

CHEM352: PHYSICAL CHEMISTRY II  
HOMEWORK SET II - DUE 17<sup>th</sup> OF MARCH, 5.00 PM  
Each problem is worth 2 pts, 20 pts in total.

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Office hours: Thu, 5-7 pm, HN-1321B

1. Show that the first three eigenfunctions of (a) harmonic oscillator and (b) rigid rotor ( $l=0,1,2$ , and  $m=0$ ) are orthonormal.
2. Show that spherical harmonics are eigenfunctions of  $\hat{L}^2$  and  $\hat{L}_z$  operators, but not of  $\hat{L}_x$  and  $\hat{L}_y$ . Is there anything specific about the z-axis?
3. (a) The spacing between absorption lines in pure rotational spectrum of  $^{11}\text{B}^{16}\text{O}$  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)  
(b) The  $J = 2 \leftarrow 1$  transition for AlH molecule in an electronic ground state ( $X^1\Sigma^+$ ) has a frequency of 755199.790 MHz, whereas  $J = 4 \leftarrow 3$  for AlD ( $X^1\Sigma^+$ ) is 786755.93 MHz. Compute the bond distance for both molecules. Why are the bond distances different? <sup>1</sup>
4. (a) A common practice in identification of bands in vibrational spectroscopy is an isotopic substitution in specific groups that shifts the position of the band but do not alter the electronic structure (force constant) of the bond. Verify this for series of isotopes of  $\text{C} = \text{O}$ :  $\bar{\nu}_{12\text{C}=16\text{O}} = 2148.21 \text{ cm}^{-1}$ ,  $\bar{\nu}_{13\text{C}=16\text{O}} = 2091.7 \text{ cm}^{-1}$  and  $\bar{\nu}_{12\text{C}=18\text{O}} = 2087 \text{ cm}^{-1}$ . The wavenumbers correspond to the vibrations in a electronic ground state ( $X^1\Sigma^+$ ).<sup>2</sup>  
(b) The excitation from singlet ( $X^1\Sigma^+$ ) to triplet state ( $a^3\Sigma^+$ ) for  $\text{C}=\text{O}$  shifts the vibrational frequency to  $1218 \text{ cm}^{-1}$ . Using your chemical intuition and IR band positions tables, rationalize this result. You can assume that the bond length in the excited molecule does not change.
5. Consider isotopic substitution, as in point (2a), for H-Br and D-Br molecules. Why is the vibrational shift of the stretching bond larger than in 4a? Next, estimate to which rotational state each molecule would be excited, if irradiated by a series of photons with the total energy equal to the vibrational excitation energy.
6. Explain why infrared spectrum of a hypothetical diatomic molecule is composed from a single band (assuming no overtones), whereas rotational spectrum features multiple equally spaced peaks? Draw respective energy diagrams.
7. Consider a hydrogen atom in an excited state with an electron occupying 2s orbital ( $\psi_{200}$  state).
  - (a) Compute position the two maxima of the probability function the electron  $r^2|\psi_{200}(r)|^2$  and the radial node where probability of finding an electron is 0.
  - (b) Finally, compute the radius of the sphere that captures 90% probability of finding the 2s electron.
8. Consider a  $\text{He}^+$  ion with an electron at  $2p_z$  orbital. What is average position  $\langle r \rangle$  and most probable distance from the nucleus for this electron? Next, calculate the kinetic energy of the electron and its associated wavelength. How does it compare to the average distance?
9. Using hydrogen-like orbitals, show that the charge density of the fully occupied subshell (for instance  $2p^6$ ) is spherically symmetrical.
10. Explain the relation between nomenclature of d-orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ ) and their respective 1-electron wavefunction.

<sup>1</sup>The data comes from doi: 10.1088/0004-637X/791/1/65

<sup>2</sup>Data comes from Ar-matrix measurements in doi: 10.1063/1.1725508 so it can differ from gas-phase value of  $2170 \text{ cm}^{-1}$ . We will learn how to read electronic terms in the next part of the semester. Meanwhile, please disregard them.