DETAILED STUDY MATERIALS: QUANTUM MECHANICS FUNDAMENTALS

I. QUANTUM HARMONIC OSCILLATOR (QHO)

A. INTRODUCTION AND SETUP

The Quantum Harmonic Oscillator (QHO) is a fundamental model in quantum mechanics, describing systems where a particle is subjected to a potential proportional to the square of its displacement from equilibrium. Examples include molecular vibrations and oscillations of atoms in a solid.

The potential energy is given by:

$V(x) = 1/2 * m * \omega^2 * x^2$

where:

- m is the mass of the particle
- ω (omega) is the angular frequency of the oscillator
- x is the displacement from equilibrium

The one-dimensional time-independent Schrödinger equation is:

$- (\hbar^2 / 2m) * (d^2\psi(x) / dx^2) + V(x) * \psi(x) = E * \psi(x)$

where:

- $\hbar$ (h-bar) is the reduced Planck's constant
- $\psi(x)$ (psi) is the wave function
- E is the energy of the state

B. SOLVING THE HERMITE DIFFERENTIAL EQUATION

Substituting $V(x)$ into the Schrödinger equation and introducing dimensionless variables:

$\xi = \sqrt{(m\omega/\hbar)} * x$

The equation can be transformed into a form related to Hermite's differential equation:

$(d^2u/d\xi^2) + ((2E / (\hbar\omega)) - \xi^2) * u = 0$

where $u(\xi)$ is proportional to $\psi(x)$. For bound states (wave functions that go to zero at infinity), solutions exist only for specific energy levels and involve Hermite polynomials, $H_n(\xi)$.

C. ALGEBRAIC SOLUTION (LADDER OPERATORS)

An elegant method uses creation ($a^\dagger$) and annihilation (a) operators:

$a = \sqrt{(m\omega/2\hbar)} * (x + i*p_x / (m\omega))$

$a^\dagger = \sqrt{(m\omega/2\hbar)} * (x - i*p_x / (m\omega))$

with the commutation relation $[a, a^\dagger] = 1$.

The Hamiltonian operator can be expressed as:

$\times = \hbar\omega * (a^\dagger a + 1/2)$

This leads to quantized energy levels:

$E_n = (n + 1/2) * \hbar\omega$

where n = 0, 1, 2, ... is the principal quantum number.

- Ground state energy (n=0): $E_0 = 1/2 * \hbar\omega$
- Excited state energies: $E_n = (n + 1/2) * \hbar\omega$

The corresponding wave functions are:

$\psi_n(x) \propto H_n(\sqrt{(m\omega/\hbar)} * x) * \exp(-m\omega x^2/2\hbar)$

D. CLASSICAL TURNING POINTS

Classical turning points are the positions where the total energy E equals the potential energy V(x). For the n-th energy level, $E_n = V(x_{tp})$:

$(n + 1/2) * \hbar\omega = 1/2 * m * \omega^2 * x_{tp}^2$

$x_{tp} = \pm \sqrt{(2n + 1) * \hbar / (m\omega)}$

These points define the classical limits of motion, within which the probability of finding the particle is non-zero. Quantum mechanically, there is a non-zero probability of finding the particle beyond these points (tunneling).

E. EXPECTATION VALUES

For the n-th energy eigenstate ψ_n:

- Expectation value of position: $\langle x\rangle_n = 0$
- Expectation value of position squared: $\langle x^2\rangle_n = ((n + 1/2) * \hbar) / (m\omega)$
- Expectation value of momentum: $\langle p_x\rangle_n = 0$
- Expectation value of momentum squared: $\langle p_x^2\rangle_n = (m\omega/2) * (2n + 1) * \hbar$

F. NUMERICAL PROBLEMS (EXAMPLES)

1. Calculate the energy levels for the first five states of a system with m = 1 amu and $\omega = 10^{13}$ rad/s. Determine the zero-point energy. [Hint: 1 amu ≈ 1.66×10^{-27} kg; $\hbar \approx 1.054 \times 10^{-34}$ J*s]

2. For the ground state (n=0) of the QHO, find the classical turning points. If m=2 kg and ω=5 rad/s, what is the energy? What are the turning points?

3. Using the ladder operators, show that $[\times, a] = -\hbar\omega a$. (This demonstrates that 'a' lowers the energy state).

II. RIGID ROTATOR

A. ANGULAR MOMENTUM COMMUTATION RULES

Angular momentum is quantized. The components of the angular momentum operator (L_x, L_y, L_z) do not commute:

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

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

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

However, the square of the total angular momentum, $L^2 = L_x^2 + L_y^2 + L_z^2$, commutes with each component:

$[L^2, L_i] = 0$ for $i = x, y, z$.

B. ANGULAR MOMENTUM OPERATORS IN SPHERICAL POLAR COORDINATES

In spherical coordinates (r, θ, ϕ), the angular momentum operators are typically expressed using derivatives with respect to angles:

$L_z = -i\hbar (\partial/\partial\phi)$

$L^2 = -\hbar^2 [1/\sin(\theta) * \partial/\partial\theta * (\sin(\theta) * \partial/\partial\theta) + 1/\sin^2(\theta) * (\partial^2/\partial\phi^2)]$

C. QUANTIZATION OF ANGULAR MOMENTUM

The simultaneous eigenstates of L^2 and L_z are characterized by quantum numbers *l* and *m*:

- Eigenvalues of L^2: $L^2 |l, m> = l(l+1)\hbar^2 |l, m>$, where $l = 0, 1, 2, \ldots$
- Eigenvalues of L_z: L_z $|l, m> = m\hbar |l, m>$, where $m = -l, -l+1, \ldots, l-1, l$

Thus, the magnitude of the angular momentum vector is $\sqrt{l(l+1)}\hbar$, and its projection onto the z-axis is $m\hbar$.

D. RIGID ROTATOR MODEL

A rigid rotator consists of two masses (m1, m2) connected by a rigid rod of length r. For a diatomic molecule, this is approximated by reducing the system to a single mass μ (reduced mass) at a fixed distance R from the origin.

$\mu = (m1 * m2) / (m1 + m2)$

The potential energy is zero (V=0) as the bond length is fixed.

E. SCHRÖDINGER EQUATION FOR RIGID ROTATOR

The Hamiltonian is simply the kinetic energy operator in terms of angular momentum:

$\times = L^2 / (2I)$

where $I = \mu R^2$ is the moment of inertia.

The Schrödinger equation is:

$(L^2 / (2I)) * \psi(\theta, \phi) = E * \psi(\theta, \phi)$

In spherical coordinates (where r is fixed):

$- (\hbar^2 / 2I) * [1/\sin(\theta) * \partial/\partial\theta * (\sin(\theta) * \partial/\partial\theta) + 1/\sin^2(\theta) * \partial^2/\partial\phi^2] * \psi(\theta, \phi) = E * \psi(\theta, \phi)$

F. SEPARATION OF VARIABLES AND SPHERICAL HARMONICS

Separating the wave function into angular parts: $\psi(\theta, \phi) = Y_{lm}(\theta, \phi)$. The solutions are the Spherical Harmonics, Y_{lm}, which are simultaneous eigenfunctions of L^2 and L_z.

The energy levels are:

$E_l = l(l+1) * \hbar^2 / (2I)$

The energy depends only on the quantum number l (the azimuthal quantum number), not on m. This leads to degeneracy.

G. DISCUSSION OF SOLUTION

The Spherical Harmonics, $Y_{lm}(\theta, \phi)$, are complex functions that describe the angular distribution of the wave function. The solution implies that the rotational energy levels of a diatomic molecule are quantized, with the spacing between levels increasing with l.

H. NUMERICAL PROBLEMS (EXAMPLES)

1. For a CO molecule (reduced mass $\mu = 1.14 \times 10^{-26}$ kg, bond length $R = 1.13 \times 10^{-10}$ m), calculate the moment of inertia. Then, find the energies for the first three rotational levels ($l=0, 1, 2$).

2. Calculate the frequency of photons that would be emitted or absorbed during transitions between the $l=1$ and $l=2$ rotational states of the CO molecule. [Hint: $E = h\nu$]

III. HYDROGEN ATOM AND HYDROGEN-LIKE IONS

A. SETUP OF SCHRÖDINGER EQUATION

For a hydrogen atom (one electron of mass m and charge -e orbiting a nucleus of charge +Ze), the potential energy is the Coulomb potential:

$V(r) = -(Ze^2) / (4\pi\varepsilon_0 r)$

where ε_0 is the permittivity of free space. The Schrödinger equation is solved in spherical polar coordinates (r, θ, ϕ), with the Hamiltonian being:

$\times = -(\hbar^2 / 2\mu) \nabla^2 + V(r)$

where μ is the reduced mass of the electron-nucleus system (for hydrogen, approximately the electron mass).

B. SEPARATION OF VARIABLES

The wave function $\psi(r, \theta, \phi)$ is separated into radial and angular parts:

$\psi(r, \theta, \phi) = R(r) * Y_{lm}(\theta, \phi)$

where $R(r)$ is the radial wave function and $Y_{lm}(\theta, \phi)$ are the Spherical Harmonics solved for the rigid rotator.

This separation leads to two equations: one for the radial part and one for the angular part (which yields the spherical harmonics and their associated quantum numbers *l* and *m*).

C. SOLUTION OF ANGULAR PART (Φ PART ONLY)

The part of the angular solution dependent on ϕ arises from the L_z operator. The quantization condition for L_z gives:

$L_z Y_{lm} = m\hbar Y_{lm}$

where m is the magnetic quantum number ($m = -l, \ldots, l$). The solution for the ϕ dependence is typically of the form $e^{im\phi}$.

D. QUANTIZATION OF ENERGY

Solving the radial equation yields the quantized energy levels for the hydrogen atom ($Z=1$):

$E_n = - (\mu * (Ze^2)^2) / (2 * (4\pi\varepsilon_0)^2 * n^2) = - (13.6 \text{ eV} * Z^2) / n^2$

where n is the principal quantum number ($n = 1, 2, 3, \ldots$). The energy depends only on *n*, leading to degeneracy.

E. REAL WAVE FUNCTIONS

The spherical harmonics Y_{lm} are complex. For some applications, real wave functions are preferred. These can be constructed as linear combinations of complex Y_{lm} functions with the same *l* but different *m* values (e.g., $Y_{l,m} + Y_{l,-m}$ and $i(Y_{l,m} - Y_{l,-m})$).

F. AVERAGE AND MOST PROBABLE DISTANCES

The radial wave function $R_{nl}(r)$ determines the probability distribution of the electron's distance from the nucleus.

- Most Probable Distance (r_{mp}): Found by maximizing the radial probability density $P(r) = r^2 |R_{nl}(r)|^2$.
- Average Distance ($\langle r\rangle_{nl}$): Calculated by integrating $r * P(r)$ over all r.

For Hydrogen ($Z=1$):

- $\langle r\rangle_{nl} = (a_0/2) * [3n^2 - l(l+1)]$, where $a_0 = 4\pi\varepsilon_0 \hbar^2 / (m_e e^2)$ is the Bohr radius.
- Most probable distance is also related to n and l, specific formulas vary. For the ground state ($n=1$, $l=0$), $\langle r\rangle_{10} = 1.5 a_0$, and $r_{mp} = a_0$.

G. SCHRÖDINGER EQUATION FOR MANY-ELECTRON ATOMS

Setting up the Schrödinger equation for atoms with more than one electron (like Helium, $Z=2$, with 2 electrons) becomes significantly more complex due to the electron-electron repulsion term in the potential:

$V_{total} = V_{nucleus} + \mathrm{Sum}(V_{electron\_nucleus}) + \mathrm{Sum}(V_{electron\_electron})$

For Helium, the interaction term is $e^2 / (4\pi\varepsilon_0 |r_1 - r_2|)$, which depends on the distance between the two electrons (r_1 and r_2).

This term makes the equation non-separable in spherical coordinates, requiring approximations (like the Hartree-Fock method or variational methods) to find solutions.

H. NUMERICAL PROBLEMS (EXAMPLES)

1. Calculate the ionization energy of the ground state of He^+ ion ($Z=2$). [Hint: Use the energy formula for hydrogen-like ions and note ionization means removing the electron to $n=\infty$]

2. For the Hydrogen atom's ground state ($n=1$, $l=0$), calculate the most probable distance and the average distance of the electron from the nucleus in terms of the Bohr radius (a_0).

3. Explain why the Schrödinger equation for Helium cannot be solved by simple separation of variables.