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COLLEGE TRB – CHEMISTRY STUDY MATERIAL

Demo file

TOPIC: Basic principles of quantum mechanics: Postulates; operator algebra; exactly- solvable systems: particle in-a-box, harmonic oscillator and the hydrogen atom, including shapes of atomic orbitals; orbital and spin angular momenta; tunneling.

Basic principles of quantum mechanics: Postulates

Specifies the State of a Quantum System – The First Postulate

- **Classical Mechanics vs Quantum Mechanics:**
  In classical mechanics, a system's state is fully determined by the specific values of coordinates and momenta—giving a precise, deterministic evolution.
  In quantum mechanics, due to the position-momentum uncertainty principle, it is impossible to know both position and momentum of a particle (like an electron) exactly at any instant. This invalidates the classical state description.

- **First Postulate of Quantum Mechanics:**
  The state of a quantum system is **completely specified by its wavefunction** $\psi(\mathbf{r}, t)$.
  All measurable information about the system is contained in ψ.
  For a single particle, ψdepends on the spatial coordinates (x, y, z) and time (t). For many particles, it depends on all their coordinates and time.

- **Meaning of the Wavefunction:**
  The square modulus $|\psi(\mathbf{r}, t)|^2$is the **probability density** of finding the particle at position $\mathbf{r}$at time t(Born interpretation).
  The wavefunction must be *square-integrable*:

$$\int_{-\infty}^{+\infty} |\psi|^2 \, d\tau = 1$$

This means the particle will be found somewhere in all space with certainty (probability 1).

- **Requirements for Valid Wavefunctions:**
    - **Single-valued:** Only one value at each point in space.
    - **Continuous:** No abrupt jumps in the function.
    - **Finite:** It does not go to infinity in any finite region.
    - It must have continuous first (and typically second) derivatives, to satisfy the Schrödinger equation.
- **Physical Meaning:**
    - A sharply peaked ψgives small position uncertainty (well-localized).
    - Sinusoidal or delocalized ψcorresponds to large uncertainty in position (Heisenberg Uncertainty in action).
- **Invalid Wavefunctions:**
    - Multi-valued, discontinuous, or infinite (not square-integrable) functions are not physically acceptable—even if they solve the math equation.

Summary:
The first postulate establishes that the wavefunction $\psi(\mathbf{r}, t)$, subject to the requirements above, provides the **complete quantum description** of a system, with probabilistic meaning given by $|\psi|^2$.

Postulate II – Observables and Operators (Correspondence Principle)

- **Observables in Quantum Mechanics:**
    - *Observable:* A physical quantity that can be measured, e.g., position, momentum, kinetic energy.
    - In classical physics, observables are always real-valued functions.
    - In quantum mechanics, **every observable corresponds to a unique linear operator** that acts on the wavefunction to extract physical information.
- **Postulate II: Correspondence Principle:**
    - **For every observable property, there is a corresponding quantum mechanical operator.**
    - This principle ensures that classical quantities are translated into quantum operators.
- **Key Operators and Formulas:**

- **Position Operator ($\hat{\mathbf{r}}$):**

$$\hat{\mathbf{r}} = (x, y, z)$$

  - Just the set of spatial coordinates as the operator.

- **Momentum Operator ($\hat{p}_x$):**

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

  - In 3 dimensions:

$$\hat{\mathbf{p}} = -i\hbar\nabla$$

- **Kinetic Energy Operator (1D):**

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

  - In 3D:

$$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$$

- **Hamiltonian Operator ($\hat{H}$) – Total Energy:**

$$\hat{H} = \hat{T} + \hat{V}$$
$$= \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]$$

- **Summary Table of Common Quantum Operators:**

Observable	Quantum Operator
Position	$\hat{\mathbf{r}} = (x, y, z)$
Momentum	$\hat{\mathbf{p}} = -i\hbar\nabla$
Kinetic Energy	$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$
Total Energy	$\hat{H} = \hat{T} + V(\mathbf{r})$

- **Key Point:**
The operator for any observable is used to extract the physical quantity from the

wavefunction, and **all operators must yield real, measurable values when acting on valid wavefunctions** (Hermitian property).

Postulates III & IV — Eigenvalue Problems and Expectation Values in Quantum Mechanics

Postulate III: Observables and Eigenvalue Equations

- **Physical Measurements Are Eigenvalues:**
  Every measurable value of an observable corresponds to an *eigenvalue* of its operator.
- **Eigenvalue Equation:**
  When an operator $\hat{A}$ acts on a special wavefunction (eigenfunction) ψ_a, it returns the function times a constant (the eigenvalue):

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

  - ψ_a — eigenstate (eigenfunction)
  - a — eigenvalue (measured quantity)
- **Physical Meaning:**
  - If a quantum system is in eigenstate ψ_a, every measurement of observable A will yield a with zero uncertainty (variance is zero).
  - For a general state (not an eigenstate), measurements yield various results distributed around an average.

Postulate IV: Expectation Value and Variance

- **Expectation Value ($\langle A \rangle$):**
  The statistical mean value of many measurements of observable A for a system in state ψ:

$$\langle A \rangle = \int \psi^* \hat{A} \psi \, d\tau$$

For an unnormalized wavefunction:

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

- **Variance and Standard Deviation:**
  The *variance* measures the spread of measurement results:

$$\text{Variance}_A = \langle A^2 \rangle - \langle A \rangle^2$$

The square root is the *standard deviation* (ΔA), indicating the typical deviation from the mean.

Expansion in Eigenstates: Orthogonality and Completeness

- **Orthogonality:**
  Eigenstates of an operator with different eigenvalues are orthogonal:

$$\int \psi_m^* \psi_n \, d\tau = \delta_{mn}$$

(δ_{mn} is the Kronecker delta.)

- **Completeness:**
  Any wavefunction can be written as a linear combination of normalized eigenstates:

$$\psi = \sum_n c_n \psi_n$$

where c_n are complex coefficients.

Example: Particle in a Box

- **Ground State Wavefunction:**

$$\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

- **Average Position:**

$$\langle x \rangle = \frac{L}{2}$$

- **Average Momentum:**

$$\langle p \rangle = 0$$

- **Average Kinetic Energy:**
  Equals the total ground state energy.

Summary:

- Measurements in quantum mechanics yield eigenvalues of operators; associated eigenfunctions define states with definite measured values.
- For general states, the average (expectation value) and the spread (variance/standard deviation) of measurement outcomes are calculated using the wavefunction and the observable's operator.
- Orthogonal eigenstates form a complete basis for expanding any possible state.

Time-Dependent vs Time-Independent Schrödinger Equation

- Time-Dependent Schrödinger Equation (TDSE):

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \hat{H}\psi(\mathbf{r}, t)$$

  - Governs how the wavefunction evolves over time.
  - Used when the system's Hamiltonian ($\hat{H}$) depends on time or for describing general quantum dynamics.

- Time-Independent Schrödinger Equation (TISE):

$$\hat{H}\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r})$$

  - Used when the Hamiltonian is constant in time (no explicit time dependence).
  - Solutions provide the *stationary state* wavefunctions (ψ_n) and their *allowed energies* (E_n).
  - These solutions can be used to build the general time-dependent solution.

Stationary States

- States that are eigenfunctions of the Hamiltonian (ψ_n):

$$\psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})e^{-iE_n t/\hbar}$$

- The probability density $|\psi_n(\mathbf{r},t)|^2$ remains constant in time.
- Energy is fixed and measurements always give E_n.
- The state evolves only by a change in phase.

Nonstationary States

- Formed by superposing several stationary states:

$$\Psi(\mathbf{r},t) = c_1\psi_1(\mathbf{r})e^{-iE_1t/\hbar} + c_2\psi_2(\mathbf{r})e^{-iE_2t/\hbar} + \cdots$$

  - The probability density changes with time (not stationary).
  - Measurement of energy can yield different allowed values, with probabilities determined by coefficients $|c_n|^2$.

Measurement and Wavefunction Collapse

- Before Measurement:
  - The state may be a superposition of several energy eigenstates.
  - Energy measurement could yield any eigenvalue E_n, each with certain probability.
- After Measurement:
  - The act of measuring energy forces the system into the corresponding eigenstate ψ_n.
  - The probability of all other energies becomes zero—the wavefunction "collapses."
  - After collapse, future measurements yield the same energy, until disturbed.
- Quantum Observer Effect:
  - Measuring disturbs/evolves the quantum state, sometimes non-continuously ("collapse").
  - This feature is unique to quantum systems and contrasts with classical physics.

Summary Chart:

Formulation	Equation	When Used	Probability Density
Time-Dependent Schrödinger Equation	$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$	Any time-dependent process	May or may not vary in time
Time-Independent Schrödinger Equation	$\hat{H}\psi_n = E_n\psi_n$	Hamiltonian has no explicit t-dependence	Stationary: constant in time

Key Points:

- Stationary states: Fixed energy, unchanging probability density.
- Nonstationary states: Changing probability density with time.
- Measurement collapses the wavefunction to a unique eigenstate.
- Quantum Observer Effect: The act of measurement itself alters the future evolution of the system.

Operator Algebra in Quantum Mechanics

- **Quantum Operators:**
  Mathematical objects representing physical observables (position, momentum, energy, etc.).
  Operate on wavefunctions to extract measurable properties.

- **Linear Operators:**
  If $\hat{A}$is an operator and $\psi_1, \psi_2$are wavefunctions:

$$\hat{A}(a\psi_1 + b\psi_2) = a\hat{A}\psi_1 + b\hat{A}\psi_2$$

  - (a, b are constants)

- **Commutators:**
  Define the relationship between two operators:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

- Fundamental for quantum theory; expresses how two observables interact.
- **Notable Example:**

$$[\hat{x}, \hat{p}_x] = i\hbar$$

- **Eigenvalue Equations:**
  For operator $\hat{A}$:

$$\hat{A}\psi = a\psi$$

  - $\psi$is the eigenfunction (state).
  - $a$is the eigenvalue (measurement result).

- **Hermitian Operators:**
  Operators representing observables must be Hermitian (real eigenvalues):

$$\langle \psi_1 \mid \hat{A}\psi_2 \rangle = \langle \hat{A}\psi_1 \mid \psi_2 \rangle^*$$

- **Uncertainty Principle (from non-commuting operators):**
  - If $[\hat{A}, \hat{B}] \neq 0$, there is an uncertainty relationship.
  - Most famously:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

Summary Table

Concept	**Formula**	**Explanation**
Commutator	$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$	Measures operator “interference”
Eigenvalue Equation	$\hat{A}\psi = a\psi$	Extracts measurable value
Hermiticity	langle psi_1	hat{A} psi_2 rangle = langle hat{A} psi_1

Concept	Formula	Explanation
Uncertainty	$\Delta x \Delta p_x \geq \hbar/2$	Limits measurable precision

Key Point:
Operator algebra forms the backbone of quantum mechanics—governing how measurements, uncertainties, and physical laws are mathematically encoded.

PREVIOUS YEARS QUESTIONS

1. In quantum mechanics, the state of a system is described by:
A) A real function
B) A probability vector
C) A wavefunction ψ
D) A classical point in phase space
Answer: C
Explanation: The wavefunction ψentirely describes a quantum system.

2. The integral $\int_{-\infty}^{+\infty} |\psi|^2 \, d\tau$gives:
A) Energy
B) Probability density
C) Total probability
D) Expectation value
Answer: C
Explanation: The wavefunction must be normalized so the total probability is 1.

3. Which of the following is a valid operator for momentum in 1D?
A) $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$
B) $\hat{p}_x = mv$
C) $\hat{p}_x = x$
D) $\hat{p}_x = \hbar\omega$
Answer: A
Explanation: The quantum momentum operator is a differential operator.

4. The time-dependent Schrödinger equation is:
A) $H\psi = E\psi$
B) $E = mc^2$
C) $i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$
D) $p = mv$
Answer: C
Explanation: This fundamental equation governs time evolution in quantum systems.

5. Observables in quantum mechanics correspond to:
A) Real numbers
B) Hermitian operators
C) Probability measures
D) None of the above
Answer: B
Explanation: Only Hermitian operators have real eigenvalues (physical measurement).

6. Probability density is given by:
A) $|\psi|$
B) $\psi^* + \psi$
C) $|\psi|^2$
D) $\psi\psi^*$
Answer: C
Explanation: $|\psi|^2$ gives the probability density.

7. The correspondence principle connects quantum mechanics with:
A) Newtonian optics
B) Classical mechanics
C) Thermodynamics
D) Relativity
Answer: B
Explanation: It ensures quantum mechanics agrees with classical at large scales.

8. Which requirement is NOT essential for a valid wavefunction?
A) Single-valued
B) Square-integrable
C) Finite
D) Must be real
Answer: D
Explanation: Wavefunctions need not be real; they can be complex.

9. The expectation value of an observable $\hat{A}$is:
A) $\langle\psi | A | \psi\rangle$
B) $\int \psi^* \hat{A} \psi d\tau$
C) Both A and B
D) None
Answer: C
Explanation: Both notations represent the same expectation value.

10. The uncertainty in an observable is related to:
A) Operator's commutator with energy
B) Square root of variance
C) Real part of wavefunction
D) Its eigenvalues only

Answer: B
Explanation: Standard deviation is square root of variance.

11. The commutator $[x, p_x]$is:
A) Zero
B) $i\hbar$
C) $-i\hbar$
D) $1/\hbar$
Answer: B
Explanation: Fundamental canonical commutation relation.

12. An eigenstate of an operator:
A) Is always normalized
B) Always has a definite measurement value
C) Has non-zero variance
D) Is uncertain
Answer: B
Explanation: Measurements always yield the eigenvalue with zero uncertainty.

13. A Hermitian operator:
A) Has only complex eigenvalues
B) Is not linear
C) Represents a physical observable
D) May have no eigenvalues
Answer: C
Explanation: Requirement for observables—they yield real values.

14. If $\hat{A}\psi = a\psi$, then $a$is called:
A) Norm
B) Expectation value
C) Eigenvalue
D) Uncertainty
Answer: C
Explanation: It is the defining property of an eigenvalue/eigenstate.

15. The uncertainty principle arises because:
A) Non-commuting operators
B) Non-Hermitian operators
C) Square-integrable functions
D) Normalized functions
Answer: A
Explanation: Only non-commuting operators have uncertainty restrictions.

16. Stationary states have probability densities that:
A) Oscillate in time
B) Are constant in time

C) Are undefined
D) Grow exponentially
Answer: B
Explanation: The modulus squared of a stationary state's wavefunction is time-independent.

17. The energy eigenvalue equation $\hat{H}\psi = E\psi$applies for:
A) Time-independent Hamiltonian
B) Time-dependent Hamiltonian
C) Only in relativity
D) Classical systems
Answer: A
Explanation: TISE applies if the Hamiltonian does not depend on time.

18. Nonstationary states are:
A) Single eigenstates
B) Superpositions of eigenstates
C) Unphysical
D) Only in classical mechanics
Answer: B
Explanation: Superpositions lead to time-dependent probabilities.

19. A measurement collapses the wavefunction to:
A) The zero vector
B) A stationary state
C) An eigenstate of the operator measured
D) A mixture of states
Answer: C
Explanation: Measurement projects the state onto the operator's eigenstate.

20. After measuring energy and obtaining E_n, future energy measurements just after will yield:
A) Any value
B) Only E_n
C) Averaged values
D) Zero
Answer: B
Explanation: The measurement outcome is certain once the system is in an eigenstate.

21. Ground state wavefunction for 1D box is:
A) $\psi_1(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$
B) $\psi_1(x) = Ae^{-\alpha x^2}$
C) $\psi_1(x) = 0$
D) $\psi_1(x) = \cos\left(\frac{\pi x}{L}\right)$

Answer: A
Explanation: Solution for infinite square well.

22. Allowed energy levels in a box:
A) Linear with n
B) Proportional to n^2
C) Proportional to $1/n$
D) Exponential in n
Answer: B
Explanation: $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$

23. Probability of finding the particle at the wall in a box is:
A) 1
B) 0
C) 0.5
D) Maximum
Answer: B
Explanation: The wavefunction is zero at the boundaries.

24. For the first excited state ($n = 2$), number of nodes is:
A) 0
B) 1
C) 2
D) Infinite
Answer: B
Explanation: For n-th state, number of nodes = $n - 1$.

25. The momentum expectation in the ground state is:
A) Maximum
B) Zero
C) Infinity
D) $\hbar k$
Answer: B
Explanation: Symmetry means equal chance for left and right momentum.

26. Ground state energy is:
A) 0
B) $\frac{1}{2}\hbar\omega$
C) $\hbar\omega$
D) $-\frac{1}{2}\hbar\omega$
Answer: B
Explanation: Zero-point energy prevents the particle from resting at the bottom.

27. Energy levels are separated by:
A) $\hbar\omega$

B) $2\hbar\omega$
C) $\frac{1}{2}\hbar\omega$
D) Arbitrary values
Answer: A
Explanation: $E_n = (n + 1/2)\hbar\omega$

28. The potential for the quantum harmonic oscillator is:
A) $V(x) = kx$
B) $V(x) = \frac{1}{2}m\omega^2 x^2$
C) $V(x) = 0$
D) $V(x) = x^2$
Answer: B
Explanation: Standard harmonic oscillator potential.

29. The potential energy is:
A) Constant
B) $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$
C) Linear in r
D) Quadratic in r
Answer: B
Explanation: Coulomb attraction between electron and nucleus.

30. The principal quantum number $n$determines:
A) Angular momentum
B) Electron spin
C) Energy levels
D) Charge
Answer: C
Explanation: Energy levels quantized by n.

31. The orbital angular momentum operator squared has eigenvalues:
A) $l\hbar$
B) $l(l + 1)\hbar^2$
C) $ml\hbar$
D) 0
Answer: B
Explanation: Standard quantization result.

32. Spin quantum number for electron is:
A) 0
B) 1/2
C) 1
D) -1/2

Answer: B
Explanation: Fundamental property of electrons.

33. Quantum tunneling is possible because:
A) Energy is not conserved
B) Particle can pass through classically forbidden regions due to wavefunction tails
C) Particles are massless
D) Only in harmonic oscillators
Answer: B
Explanation: Non-zero probability from the wavefunction inside barriers.

34. Tunneling probability is approximately:
A) Linear in κ
B) $e^{-2\kappa a}$
C) Always 1
D) $1/a$
Answer: B
Explanation: Probability decays exponentially with barrier thickness.

35. Variational principle states:
A) Estimated ground state energy is always higher than the true energy
B) Lower than true energy
C) Exact for all states
D) Correct only for hydrogen
Answer: A
Explanation: $E_0 \leq E_{\text{trial}}$

36. The trial wavefunction should be:
A) Arbitrary
B) Normalized and reasonable
C) Infinite
D) Sinusoidal only
Answer: B
Explanation: A physically reasonable guess improves estimation.

37. The first-order correction to energy is:
A) $\langle\psi^{(0)} \mid \hat{H}' \mid \psi^{(0)}\rangle$
B) E_n^2
C) 0
D) V_0
Answer: A
Explanation: This is standard from perturbation theory.

38. Perturbation theory is usually applied when:
A) Exact solutions are easy
B) The Hamiltonian has a small extra term

C) Potential is infinite everywhere
D) Trial wavefunctions are unknown
Answer: B
Explanation: Used when a small "perturbing" term is present.

39. Which statement about the rigged Hilbert space formalism in quantum theory is correct?
A) It allows for the treatment of unbounded operators and generalized eigenstates
B) It only describes bounded Hermitian operators
C) It is equivalent to classical Hilbert space theory
D) It is not used in quantum scattering theory
Answer: A
Explanation: Rigged Hilbert spaces admit generalized eigenstates (e.g., Dirac delta), needed for continuous spectra and scattering theory.

40. The Berry phase acquired by a quantum system after adiabatic, cyclic evolution is:
A) Always zero
B) Given by the integral of the Berry connection over a closed loop in parameter space
C) Independent of the path in parameter space
D) Always imaginary
Answer: B
Explanation: Berry phase is geometric, calculated via path integral of the Berry connection over a closed loop.

41. For a two-level atom interacting with a classical field, which phenomenon arises from time-dependent perturbation theory?
A) Spontaneous emission
B) Rabi oscillations
C) Vacuum fluctuations
D) Quantum Zeno effect
Answer: B
Explanation: Rabi oscillations describe coherent population transfer due to a resonant classical field.

42. In the formalism of second quantization, which operator satisfies canonical commutation relations for bosons?
A) Fermionic creation operator
B) Bosonic annihilation operator
C) Pauli matrices
D) Position operator
Answer: B
Explanation: Bosonic operators obey $[a, a^\dagger] = 1$.

43. Which statement about the density matrix $\rho$is true?
A) It is always pure
B) $\mathrm{Tr}(\rho^2) \leq 1$
C) It cannot describe mixed states
D) It is non-Hermitian
Answer: B
Explanation: For pure states $\mathrm{Tr}(\rho^2) = 1$, for mixed <1; density matrices are Hermitian.

44. Which of the following is *not* a necessary condition for the Lindblad master equation to yield a completely positive map?
A) Lindblad operators must be Hermitian
B) The equation is Markovian
C) The coefficients must be positive semi-definite
D) The evolution must be trace-preserving
Answer: A
Explanation: Lindblad operators need not be Hermitian; positivity, Markovian property, and trace preservation are required.

45. Consider the quantum harmonic oscillator. The operator $\hat{a}^\dagger \hat{a}$has eigenstates:
A) All eigenstates of the Hamiltonian
B) Only ground state
C) Only excited states
D) No eigenstates
Answer: A
Explanation: $\hat{a}^\dagger \hat{a}$is the number operator, its eigenstates are energy eigenstates.

46. In the path integral approach, the transition amplitude between two points is given by:
A) The sum over all classical paths only
B) The least action path
C) Sum/integral over all possible paths weighted by $e^{iS/\hbar}$
D) Only the shortest path
Answer: C
Explanation: Path integrals sum over all paths, each weighted by the action exponent.

47. Which phenomenon cannot be explained without quantum field theoretic (QFT) concepts?
A) Spin-orbit coupling
B) Superposition

C) Spontaneous emission
D) Tunneling
Answer: C
Explanation: Spontaneous emission arises from field quantization and vacuum fluctuations.

48. The Wigner function characterizes quantum states in:
A) Real Hilbert space
B) Phase space
C) Only coordinate space
D) Only momentum space
Answer: B
Explanation: Wigner function is a quasi-probability distribution in phase space.