CHEM352: Physical Chemistry II
Homework Set III - due 19^{th} of May, 12.00 pm
Each problem is worth 2 pts, 20 pts in total.

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Office hours: Thu, 5-7 pm, Zoom

1. Write the complete hamiltonian and the wavefunction (using Single Slated Determinant) of a Berylium atom.

2. Using variational method, calculate the ground-state energy of a particle constrained to move within the region $0 \leq x \leq a$ in a potetnial given by:

$$V(x) = V_0 x \qquad 0 \leq x \leq \frac{a}{2}$$
$$V(x) = V_0(a - x) \qquad \frac{a}{2} \leq x \leq a$$

   As a trail function a combination of the first two wavefunctions of a particle in a box.

3. - Using perturbation theory, calculate the first-order correction to a particle constrained to move within the region $0 \leq x \leq a$ in a potetnial given in the problem 2.
   - Some potential-wells, for instance strong symmetric H-bonded systems, can be described by a quartic ($V(x) = cx^4$) instead of quadratic potential. Using first-order perturbation theory, calculate the energy correction to the ground-state energy of a quartic oscillator (assuminc quadratic oscillator as an unperturbed system).

4. Derive atomic terms for p^4 and d^2 electronic configurations. Order them according to the Hund's rule.

5. - Consider the 1s np $^3P \rightarrow$ 1s nd ^3D transition in helium atom. Draw an energy-level diagram and show the allowed transtions.
   - The first ionization potential of helium atom is 24.6 eV and the wavelenght of the electronic excitation to the [1s2p] $^1P_1$ state is 58.44 nm. What is the ionization energy of this [1s2p] $^1P_1$ state of a helium atom?
   - The transition $Al[Ne]3s^2 3p^1 \rightarrow Al[Ne]3s^2 4s^1$ has two lines at $\widetilde{\nu}$ = 25354.8 cm^{-1} and $\widetilde{\nu}$ = 25242.7 cm^{-1} and transition $Al[Ne]3s^2 3p^1 \rightarrow Al[Ne]3s^2 3d^1$ has three lines at 32444.8, 32334.0 and 32332.7 cm-1. Draw the enenrgy diagram of an atom and assign the transition to the respective energies using the selection rules.

6. - Plot a molecular orbital diagram for N_2 molecule.
   - Write down the ground-state electronic configuration for a following series of species: N_2^+, N_2, N_2^- and N_2^{2-}. Assign the bond order and determine the molecular term symbol.
   - Sketch the molecular orbital energy diagram for a radical OH molecule and compare it with a diagram of HF. Show HOMO, LUMO and potential nonbonding orbitals. Derive molecular term of both molecules and order them according to the energy.

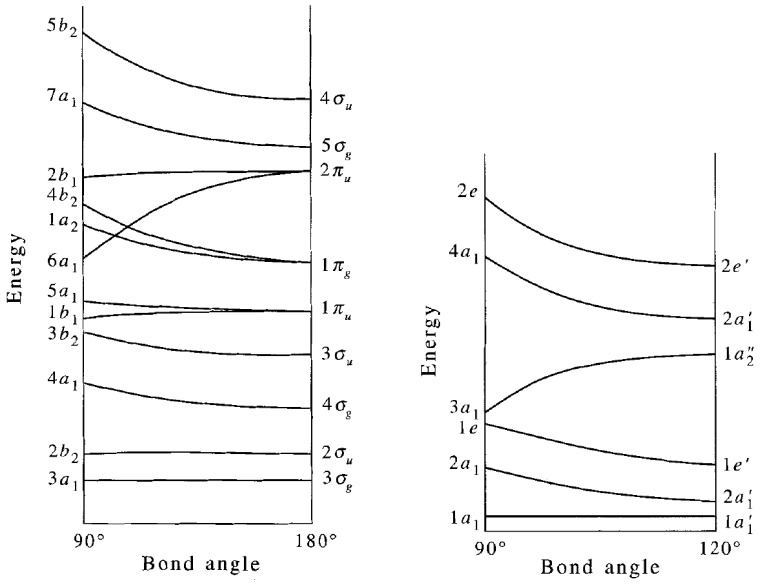
7. - The energies E_j of the j-th molecular orbitals in a linear conjugated polyene composed of N carbon atoms is given by:

$$R_j = \alpha + 2\beta \cos \frac{j\pi}{N_1}$$

   Validate the formula for butadiene and hexatriene. Next, show that extrapolation of the model to hypothetical 1-dimensional solid leads to formation of essentially a continuous band of the width of 4β.

- Consider allyl cation, $CH_2 = CH - CH_2^+$ which features delocalized π-network. Using Hückel model, derive the molecular orbital energies. Next, derive the energies for cyclopropene cation and compare energetics of these two molecules. How does the relative stability changes if we consider allyl and cyclopropene anions?

8. Use the Walsh correlation diagram for the valence electrons of XY_2 (left) and XH_3 (right) molecules to predict whether following molecules are linear or bent: CO_2, CO_2^-, CO_2^+, CF_2, CN_2, NO_2^+, NO_2; and planar or pyramidal: BH_3, CH_3, CH_3^+, CH_3^-, NH_3. 'e' means that the state is double-degenerate.



9. The follwoing data are obtained for the vib-rot spectrum of $H^{79}Br$. Determine $\bar{B}_0$, $\bar{B}_1$, $\bar{B}_e$ and $\bar{\alpha}_e$ and ν_e.

Line	Freq $[cm^{-1}]$
R(0)	2642.60
R(1)	2658.36
P(1)	2609.67
P(2)	2592.51

10. Explain what is electon correlation energy.