Computational Chemistry and Materials Modeling
Homework 2, due date is set in Storion web page
Topic: quantum chemistry

Notes: *In multiple choice problems explain your answer. Add references if needed. Upload solution as a single file "YourName.pdf" or "YourName.zip".*

1. (1 pt.) Which of the following is an eigenfunction of the operator $\mathrm{p}_r = -\mathrm{i}\hbar r^{-1}\frac{\mathrm{d}}{\mathrm{d}r}$: (A) $\mathrm{e}^{\mathrm{i}kr}$, (B) $\sin kr$, (C) $r^{-1}\mathrm{e}^{\mathrm{i}kr}$, (D) $r\mathrm{e}^{\mathrm{i}kr}$, (E) $\mathrm{e}^{\mathrm{i}kr^2}$.

2. (1 pt.) Write the Slater determinant for a system with three electrons.

3. (2 pts.) Specify core and valence electrons for O, N, F, C, Au and U elements. Please, use the following notation: $2s^1$, $3p^4$, $5d^{10}$, etc.

1. (1 pt.) Which of the following is NOT a correct aspect of the Born-Oppenheimer approximation. Please, justify your answer:

(A) The electrons in a molecule move much faster than the nuclei.

(B) Excited electronic states have the same equilibrium internuclear distance as the ground electronic state.

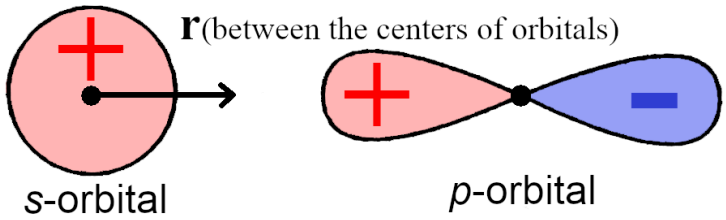
(C) The electronic and vibrational motions of a molecule are approximately separable.

(D) Electronic energy curves serve as potential energy functions for nuclear vibrational motion.

(E) The typical amplitude of nuclear vibration is much smaller than that characterizing the motion of electrons.

5. (1 pt.) Write down all terms of the Hamiltonian operator in the Born-Oppenheimer approximation for the methane molecule as a function $H(M_\mathrm{i}, m_\mathrm{i}, Z_\mathrm{i}, \vec{R}_\mathrm{i}, \vec{r}_\mathrm{i})$, where M_i, Z_i and $\vec{R}_\mathrm{i}$ are the mass, charge and position of nuclei i, respectively; m_i and $\vec{r}_\mathrm{i}$ are the mass and position of electron i, respectively. Limit the calculations only to the **valence** electrons.

6. (1 pt.) Qualitatively draw overlapping integral for s and p orbitals as a function of distance between the centers of orbitals ($\vec{r}$).



7. (1 pt.) Estimate relative concentration of *cis* and *trans* conformers of butadiene molecule at the room temperature (conformations and conformer energies can be either calculated or taken from a database). Note, use the Boltzmann distribution.

8. (2 pts.) Write the secular equation for the cyclobutadiene molecule ($\mathrm{C_4H_4}$) in the Huckel model.
(+2 pts.) Solve the obtained equation, find energy levels and HOMO–LUMO gap.

Maximum score is 10 points (equals 100% grade)