Materials Design: Theoretical Methods. 07/04/2013, 9.00 – 12.00, 5113.0201

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

Question 1 (8 punten (2,2,2,2))

a) Calculate the commutator $\left[\hat{y}^2, \frac{d}{dy}\right]$.

b) f en g are degenerate eigenfunctions of operator A with eigenvalue a. Is $h=c_1f + c_2g$ (met $c_1 \neq c_2$) also an eigenfunction of A? If yes, what is the eigenvalue?

c) A system is described by the wavefunction $\psi = \phi_1 + 2\phi_2$. $\langle\phi_1|\phi_1\rangle = \langle\phi_2|\phi_2\rangle = 1.0$ and $\langle\phi_1|\phi_2\rangle = 0.3$. 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 $\psi = \sin(3x)$. 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 punten (2,2,2,2))

Using perturbation theory, the effect of a uniform magnetic field in the z-direction is calculated for the hydrogen atom. The magnetic field can be described with $\frac{1}{2}L_zB$.

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

b) Which function is $\psi^{(0)}$?

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

d) $E^{(2)}$ is given by $E^{(2)} = -\sum_{i\neq 0} \frac{\langle\psi_i^{(0)}|V|\psi^{(0)}\rangle^2}{E_i^{(0)} - E^{(0)}}$. Which functions belong to the set $\psi_i^{(0)}$?

Question 3 (8 punten (4,4))

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

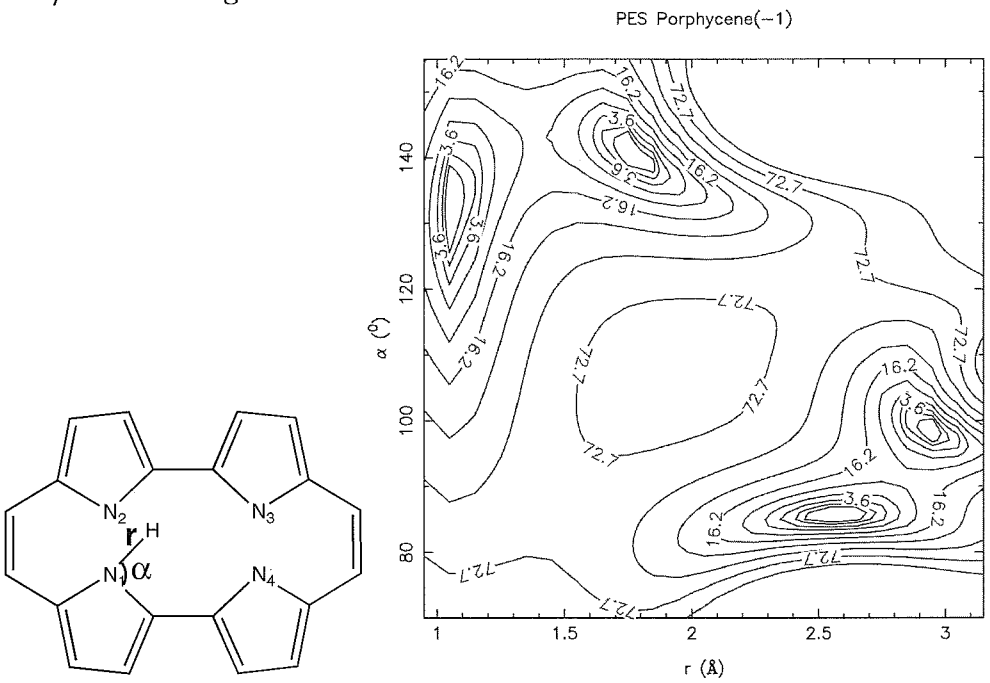
$\langle\varphi_1|H|\varphi_1\rangle = -1.5$; $\langle\varphi_2|H|\varphi_2\rangle = -1.0$; $\langle\varphi_1|H|\varphi_2\rangle = -0.25$

a) Calculate the energy of the ground state.

b) Calculate the corresponding wavefunction.

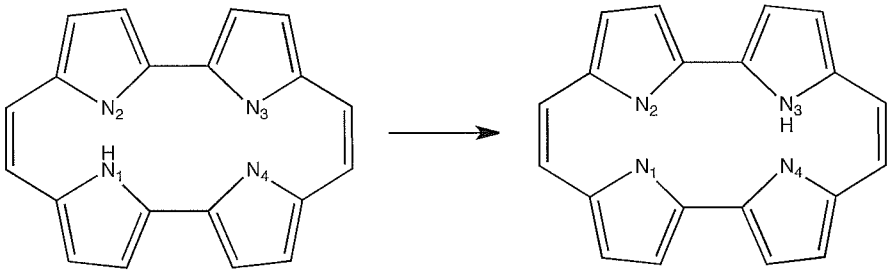
Question 4 (7 punten (3,2,2))

A student studies the different isomers of porphycene(-1). Therefore, she calculates with the Hartree-Fock method and the STO-3G basis set the energy as a function of r en α (see figure). She has set the lowest minimum at 0.00 kcal/mol in the figure.



a) She sees in the figure that there are several minima and transition states. Give an estimate for r en α of all minima and transition states, and indicate in the Figure (see the answer sheet) the minima and transition states. Number your minima in such a way that minimum 1 corresponds to the structure with the hydrogen attached to nitrogen 1 etc.

b) Indicate in the Figure on the answer sheet the reaction path for the following reaction and, if applicable, give the structure(s) of the intermediate(s):



c) Mention two different possibilities to improve her calculations.

Question 5 (12 punten (2,2,2,2,2,2))

A student wants to do a closed shell Hartree-Fock calculation on the CO molecule. She can choose between a minimal STO-3G basis set or the 6-311G* 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 6-311G* basis set, how many basis functions does she have in her calculation?

c) The Hartree-Fock energy is in this case given by $E_{HF} = \sum_i 2h_{ii} + \sum_i \sum_j 2(ii \mid jj) - (ij \mid ji)$. Explain what the various terms are in the expression for the Hartree-Fock energy, and indicate the limits of the summations.

d) Give the Hartree-Fock wavefunction for the CO molecule. Use for the molecular orbitals the abbreviations *a*, *b*, etc.

e) Is the final Hartree-Fock wavefunction an eigenfunction of the Hamiltonian for the CO molecule and are the molecular orbitals eigenfunctions of the Fock operator? If so, what are the eigenvalues of these operators?

f) The expression for a Fock matrix element in this case is $F_{ij} = h_{ij} + \sum_n 2(nn \mid ij) - (in \mid nj)$ or $F_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} P_{\rho\sigma}[(\mu\nu \mid \rho\sigma) - \frac{1}{2}(\mu\rho \mid \sigma\nu)]$.

What is the matrix **P**, and explain the factor of ½ in front of (μρ|σν) in the second expression for the Fock matrix.

Question 6 (10 punten (2,4,4))

Different spinfunctions can be generated for a system with three electrons in three singly-occupied orbitals.

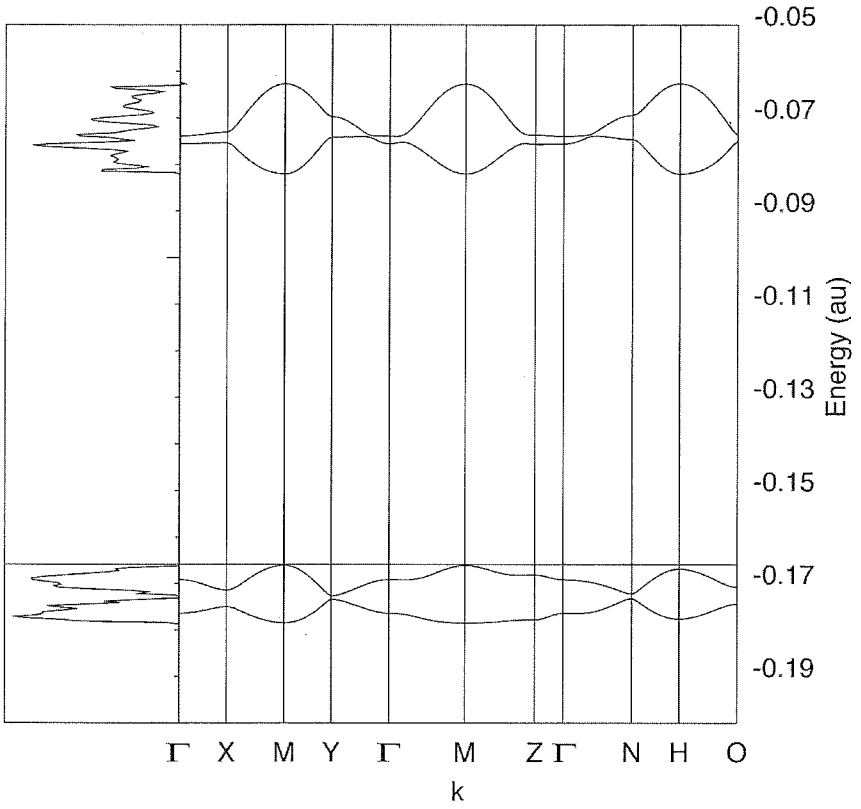
a) Give the number of different spinfunctions that can be generated.

b) Give for all spinfunctions that can be generated the eigenvalues of the S^2 en S_z operators.

c) Give the unnormalised spinfunction with $M_S = 1/2$ for the highest possible multiplet.

Question 7 (10 punten (2,4,4))

A student has calculated a band structure and DOS (see figure) for tetracene ($C_{18}H_{12}$). The Fermi-level is indicated with a red line.



a) Did he do the calculation on a conductor or insulator according to the band structure and DOS?

b) He used a basis set that has 5 basis functions per carbon atom and 1 basis function per hydrogen atom. There are 4 tetracene molecules in the unit cell. How many bands do you expect to see, and why are there only four bands in the shown band structure plot?

c) Give a sketch of the band structure plot that you would obtain if the molecules had no mutual interaction at all.

The End

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

Final mark: 0.25 * practicum + 0.75 * examination