Final Exam

CHMY 564-17
Fri. 28 April – Wed, 3 May 2017
200 points

This is a take-home exam, on which you are to work completely independently (you may direct questions of clarification to the Professor only). You may use only your notes, handouts, readings from this course, and personal textbooks.

The exam must be **turned in no later than Wed, May 3 at 12 noon.** The cumulative time limit is **8** hours of ***active*** work. You may break the time into sections such that periods of time (sleeping, etc) for which you are not consciously solving an exam problem do not count as part of the 8 hours.

This exam is worth 200 points. The midterm and the homework will each be worth 100 points. Therefore, this exam represent 50% of your grade.

(20 pts) 1. In a paragraph of no more than 100 words, explain the essence of quantum mechanics to a very bright high school student who has taken chemistry, knows about the atomic orbitals, and Coulomb's Law, but nothing about quantum mechanics.

(20 pts) 2. For a 1-electron ion whose nuclear charge is Z= +5, in what region of space (r = distance from the nucleus) will the electron be tunneling, according to the virial theorem?

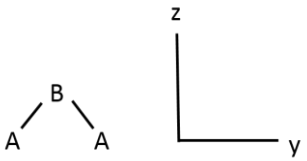
(30 pts) 3. For a particle of mass = 1 atomic unit in a 1-dimensional infinite square well that extends from 0 to +1 atomic length units:

(a) Write the lowest energy wavefunction as a linear combination of momentum eigenfunctions.

(b) What is the probability of observing a momentum = π a.u. if the universe is a box of length 10^6 a.u., meaning that all momentum eigenfunctions have a normalization constant = 10^{-3} a.u.$^{-1/2}$. That is you would turn an integration from – infinity to + infinity to -0.5×10^6 to $+0.5 \times 10^6$ atomic length units.

(40 pts) 4. For a non-linear triatomic molecule BA_2 lying in the yz plane, the normal mode frequencies, ν_1, ν_2, and ν_3 are found to be 500, 3000, and 3500 cm^{-1} respectively and belong to the A_1, A_1, and A_2 irreducible representations of the C_{2v} point group respectively.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz



(a) If the displacement parameters λ_1 =1.5, λ_2 =3, and λ_3 = 0. for electronic excitation to a certain excited electronic state, make a table for the relative vibronic transitions from the 0 vibrational level of the ground state that includes all combinations and overtones with vibrational energy below 20,000 cm^{-1} that also have Franck-Condon factors more than 0.1.

(b) For an electronic transition from the ground electronic state (A_1) to an excited state with symmetry B_1 , in what direction will the transition moment point?

(c) For an electronic transition from an A_2 MO to a B_1 MO, in what direction will the transition dipole point?

(d) Draw an examples an A_2 MO and a B_1 MO

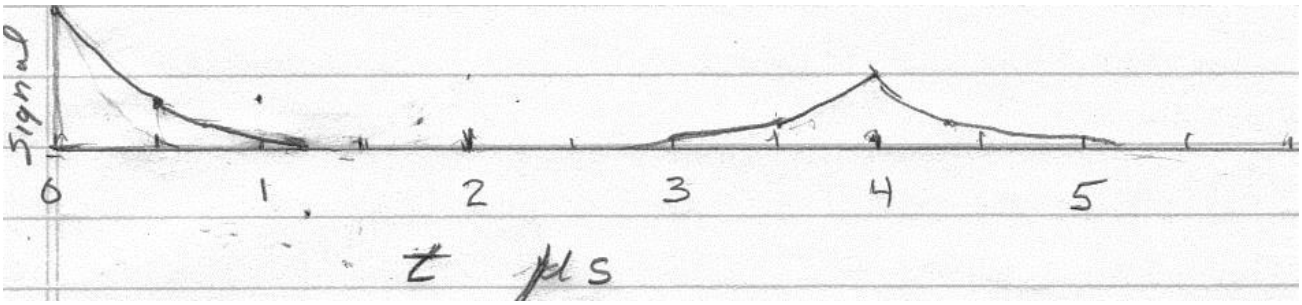
(e) For transitions from the ground state, which excited state symmetries will be allowed in 1-photon spectroscopy?

(f) For transitions from the ground state, which excited state symmetries will be allowed for 2-photon absorption and Raman spectroscopies?

(40 pts) 5. (a) If $\Psi = 2^{-1/2}(|1> + i|2>)$ at time = 0, and $H_{11} = 0$, $H_{22} = 0$, and $H_{12} = i$ what are ρ_{11}, ρ_{22}, ρ_{12}, ρ_{21}, ρ_x, ρ_y, ρ_z, Ω_x, Ω_y, and Ω_z, where the latter 6 are in the FVH formalism.

(b) What will these values be at later times such that $\omega t = \pi/2, \pi\ 3\pi/2$ and 2π, where $\omega = 2\pi H_{12}/h$.

(30 pts) 6. Consider the following spin echo experiment.



Using a ruler for accuracy, what are T_1, T_2, and T_2* relaxation times in microseconds?

(20 pts) 7. (a) Perform Gaussian 09 calculations using (1) the most minimal basis set HF method and (2) the most correlated basis set DFT calculation we used during homework to find optimized geometry and energy for the neutral Be atom and neutral Be_2 molecule. In each for the two cases, compute the bond dissociation energy in kJ/mol and comment on the difference and reasons for the difference.

(b) From the MO pictures, comment on the reason for the exceptionally low bond strength observed for this molecule.