

Computational Chemistry and Materials Modeling
Homework 2, due date is set in Canvas LMS
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. Which of the following is NOT a correct aspect of the Born-Oppenheimer approximation:
 - (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.

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

3. Calculate π -conjugated MOs and MO energies of the benzene molecule in the tight-binding approximation (Huckel Hamiltonian) taking 4 eV for the nearest neighbor $pp\pi$ couplings. Compare with PM7 calculations. Determine the best values of the parameters of the tight-binding Hamiltonian.

4. Calculate the valence band of Si using the simplest model (one bonding orbital per bond) determining its parameters from experiment (e.g. the bandwidth is 12.60 eV).

5. 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).