavefunction. A Slater determinant guarantees this property.

$$\Psi = (1/\sqrt{N!})\ \det[\chi_i(x_j)]$$

If two spin orbitals are identical, two determinant columns match and the determinant becomes zero. This is Pauli in algebraic form.

Orbital approximation :-

Each electron moves in an average field of the nucleus and all other electrons.

Bottom recall :-

A Slater determinant changes sign when two electron labels are exchanged.

MULTI-ELECTRON ATOMS

Why difficult ?

Electron-electron repulsion couples all coordinates. Exact separation like hydrogen is no longer possible.

Shielding and effective charge :-

Inner electrons screen nuclear attraction. A valence electron experiences an effective charge smaller than Z.

$$Z_{eff} = Z - S$$

Penetration order :-

same n : s > p > d > f penetration

Greater penetration lowers orbital energy. This removes the hydrogenic degeneracy between subshells with the same n.

Aufbau, Hund, Pauli :-

→ fill lower-energy orbitals first

→ maximize unpaired parallel spins in a subshell

→ pair only after each orbital is singly filled

Exchange stabilization helps explain Hund's rule, but the full energy also includes Coulomb repulsion.

Bottom recall :-

Shielding lowers effective nuclear charge and removes hydrogenic subshell degeneracy.

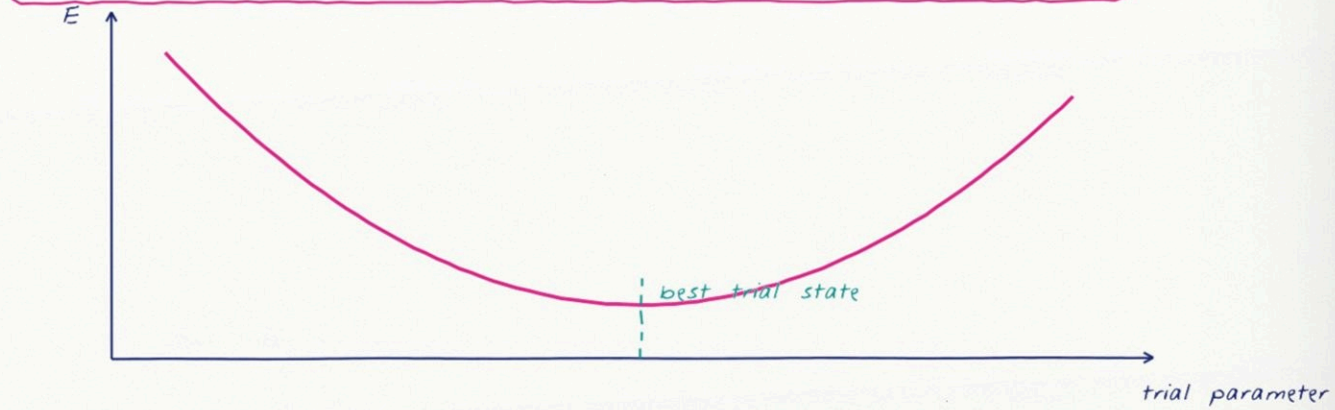
→ Shielding lowers effective nuclear charg...

VARIATION METHOD

Principle :-

For any normalized trial wavefunction, the calculated energy is never below the exact ground-state energy.

$$E_{trial} = \langle \phi \quad H \quad \phi \rangle \geq E_0$$



Procedure :

→ choose a physically sensible trial function

→ normalize it and evaluate expectation energy

→ vary its parameter to minimize the energy

What improves accuracy ?

A flexible trial form with correct symmetry, boundaries and cusp behavior usually gives a better upper bound.

Mistake : the theorem guarantees an upper bound only for the ground state unless extra orthogonality constraints are used.

Bottom recall :-

A variational energy is an upper bound to the exact ground-state energy.

→ A variational energy is an upper bound t...

LINEAR VARIATION & SECULAR EQN

Trial expansion :-

Build a trial state as a linear combination of known basis functions. The coefficients become the variables.

$$\text{phi} = \text{Sum } i \; c_i \; \text{chi}_i$$

Stationary condition :-

Minimizing the energy with respect to every coefficient gives simultaneous homogeneous equations.

$$\text{Sum } j \; (H_{ij} - E \; S_{ij}) c_j = 0$$

Nonzero solution :-

$$\det \; H - ES \; = 0$$

→ $H_{ij} = \langle \text{chi}_i \; H \; \text{chi}_j \rangle$

→ $S_{ij} = \langle \text{chi}_i \; \text{chi}_j \rangle$

If the basis is orthonormal, S becomes the identity matrix. Solving the secular determinant gives approximate energies.

This machinery leads directly to LCAO molecular orbital theory.

Bottom recall :-

A nonzero coefficient solution requires the secular determinant to vanish.

→ A nonzero coefficient solution requires...

PERTURBATION THEORY

Split the Hamiltonian :-

Start from an exactly solvable system H-zero, then add a small correction lambda times H-prime.

$$H = H_0 + \lambda H'$$

First-order energy :-

$$E_n^{(1)} = \langle n^{(0)} | H' | n^{(0)} \rangle$$

The first correction is the expectation value of the perturbation in the unperturbed state.

First-order state :-

$$|n^{(1)}\rangle = \text{Sum } m \neq n \quad |m\rangle H'_{mn} / (E_n^0 - E_m^0)$$

When it fails :-

Ordinary nondegenerate theory fails when energy denominators vanish or the perturbation is not small.

For degeneracy, first diagonalize H-prime inside the degenerate subspace.

Two quick checks :-

→ constant H-prime shifts every level equally

→ odd H-prime gives zero in a parity eigenstate

A correction comparable to the unperturbed level spacing signals that the expansion may be unreliable.

→ First-order energy is the perturbation e...

ATOMIC UNITS

Purpose :-

Atomic units set natural electronic constants equal to one. This removes repeated constants and exposes the physics.

$$m_e = e = \hbar = 4\pi\varepsilon_0 = 1$$

Important atomic units :

→ length : $a_0 = 0.529$ angstrom

→ energy : $E_h = 27.2114$ eV

→ energy : 1 Hartree = 2 Rydberg

→ time : $\hbar/E_h = 2.42 \times 10^{-17}$ s

Hydrogen Hamiltonian :-

$$H = -(1/2)\,\nabla^2 - 1/r$$

Dimensional check :-

Convert only at the end. In atomic units, hydrogen ground energy is -1/2 Hartree, equal to -13.6 eV.

Mistake : one Rydberg is 13.6 eV, while one Hartree is 27.2 eV.

Conversion habit :-

Write the answer first in atomic units, attach the correct unit type, then multiply by the single conversion factor.

Bottom recall :-

One Hartree equals two Rydberg and about 27.2 electron volts.

→ One Hartree equals two Rydberg and about...

WORKED GATE ROUTES

Route 1 : box scaling

A one-dimensional box width changes from L to 2L. Since energy varies as 1/L squared, every level becomes one-fourth.

$$E_n(2L) / E_n(L) = 1/4$$

Route 2 : box transition

For n = 1 to n = 3, subtract energies before simplifying. The gap is proportional to 9 - 1 = 8.

$$\delta E = 8\pi^2 \hbar a r^2/(2mL^2)$$

Route 3 : isotope shift

Replacing H by D nearly doubles reduced mass. Vibrational frequency scales as inverse square root of reduced mass.

$$V_D/V_H \text{ approx } 1/\text{root}(2)$$

Route 4 : perturbation

For an odd perturbation in an even or odd state, the first-order energy correction vanishes by parity.

odd integrand over symmetric range = 0

Bottom recall :-

Scaling, parity and limiting cases should be checked before numerical substitution.

→ Scaling, parity and limiting cases shoul...

QUICK RECALL & GATE MISTAKES

Must-know results :-

→ box : E proportional to n squared / L squared

→ oscillator : E = (v+1/2)hbar omega

→ rotor : E = hbar squared J(J+1)/2I

→ hydrogenic : E = -13.6 Z squared/n squared

→ nodes : radial n-l-1, angular l

Classic mistakes :-

→ expectation value need not be an eigenvalue

→ psi can be negative; psi squared cannot

→ finite walls allow nonzero exponential tails

→ include spin degeneracy only when requested

→ variation gives an upper bound to ground E

Thirty-second checklist :-

Check normalization, boundary conditions, quantum-number ranges, degeneracy, units and the sign of energy before choosing an answer.

Preferred solve order :

→ identify model, symmetry and boundary

→ write symbolic result before numbers

→ test limiting behavior and units

Revise the model, not just the formula!

→ Final revision must test normalization,...