Materials Design: Theoretical Methods. 06/05/2013, 18.30 – 21.30, A. Jacobshal

- Read the exercises carefully;
- **Explain all your answers (no explanation, no points!).**

Question 1 (8 points (2,2,2,2))

a) Calculate the commutator $\left[\hat{x},\hat{x}\frac{d}{dx}\right]$.

b) Operator A and B commute ([A,B]=0). The function f is an eigenfunction of operator A with eigenvalue a. However, $Bf = f + g$. Is the function g an eigenfunction of A, and if so, what is its eigenvalue?

c) A system is described by the wavefunction $\psi = \phi_1 + 2\phi_2$. The functions ϕ_i are orthonormal. Is this wavefunction normalised to 1? If not, normalise the wavefunction to 1.

d) A particle (in a one-dimensional world) is described by the wavefunction $\psi = e^{i2x}$. If you would measure the linear momentum ($\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$), what value would you measure? If you repeat this experiment many times, what would be the average value for the linear momentum?

Question 2 (8 points (2,2,2,2))

Using perturbation theory, the effect of an unspecified field in the z-direction is calculated for the hydrogen atom. This unspecified field can be described with zL_zF.

a) Give the expressions for H^0 and V.

b) Which function is $\psi_0^{(0)}$? Be as specific as possible.

c) Give the expression for $E^{(1)}$.

d) $E^{(2)}$ is given by $E^{(2)} = -\sum_{i\neq 0} \frac{\left\langle \psi_i^{(0)} \middle| V \middle| \psi_0^{(0)} \right\rangle^2}{E_i^{(0)} - E_0^{(0)}}$. Which functions (be as specific as possible) belong to the set $\psi_i^{(0)}$?

Question 3 (8 points (4,4))

To solve a quantum chemical problem, one uses variation theory with the trial function $\psi = a\varphi_1 + b\varphi_2$ (φ_1 and φ_2 are orthonormal basis functions). One calculates the matrix elements of the Hamiltonian and finds (in eV):

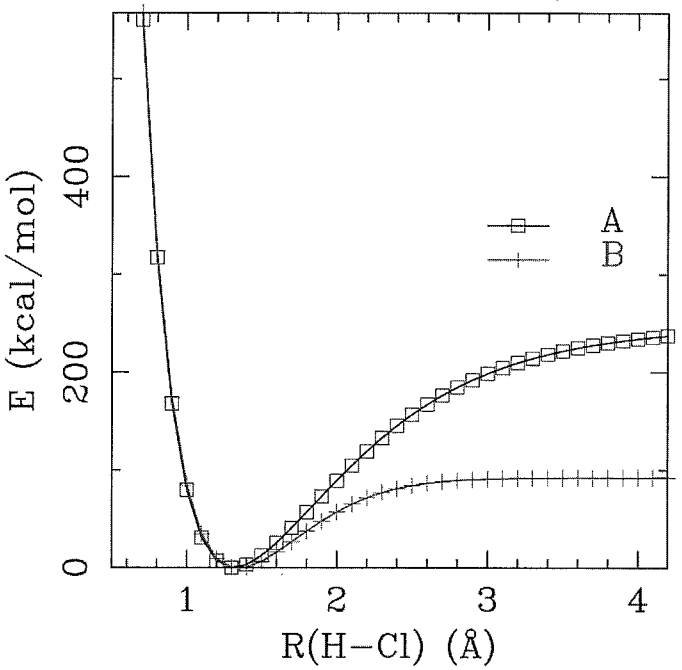
$\langle \varphi_1 | H | \varphi_1 \rangle = -1.0$; $\langle \varphi_2 | H | \varphi_2 \rangle = -0.0$; $\langle \varphi_1 | H | \varphi_2 \rangle = -1.0$

a) Calculate the energy of the ground state.

b) Calculate the corresponding wavefunction.

Question 4 (9 points (3,2,2,2))

A student studies the dissociation of HCl. Therefore, she calculates with both the Hartree-Fock method and the configuration interaction method with the SV 3-21G basis set the energy as a function of the H-Cl distance ***R*** (see figure). She has set both minima at 0.00 kcal/mol in the figure.



a) Which line corresponds to the Hartree-Fock calculation and which to the configuration interaction calculation and why?
b) What is the best estimate for the dissociation energy for HCl?
c) Mention two different possibilities to improve her estimate of the HCl dissociation energy.
d) Which of the two methods, Hartree Fock or configuration interaction, gives the lowest total energy at the minimum in the curve?

Question 5 (10 points (2,4,4))

a) Give the number of different spinfunctions that can be generated for a system with 5 electrons in 5 singly occupied orbitals.
b) Use a branching diagram to determine how many different doublets, quartets and sextets can be made for 5 electrons in 5 singly occupied orbitals.
c) Give the unnormalised spinfunction with M_S = -3/2 for the highest possible multiplet.

Question 6 (10 points (2,2,2,2,2))

A student wants to do a Hartree-Fock calculation on the NO molecule. She can choose between a 6-31G basis set and the 6-31G* basis set.

a) What is the difference between these two basis sets, and which basis set gives a lower Hartree-Fock energy?

b) If she uses the 6-31G* basis set, how many basis functions does she have in her calculation?

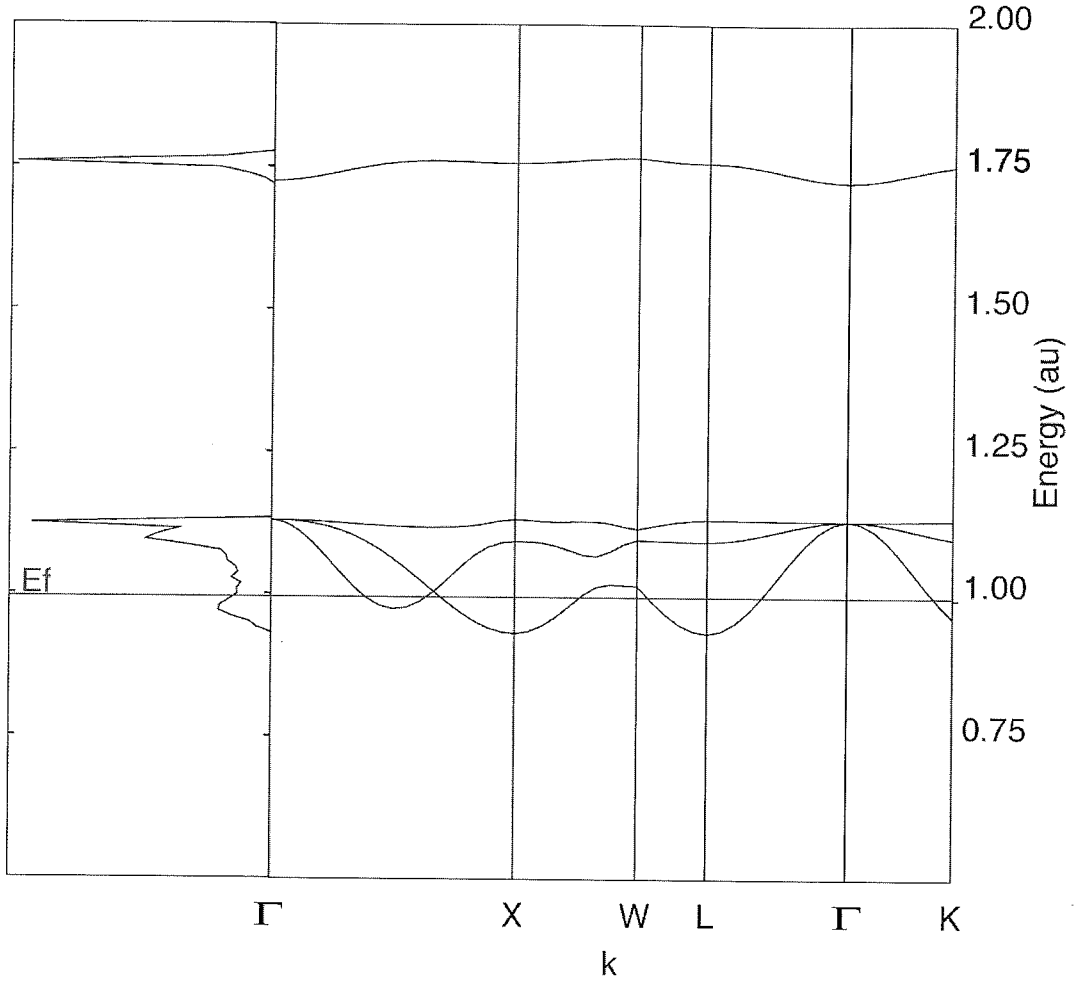
c) The Hartree-Fock energy in terms of spinorbitals is given by $E_{HF} = \sum_I h_{II} + \sum_I \sum_J (II \mid JJ) - (IJ \mid JI)$. Explain what the various terms are in the expression for the Hartree-Fock energy, and explain over what the summations go.

d) The student performs a restricted Hartree-Fock calculation. Give an expression for the restricted Hartree-Fock wavefunction for the NO molecule. Use for the molecular orbitals the abbreviations *a*, *b*, etc.

e) If the student would do an unrestricted Hartree-Fock calculation, would she get a lower, higher or the same energy? Explain your answer!

Question 7 (10 points (4,6))

A student has calculated a band structure and DOS (see the Figure) for Li (all valence bands are shown). The Fermi-level is indicated with a red line.



a) According to the band structure and DOS, did he do the calculation on a conductor or insulator?

b) He used a basis set that has five basis functions per lithium atom. How many atoms are in the unit cell? Why are there only four bands in the Figure?

The End

Examination mark: $\frac{\#p+7}{7}$

Final mark: 0.25 * practicum + 0.75 * examination