EXAM 07-04-2026

FROM ATOMS TO SOLIDS. # QUESTIONS: 4

The grade is calculated by: GRADE=1+(TotalPoints/10)
Note that this exam is printed on both sides. Do not forget to turn the page!

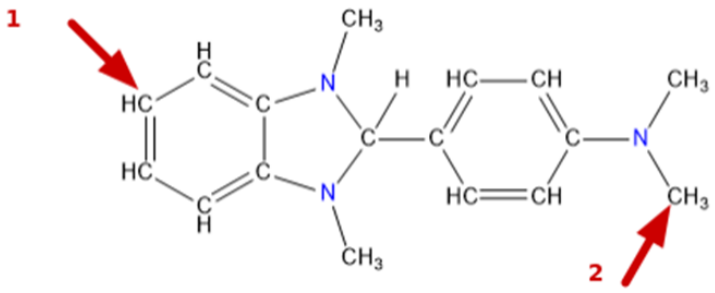
1. Born-Oppenheimer approximation and valence bond theory (22 points)

a. (8 points) Write down the explicit nonrelativistic Hamiltonian of the CO molecule, (Z(C)=6, Z(O)=8) (use either SI or atomic units and summations, rather than writing out all the terms explicitly). Explain each of the terms.

b. (4 points) How is this Hamiltonian separated within the Born-Oppenheimer approximation?

c. (4 points) What is the form of the molecular wavefunction within the Born-Oppenheimer approximation?

d. (6 points) The structural formula of a molecule used in semiconductor technology is shown below. What is the hybridization of the carbon atoms indicated by arrows 1 and 2? explain your answer.



2. Homonuclear molecules and orbital diagrams (22 points)

a. (10 points) Draw a molecular orbital diagram of the S_2 molecule (Z(S)=16, the configuration of atomic S is $1s^2 2s^2 2p^6 3s^2 3p^4$). For simplicity, consider the bonding of the 3s and 3p orbitals separately. Your diagram must include labelled atomic and molecular orbitals (bonding, anti-bonding, gerade/ungerade) and include electrons in the appropriate orbitals. Note that for S_2 the bonding σ orbital is lower in energy than the bonding Π orbital, while the antibonding σ orbital is higher in energy than the antibonding Π orbital.

b. (4 points) Explain why we do not consider the $1s$, $2s$, and $2p$ orbitals in this analysis.

c. (4 points) Determine the ground state term symbols of S_2 and S_2^+.

d. (4 points) Determine the bond order of S_2 and S_2^+.

3. Variation theory and heteronuclear molecules (20 points)

Use variation theory to calculate the form of the Π orbitals and the corresponding orbital energies of the CO molecule (Z(C)=6, Z(O)=8). Consider only the p_x orbitals of C and O. The ionization energies of C and O are 11.3 eV and 13.6 eV, respectively. Use β = -1.5 eV and S = 0; assume the orbitals to be normalized.

a. (8 points) Calculate the energies of the bonding and antibonding Π orbitals.

b. (8 points) Calculate the composition of the bonding orbital of CO. Is it as you expected? Explain your answer.

b. (4 points) Consider a similar treatment for the Π orbitals of the BO molecule (Z(B)=5). Would the bonding orbital in BO have a larger or a smaller contribution of the p_x orbital of oxygen than in CO? Explain your answer.

4. Molecular spectroscopy (26 points)

a. (6 points) Consider electric dipole (E1) transitions between rotational states of a diatomic molecule. Show that such transitions are only allowed (within the Born-Oppenheimer approximation) if the molecule has a permanent dipole moment.

b. (4 points) Give one example of a molecule that will show a pure rotational spectrum and one that won't.

c. (6 points) Make a schematic drawing of the ground and excited state potential energy curves for a molecule, X_2. Label the axes appropriately, and indicate in the figure the equilibrium distances R_e (assume that the equilibrium bond length is larger in the excited than in the ground state), the dissociation energy D_0 and the bond energy D_e of the ground electronic state. Indicate a few vibrational and rotational energy levels in the potential curves, roughly to scale.

d. (6 points) For the HF molecule, the bond energy is $D_e = 6.124$ eV and the vibrational constants are $\omega_e = 4138$ cm^{-1}, and $\omega x_e = 89.9$ cm^{-1} (the conversion factor between eV and cm^{-1} is 1 eV =8066 cm^{-1}). Calculate the dissociation energy, D_0, of HF. You can use the following expression for the vibrational energy.

$$E_v = \omega_e \left(v + \frac{1}{2}\right) - \omega x_e \left(v + \frac{1}{2}\right)^2 \tag{1}$$

e. (4 points) Consider the DF molecule. Discuss (qualitatively, no calculations needed), whether this molecule will have a higher or lower dissociation energy D_0 than HF. Assume that the potential energy curve and thus the D_e is identical for the two molecules.