Quantum Mechanics 4

Physical Chemistry Tutorials

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Question 1

a) The Schrödinger equation for a particle confined to a ring of radius r and subject to a constant potential V may be written in the form:

$$\left(\frac{-\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}+V\right)\Psi = E\Psi$$

where I is the moment of inertia of the particle. Show by direct substitution that

$$\Psi = Ne^{im\phi}$$

is a solution of the Schrödinger equation (where N and m are constants) and, by applying the boundary conditions, determine the quantised values of energy.

b) If Ψ is an eigenfunction of the operator $\hat{\Omega}$ with eigenvalue ω, show that the expectation value of that operator is equal to ω.

c) A linear combination of the form $\Psi' = Ae^{i\phi} + Be^{-i\phi}$, where A and B are non-zero constants, is a solution of the Schrödinger equation above, and is an eigenfunction of the l_z^2 operator, but is not an eigenfunction of the l_z operator ($l_z = -i\hbar\frac{d}{d\phi}$).

i. Determine the expectation value, $\langle l_z^2 \rangle$, for the function Ψ'.

ii. Show that the normalization integral for Ψ' is equal to $2\pi(A^2 + B^2)$.

iii. Determine the ratio of the coefficients A/B if the expectation value $\langle l_z \rangle = \hbar/3$.

iv. What would be the quantum mechanical uncertainty in the measurement of l_z?

d) When an electron confined to a ring interacts with radiation polarised in the x direction, the transition dipole operator is of the form

$$\hat{\mu} = \mu_0\cos(\phi) = \tfrac{1}{2}\mu_0\left(e^{i\phi} + e^{-i\phi}\right)$$

Show that the integral

$$\int_0^{2\pi} e^{-im\phi}e^{i\phi}e^{im'\phi}\,d\phi$$

is equal to zero unless m'=m-1, and hence deduce that the selection rules for transitions induced by this radiation between the states of the electron confined to the ring are Δm= ±1.

Question 2

What is meant by the Hamiltonian operator, and why is it important in quantum mechanics?

A one-dimensional particle is confined to a region $0 < x < L$ of zero potential energy, by infinite potential barriers at $x=0$ and L.

a) Write down the Hamiltonian for the particle, and solve fully the Schrodinger equation for the energy levels and wavefunctions of the system.

b) Compare briefly the predicted behaviour of the quantum system with its classical counterpart.

c) How would the energy levels be modified if the potential for $0<x<L$ was a non-zero constant, V_o?

d) Write down the corresponding expression for the energy levels of a two-dimensional particle confined to the zero-potential region $0 < x < L_1$ and $0 < y < L_2$. Under what conditions does degeneracy occur, and what property of the system does this reflect?

Question 3

a) What is meant by the statement: 'ψ is an eigenfunction of the Hamiltonian with eigenvalue E'?

b) Explain briefly why the determination of eigenfunctions and eigenvalues is important in chemistry.

c) The Hamiltonian for the bending vibration of CO_2 can be written:

$$\hat{H} = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial R^2} + \frac{1}{R}\frac{\partial}{\partial R} + \frac{1}{R^2}\frac{\partial^2}{\partial \phi^2}\right) + \frac{1}{2}kR^2$$

where the cylindrical coordinates (R, φ) describe the displacement of the carbon atom from the symmetry axis. Show that $\Psi = Ae^{-bR^2}$ is an eigenfunction of the Hamiltonian and find the corresponding eigenvalue.

d) Give reasons for believing that this is the ground state and, from your knowledge of molecular vibrations, what would you expect for the energy, degeneracy and wavefunction of the first excited state?