
Faculty of Science

Exam

Quantum Theory of Molecules and Matter Master Chemistry (joint degree)

Tentamen

Date: 25 October 2017

Time: 13-16 hours

Number of pages: 7 (including front page)

Number of open questions: 8

For each question the maximum number of points is indicated. Total number of points:
100

BEFORE YOU START

- Check if your version of the exam is complete.
- Write down **your name, student ID number**, and if applicable the **version number** on **each sheet** that you hand in. Also **number the pages**.
- Your **mobile phone** has to be switched off and be put in your coat or bag. Your **coat and bag** should be on the ground.
- **Tools allowed:** Kladpapier, Rekenmachine (grafisch), Rekenmachine (niet-grafisch), Studieboek of reader. Other tools are not allowed.

PRACTICAL MATTERS

- The first 30 minutes and the last 15 minutes you are not allowed to leave the room, not even to visit the toilet.
- 15 minutes before the end, you will be warned that the time to hand in is approaching.
- If applicable, fill out the evaluation form at the end of the exam.
- You are obliged to identify yourself at the request of the examiner (or his representative) with a proof of your registration and a valid ID.
- During the examination it is not permitted to visit the toilet, unless the invigilator gives permission to do so.
- You may take this exam paper with you when you are done.

Good luck!

Exercise 1 (6 points)

Paola

Consider an electron in the H atom whose state is described by the following wavefunction:

$$\psi(r, \vartheta, \varphi) = R_{32}(r)Y_{21}(\vartheta, \varphi) + (1 - i)R_{31}(r)Y_{11}(\vartheta, \varphi) + (1 + i)R_{30}(r)Y_{00}(\vartheta, \varphi)$$

where $R_{n\ell}(r)$ are the solutions of the radial part of the H atom Hamiltonian and $Y_{\ell m}(\vartheta, \varphi)$ are spherical harmonics

¹(a) Is $\psi(r, \vartheta, \varphi)$ normalized? If not, normalize it.

¹(b) Is $\psi(r, \vartheta, \varphi)$ an eigenfunction of the Hamiltonian for the electron in the H atom? Explain your answer

¹(c) Is $\psi(r, \vartheta, \varphi)$ an eigenfunction of the square of the electron angular momentum operator ℓ^2 ? Explain your answer.

¹(d) Is $\psi(r, \vartheta, \varphi)$ an eigenfunction of the z component of the electron angular momentum operator ℓ_z ? Explain your answer.

For the following question, consider the normalized wavefunction from question (a):

²(e) If we measure the energy of the electron in the state $\psi(r, \vartheta, \varphi)$ which values can we obtain? With which probabilities? Answer to the same question for a measure of ℓ^2 and ℓ_z .

Exercise 2 (8 points)

Paola

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Consider the raising angular momentum operator

$$\ell_+ = \ell_x + i\ell_y$$

²(a) Compute the commutator $[\ell_+, \ell_x^2]$

²(b) Compute the matrix element $\langle 3\ 1 | \ell_y | 3\ 2 \rangle$, where the notation $|\ell\ m\rangle$ indicates eigenstates of ℓ^2 and ℓ_z .

⁴(c) A system has orbital angular momentum $\ell = 3$ and spin angular momentum $s = 1$. Write all the microstates of the system in the uncoupled representation $|\ell\ m_\ell\ s\ m_s\rangle$ and in the coupled representation $|\ell\ s\ j\ m_j\rangle$.

Exercise 3 (10 points)

H. Zhang

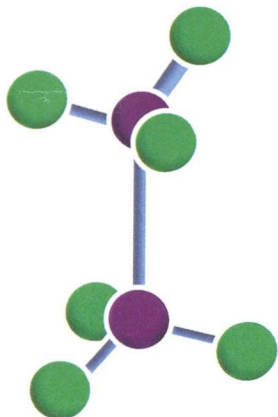
⁴(a) Determine the values of the missing characters X1 to X4 in the following D_{3d} character table. Explain your answer from the point of view of group theory.

Character table D_{3d} point group

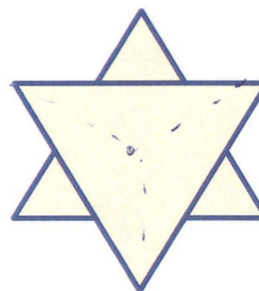
| | E | $2C_3$ | $3C'_2$ | i | $2S_6$ | $3\sigma_d$ | linear, rotations | quadratic |
|----------|----|--------|---------|----|--------|-------------|-------------------|--------------------------|
| A_{1g} | 1 | 1 | 1 | 1 | 1 | 1 | | x^2+y^2, z^2 |
| A_{2g} | 1 | 1 | -1 | 1 | 1 | -1 | R_z | |
| E_g | 2 | -1 | 0 | 2 | -1 | 0 | (R_x, R_y) | $(x^2-y^2, xy) (xz, yz)$ |
| A_{1u} | 1 | 1 | 1 | -1 | -1 | -1 | | |
| A_{2u} | 1 | 1 | -1 | -1 | -1 | 1 | z | |
| E_u | X1 | X2 | X3 | X4 | 1 | 0 | (x, y) | |

0145

⁴(a) Determine the point group to which the staggered form of ethane (C_2H_6) belongs.



(i) Structure of staggered form ethane



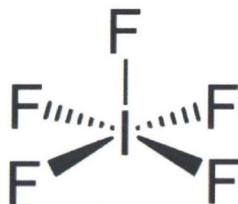
(ii) Top view of the staggered form ethane

²(b) Does the staggered form ethane have a permanent dipole moment? Explain your answer from the point of view of group theory.

Exercise 4 (15 points)

Zhong

It is known that the molecule IF_5 shown below belongs to the point group C_{4v} :



Structure of IF_5

¹⁰(a) Which symmetry species do the vibrational modes of IF_5 span?

⁵(b) Determine for each of the vibrational modes if the mode is infrared active.

Note: Based on Cartesian coordinates the contribution of each unshifted atom to the character of the reducible representation

| operation | Contribution to character |
|-----------|---------------------------|
| E | 3 |
| i | -3 |
| σ | 1 |
| C_n | $2\cos(2\pi/n)+1$ |
| S_n | $2\cos(2\pi/n)-1$ |

$C_2 = -1$ $C_4 = 1$

Exercise 5 (12 points)

Burna

Consider a particle with mass m in a one-dimensional box of length L for which the potential energy is given by

$$V(x) = \begin{cases} 0, & 0 \leq x \leq L \\ \infty, & \text{otherwise} \end{cases}$$

As has been derived in Chapter 2, the eigenfunctions of this problem are given by

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$$

The potential energy is now perturbed by an additional potential of which the height is $+a$ for $0 \leq x \leq L/2$ and $-a$ for $L/2 < x \leq L$.

- ⁵(a) What is the first-order correction to the energy of the ground state due to this perturbation?
- ⁷(b) Derive an expression for the wavefunction of the ground state that has been corrected for the contribution of the first excited state.

N.B. Use $\sin(2\theta) = 2\sin(\theta)\cos(\theta)$!

e Exercise 6 (13 points) *Berno*

In the following exercise we will use hydrogen eigenfunctions that are given in this exercise as $\psi_{n,l,m_l}(r, \theta, \phi)$

$$\begin{aligned}\psi_{100}(r, \theta, \phi) &= (\pi a_0^3)^{-1/2} \exp\left(-\frac{r}{a_0}\right) \\ \psi_{211}(r, \theta, \phi) &= -(\pi a_0^3)^{-1/2} \frac{r}{8a_0} \sin \theta \exp(i\phi) \exp\left(-\frac{r}{2a_0}\right) \\ \psi_{210}(r, \theta, \phi) &= (8\pi a_0^3)^{-1/2} \frac{r}{2a_0} \cos \theta \exp\left(-\frac{r}{2a_0}\right) \\ \psi_{21-1}(r, \theta, \phi) &= (\pi a_0^3)^{-1/2} \frac{r}{8a_0} \sin \theta \exp(-i\phi) \exp\left(-\frac{r}{2a_0}\right)\end{aligned}$$

Given is that

$$\int_0^\infty \exp(-br)r^n dr = n!/b^{n+1}, \quad n > -1$$

A hydrogen atom is placed in a uniform but time-dependent electric field in the z-direction with a magnitude of

$$\begin{cases} \mathcal{E} = 0 & \text{for } t < 0 \\ \mathcal{E} = \mathcal{E}_0 \exp(-t/\tau) & \text{for } t \geq 0 \quad (\tau > 0) \end{cases}$$

leading to a perturbing Hamiltonian that is given by

$$\hat{H}^{(1)}(t) = -e(-\mathcal{E}_0 z \exp(-t/\tau))$$

At time $t=0$, the hydrogen atom is in the ground (1s) state.

6(a) Show that the transition probability amplitude for finding the atom at time $t = t$ in its excited 2p state is given by

$$c_{1s \rightarrow 2p} = \frac{1}{i\hbar} \int_0^t \langle 210 | \hat{H}^{(1)}(t') | 100 \rangle \exp(i\omega t') dt'$$

where $\omega = (E_{2p} - E_{1s})/\hbar$.

N.B. You thus have to show in this part as well that the transition probabilities to the other 2p states are zero.

7(b) Calculate the probability to find the hydrogen atom at time $t = \infty$ in its excited 2p state in terms of the symbols used in this exercise ($\mathcal{E}_0, E_{1s}, E_{2p}, a_0$, etc.)

Exercise 7 (20 points)

Paola

Consider a Sulfur (S) atom in the ground-state configuration $1s^2 2s^2 2p^6 3s^2 3p^4$.

- ⁴(a) Give the terms (and their degeneracy) that arise from this configuration.
- ³(c) Give the levels that are obtained when we consider also the spin-orbit coupling. Which one has the lowest energy?
- ³(b) Answer to questions a) and b) for the excited configuration $1s^2 2s^2 2p^6 3s^2 3p^2 4s^2$.
- ⁴(d) Predict the lowest energy term for the Europium (Eu atom) in its ground state configuration $[\text{Xe}] 4f^7 6s^2$ (*hint*: you don't need to construct the microstates for this case, since **only the lowest energy term** is requested. Explain your reasoning.)
- ⁶(e) Give the ground state configurations and terms of the molecules F_2 and F_2^+ , and give their bond orders.

Exercise 8 (15 points)

Paola

Consider an approximation for the K atom in which the effect of the core electrons is modeled with an effective central potential, so that only the 4s electron needs to be treated explicitly. Study the molecules K_2^+ and K_2 within this approximation:

- ²(a) Denoting $A(\mathbf{r})$ and $B(\mathbf{r})$ the (approximate) 4s orbitals centered in the two atoms, write the two LCAO bonding and antibonding orbitals. Write the (approximate) ground-state wave functions for the two molecules K_2^+ and K_2 in terms of these orbitals. Do not forget the spin part.
- ³(b) For the molecule K_2 write also the other three LCAO wavefunctions for the singlet and triplet states constructed from the excited configurations $1\sigma_g^1 1\sigma_u^1$ and $1\sigma_u^2$. Do not forget the spin part.
- ³(c) Consider the singlet and triplet states of question b) arising from the configuration $1\sigma_g^1 1\sigma_u^1$. Which of the two states has lower energy? Why?

Consider now the Heitler-London approximate wavefunction at large internuclear separations R (where we can set the overlap integral $S \approx 0$):

$$\psi_{HL}(1,2) = \frac{1}{\sqrt{2}} [A(\mathbf{r}_1)B(\mathbf{r}_2) + B(\mathbf{r}_1)A(\mathbf{r}_2)] \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

- ²(d) Explain the physical meaning of this wavefunction.
- ⁵(e) Show explicitly that this wavefunction can be written as a linear combination of the two LCAO singlet wavefunctions of g symmetry, $1\sigma_g^2$ and $1\sigma_u^2$, computed in b), by finding the coefficients appearing in the linear combination. You can keep the overlap integral $S = 0$ in all your calculations.

