Name: ____________________

The exam consist of 5 questions, 25 points each. Only 4 highest score questions will make the final score.

Total - 100 Pts.

Problem I 25 Pts

The normalized spherical harmonics (eigenfunctions of the rigid rotator) are defined by following equation:

$$Y_l^m(\theta,\phi) = \left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)e^{im\phi}$$

where $P_l^{|m|}(\cos\theta)$ are associated Legendre's polynomials specified by ($x = \cos\theta$):

$$P_l^{|m|}(x) = (1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_l(x)$$
$$P_l(x) = \frac{1}{2^l l!}\frac{d^l}{dx^l}(x^2-1)^l$$

1. Derive formulae for spherical harmonics (S.H.) for following l and m values:

$$l = 0, 1$$
$$m = 0, \pm1, \ldots, \pm l$$

2. Using above functions, show that the S.H. are orthogonal with respect to both l and m numbers.

3. The angular momentum operator $\hat{L}_z$ is defined as follow:

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

Using Y_1^m and different values of m, show that S.H. are eigenfunctions of the $\hat{L}_z$ operator. What are their eigenvalues?

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Problem II 25 Pts

1. Sketch an energy diagrams for (1 dimensional) particle in a box, harmonic oscillator and rigid rotator systems. Label the n, ϑ and J states and energy values associated with them. Derive the expression for the energy spacing between levels for each system. Indicate the symmetry (odd or even) of the wave functions associated with each level.
2. Which type of molecular motions (or molecular degrees of freedom) these models are applicable to?

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Problem III — 25 Pts

The wave function and of the particle in the 3 dimensional box with lengths of a, b and c has following forms:

$$\Psi(x, y, z) = A_x A_y A_z \sin\frac{n_x \pi x}{a} \sin\frac{n_x \pi y}{b} \sin\frac{n_z \pi z}{c}$$

where n_x, n_y and n_z are independent, positive integers.

1. Compute the value of the normalization constant $(A_x A_y A_z)$
2. Derive the expression for the energy of the particle in the 3D box. You can present the solution to 1D system and show the generalization for 3 dimensions.
3. For size of the box $a = b = 1.5c$, sketch the particle's energy diagram.

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Problem IV 25 Pts

1. A $^{40}Ca^{1}H$ molecule has a fundamental vibrational band absorption at $\bar{\nu} = 1298$ cm^{-1}. Assuming the harmonic potential, compute the bond strength and zero-point energy of this molecule. ($m_H = 1.672 \cdot 10^{-27}$ kg, $m_{Ca} = 6.655 \cdot 10^{-26}$ kg).

2. The spacing between absorption lines in pure rotational spectrum of $^{11}B^{2}D$ is 392.14 MHz. Calculate the bond length of this molecule. ($m_D = 3.345 \cdot 10^{-27}$ kg, $m_B = 1.795 \cdot 10^{-26 kg}$)

3. Assuming the particle in the box model, compute the energy of the electron excitation in ethylene molecule. Assume respective geometrical parameters for the box size. ($e = 1.602 \cdot 10^{-19}$ C, $m_e = 9.109 \cdot 10^{-31}$ kg)

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Problem V — 25 Pts

Choose One!

- Assuming the Bohr model of atom, derive the Rydberg formula for energy of an electron around a nucleus of atomic number Z. If Z=2, for what series (n_f) the light falls in the visible part of the spectrum.

- The $\Psi_{\vartheta=2}$ for harmonic oscillator is:

$$\Psi_{\vartheta=2}(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} \left(2\alpha x^2 - 1\right) e^{-\alpha x/2}$$

  where $\alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/2}$. Compute the $< p >$ and $< p^2 >$ and justify why the second integral is different than 0. Next, show that the transition dipole moment (T.D.M.) integral between $\Psi_{\vartheta=1} \rightarrow \Psi_{\vartheta=2}$ is different from 0 (absorption is possible):

$$T.D.M. : \int_{-\infty}^{+\infty} \Psi_{\vartheta=1} * \hat{x} \Psi_{\vartheta=2} dx \neq 0$$

$$\Psi_{\vartheta=1} = \left(\frac{4\alpha^3}{\pi}\right) x e^{-\alpha x^2/2}$$