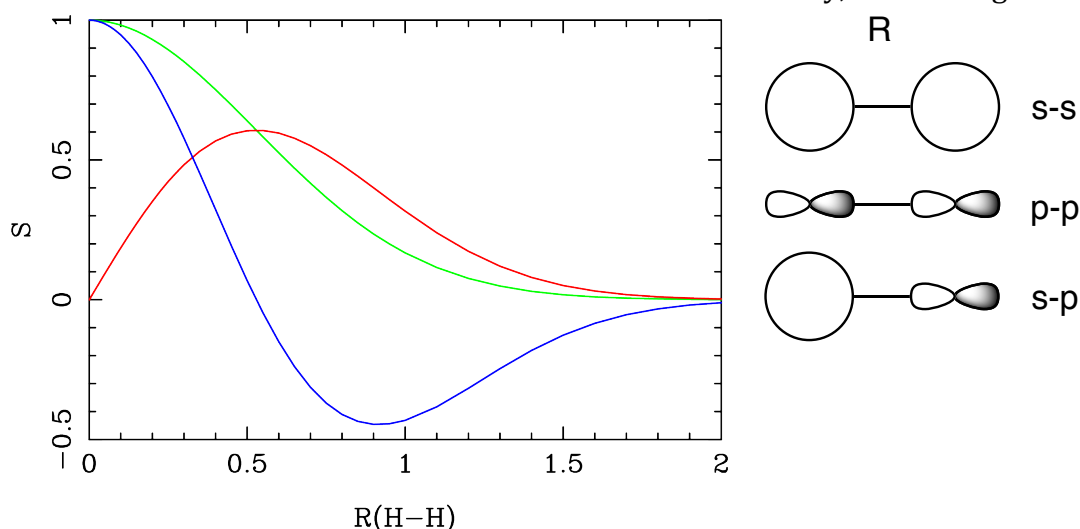


Examination Quantum Chemistry. 09/03/2020, 14.30 - 18.00

- This exam has 7 questions on 4 pages;
- **Explain all your answers (no explanation, no points!).**
- **Do not forget your name and s-number!**
- Review: Dr. J.E.M.N. Klein
- Grade: $\frac{\# p + 7}{7}$, maximum number of points is 63.

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

The overlap between two hydrogen s-orbitals, p-orbitals and an s- and p-orbital is calculated as a function of the H-H distance. Unfortunately, the labels got lost.



- Explain which curve belongs to which overlap.
- Sketch the energy difference between the bonding and the anti-bonding σ orbitals for H_2 as a function of the interatomic distance. Explain why you have drawn the curve as you did.
- Is the restricted Hartree-Fock method appropriate to describe this dissociation?
- Explain what you expect for the calculated dissociation energy using the restricted Hartree-Fock method compared to experiment. Do you expect it to be too small, too high, or correct, and why?

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

- Mention one difference between HF and DFT.
- Mention one functional that can be used in a DFT calculation.
- Does the following two-electron wavefunction, $\Psi(1,2) = |a\bar{a}| + |b\bar{b}|$, obey the Pauli principle?
- Is the wavefunction mentioned in question c) normalised to 1? If not, normalise it to 1 (the orbitals a and b are orthonormal).

Question 3 (8 points (1,1,2,2,2))

- a) A system is in a particular quantum state described by the wavefunction

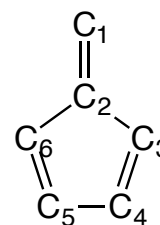
$$\psi = \frac{1}{\sqrt{2}}(f + g). \text{ The functions } f \text{ and } g \text{ are eigenfunctions of the operator}$$

$$A: Af = a_1f; Ag = a_2g \quad (a_1 \neq a_2).$$

- i. Is the function ψ an eigenfunction of operator A? If so, what is the eigenvalue?
 - ii. Calculate the expectation value for operator A.
- b) Explain why the dissociation energy for D_2 ($D = {}^2H$) is slightly different from that of H_2 .
- c) Give a short description of the CI method.
- d) Mention an example of a chemical problem for which the use of the MCSCF method is recommended.

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

Hückel theory is used for the study of the following molecule:



- a) Give the secular determinant for this system.

The results of a Hückel calculation are summarised in the Table.

Table

	MO 1	MO 2	MO 3	MO 4	MO 5	MO 6
ϵ	$\alpha + 2.11\beta$	$\alpha + 1.00\beta$	$\alpha + 0.62\beta$	$\alpha - 0.25\beta$	$\alpha - 1.62\beta$	$\alpha - 1.86\beta$
C_1	-0.2473	-0.5000	0.0000	-0.7495	0.0000	-0.3566
C_2	-0.5230	-0.5000	0.0000	0.1904	0.0000	0.6635
C_3	-0.4294	0.0000	-0.6015	0.3505	0.3717	-0.4390
C_4	-0.3851	0.5000	-0.3717	-0.2795	-0.6015	0.1535
C_5	-0.3851	0.5000	0.3717	-0.2795	0.6015	0.1535
C_6	-0.4294	0.0000	0.6015	0.3505	-0.3717	-0.4390

- b) What is the total Hückel energy for this system?
- c) The energy of the double bond in ethene is $\alpha + \beta$. What is the resonance or delocalisation energy for this molecule?
- d) Calculate the charge of the C_1 atom.
- e) Calculate the C_2 - C_3 π -bond order.

Question 5 (11 points (2,2,2,2,1))

The bonding orbital of H_2^+ is written as, $\psi = c_1 s_A + c_2 p_A + c_3 s_B + c_4 p_B$, with $s_{A/B}$ the 1s orbital centred on atom A/B, and $p_{A/B}$ the p-orbital, aligned along the intermolecular axis, on atom A/B, respectively. The atomic orbitals are considered to be orthonormal and the following integrals have been calculated (all in Hartree):

$$\int s_A H s_A d\tau = \int s_B H s_B d\tau = -0.5$$

$$\int p_A H p_A d\tau = \int p_B H p_B d\tau = -0.125$$

$$\int s_A H p_A d\tau = \int s_B H p_B d\tau = 0.0$$

$$\int s_A H s_B d\tau = -0.4$$

$$\int s_A H p_B d\tau = \int p_A H s_B d\tau = -0.3$$

$$\int p_A H p_B d\tau = -0.2$$

- a) Give the secular determinant for this problem.

The use of symmetry can greatly reduce the complexity of the problem. We treat the molecule in the subgroup C_i of the full point group. The character table for C_i is:

$C_i = S_2$ (1)	E	i		
A_g	1	1	R_x, R_y, R_z	$x^2, y^2, z^2,$ xy, xz, yz
A_u	1	-1	x, y, z	

- b) Make the symmetry adapted linear combinations (SALCs) of the basis functions that we have in this case, and indicate according to which irreducible representation they transform.
- c) Give the secular determinant in this SALC basis.
- d) Determine the ground state energy of H_2^+ .
- e) Calculate the ground state wavefunction for H_2^+ . Express the final orbital in terms of the original atomic orbital basis.
- f) What would happen with the energy if we add a set of d-orbitals to each hydrogen atom?

Question 6 (8 points (2,2,2,2))

One spinorbital of the hydrogen atom can be written as:

$$\psi(r, \vartheta, \phi) = \alpha N r^3 e^{-r/4} \sin^3 \vartheta e^{-3i\phi}.$$

- What do the variables r , ϑ , ϕ of the function $\psi(r, \vartheta, \phi)$ indicate?
- How many radial and angular nodes has this orbital?
- What are the four quantum numbers for an electron described by this wavefunction?
- Is there also a hydrogen orbital that is degenerate with this orbital, that has 4 angular nodes?

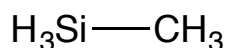
Question 7 (10 points (2,2,2,2,2))

Given the character table of the C_{3v} point group.

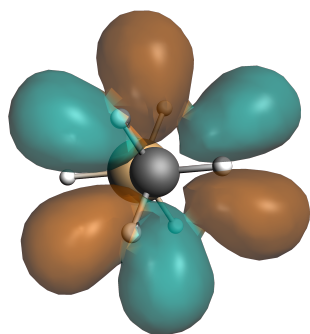
C_{3v} ($3m$)	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, 2xy)(xz, yz)$

- How many classes does the C_{3v} point group have?
- Show that C_3^+ and C_3^- are conjugated elements.
- Is the C_{3v} point group an Abelian group?

A conformation of the H_3Si-CH_3 molecule belongs to the C_{3v} point group (with the C_3 axis aligned along the z -axis).



- Argue on the basis of symmetry whether this molecule can have a permanent dipole.
- According to which irreducible representation does the following orbital transform?



The End