
Faculty of Science

Exam

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

Tentamen

Date: 21 October 2019

Time: 13-16 hours

Number of pages: 6 (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 (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 (8 points)

For a particle confined to the region $0 \leq x \leq a$ on the x-axis (1D box with length a), consider the wavefunction

$$\phi(x) = C(ax - x^2).$$

²(a) Determine the value of the constant C in order to normalize this wavefunction. Is there only one possible choice for C ?

Consider now the following wavefunction for an electron in the H atom:

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{5}} [R_{21}(r)Y_{1,1}(\theta, \phi) + 2iR_{31}(r)Y_{1,-1}(\theta, \phi)].$$

$R_{n\ell}(r)$ are the solutions of the radial part of the H atom Hamiltonian \hat{H} and $Y_{\ell,m}(\theta, \phi)$ are spherical harmonics. In addition to \hat{H} , consider the operators \hat{L}^2 and \hat{L}_z (square and z-component of the orbital angular momentum).

²(b) Is $\psi(r, \theta, \phi)$ an eigenfunction of any of these operators? Explain your answer.

²(c) Compute the expectation value $\langle \hat{L}_z \rangle$ in the state $\psi(r, \theta, \phi)$.

²(d) If we measure the energy of the electron in the state $\psi(r, \theta, \phi)$ which values can we obtain? With which probabilities?

Exercise 2 (7 points)

Consider the lowering angular momentum operator

$$\ell_- = \ell_x - i\ell_y$$

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

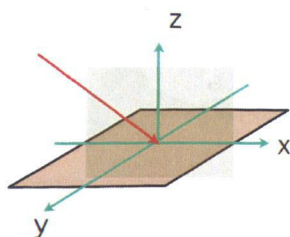
²(b) What is the effect of ℓ_- when is applied to the states $|3\ 2\rangle$ and $|3\ -3\rangle$? (the notation $|\ell\ m\rangle$ indicates eigenstates of ℓ^2 and ℓ_z).

³(c) A system has orbital angular momentum $\ell = 1$ and spin angular momentum $s = \frac{3}{2}$. Write all the microstates of the system in the uncoupled representation $|\ell\ m_\ell\ s\ m_s\rangle$ and in the coupled representation $|\ell\ s\ j\ m_j\rangle$.

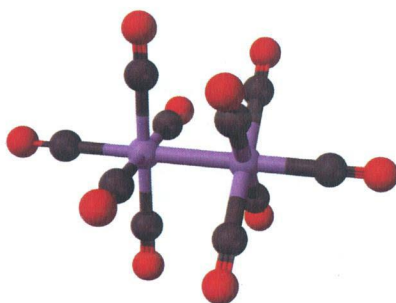
Exercise 3 (10 points)

⁴(a) A Ni atom belongs to the C_{4v} point group when it sits in a fourfold site on an Cu (100) surface as shown below. Determine which electric dipole transitions from its ground $p_{x,y}$ orbital to d orbitals are allowed in the z -direction.

Noe: electric dipole moment operator given by $\hat{\mu}_z = e\vec{z}$



³(b) Determine the point group of the molecule dimanganese decacarbonyl (staggered rotamer with the structure shown below).

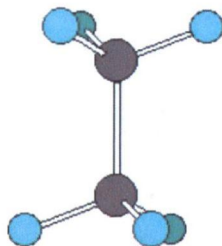


³(c) Fill in the values of the first two columns and the first row of the character table of D_{4h} :

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}										
A_{2g}			1	-1	-1	1	1	1	-1	-1
B_{1g}			1	1	-1	1	-1	1	1	-1
B_{2g}			1	-1	1	1	-1	1	-1	1
E_g			-2	0	0	2	0	-2	0	0
A_{1u}			1	1	1	-1	-1	-1	-1	-1
A_{2u}			1	-1	-1	-1	-1	-1	1	1
B_{1u}			1	1	-1	-1	1	-1	-1	1
B_{2u}			1	-1	1	-1	1	-1	1	-1
E_u			-2	0	0	-2	0	2	0	0

Exercise 4 (15 points)

It is known that staggered ethane (C_2H_6) belongs to point group D_{3d} .



Character table for point group D_{3d}
(x axis coincident with C_2 axis)

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
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	-	-	$x(x^2-3y^2)$
A_{2u}	+1	+1	-1	-1	-1	+1	z	-	$y(3x^2-y^2), z^3, z(x^2+y^2)$
E_u	+2	-1	0	-2	+1	0	(x, y)	-	(xz^2, yz^2) $[xyz, z(x^2-y^2)]$ $[x(x^2+y^2), y(x^2+y^2)]$

Character contribution table for Cartesian coordinates

operation	contribution to character
E	3
i	-3
σ	1
C_n	$2\cos(360/n)+1$
C_2	-1
C_3	0
C_4	1
C_6	2
S_n	$2\cos(360/n)-1$
S_3	-2
S_4	-1
S_6	0

- ²(a) How many vibrational modes does a staggered ethane molecule have?
- ⁴(b) Determine the symmetry species of the vibrational modes.
- ⁴(c) Which of these vibrational modes are bending modes?
- ⁵(d) Which of the vibrational modes are Raman active?

Exercise 5 (8 points)

In the following we consider an infinite square well (see Exercise 1) in which we put as a perturbation a delta-function bump in the center

$$\hat{H}^{(1)} = \alpha \delta\left(x - \frac{a}{2}\right); \quad \delta\left(x - \frac{a}{2}\right) = \begin{cases} 1 & \text{if } x = a/2 \\ 0 & \text{if } x \neq a/2 \end{cases}$$

- ³(a) Find the first-order correction to the allowed energies E_n . Make a distinction between even and odd values of n .
⁵(b) Find the first three nonzero terms in the expansion (6.22) of the correction to the ground state of the system.

Exercise 6 (17 points)

Consider a particle of mass m in a one-dimensional harmonic oscillator potential $V = \frac{1}{2}m\omega_0^2 x^2$. At $t = 0$, it is in the ground state. For $t > 0$, a time-dependent perturbing potential $H^{(1)}(t) = F_0 x \cos \omega t$ is applied where F_0 is constant in both space and time. In the following we will use the bracket notation in which we indicate with $|v\rangle$ the eigenfunction $\psi_v(x) = N_v H_v(\alpha x) e^{-\alpha^2 x^2/2}$ with eigenvalue $E_v = (v + \frac{1}{2})\hbar\omega_0$.

- ⁵(a) Show that

$$c_v(t) = -\frac{i}{\hbar} F_0 \int_0^t \langle v|x \cos(\omega t') |0\rangle e^{i\omega_{v0} t'} dt'$$

in which $c_v(t)$ denotes the coefficient of a particular state $|v\rangle$ in the time-dependent perturbed wave function that is initially zero, and in which $\omega_{v0} = \frac{E_v - E_0}{\hbar}$.

- ⁵(b) Given that

$$\langle v|x|0\rangle = \left(\frac{\hbar}{2m\omega_0}\right)^{\frac{1}{2}}$$

if $v = 1$ and otherwise 0, show that the time-dependent perturbed wavefunction of the ground state only contains contributions from states $|0\rangle$ and $|1\rangle$, and is given by

$$\Psi(t) = e^{-i\omega_0 t/2} |0\rangle + c_1(t) e^{-i3\omega_0 t/2} |1\rangle$$

- ⁷(c) Derive an expression for $c_1(t)$ in terms of F_0 , \hbar , ω , ω_0 , and $\langle 1|x|0\rangle$.

Exercise 7 (20 points)

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

- ⁶(a) Give the terms ^{2S+1}L that arise from this configuration.
- ⁶(b) Give the levels $^{2S+1}L_J$ that are obtained when we consider spin-orbit coupling. Which one has the lowest energy?
- ⁴(c) An excited configuration of the same atom is $1s^2 2s^2 2p^6 3s^2 3p 4s^2 4p$. How do the answers to (a) and (b) change in this case?
- ⁴(d) Give the ground state configurations and terms of the molecules B_2 and B_2^- and give their bond orders.

Exercise 8 (15 points)

Consider an approximation for the Li atom (ground-state configuration: $1s^2 2s$) in which the effect of the 1s electrons is modeled with an effective central potential, so that only the 2s electron needs to be treated explicitly. Study the molecules Li_2^+ and Li_2 within this approximation:

- ⁴(a) Denoting $A(\mathbf{r})$ and $B(\mathbf{r})$ the (approximate) 2s orbitals centered in the two atoms, write the LCAO ground-state wave function for the two molecules Li_2^+ and Li_2 . Do not forget the spin part.
- ³(b) Which of the two molecules do you expect to be better described by the LCAO wavefunction? Why?
- ⁶(c) Write in terms of the $1\sigma_g$ and $1\sigma_u$ molecular orbitals the corresponding four possible LCAO wavefunctions for the molecule Li_2 (corresponding to the configurations $1\sigma_g^2$, $1\sigma_u^2$, $1\sigma_g^1 1\sigma_u^1$). Indicate explicitly the total spin of the electrons in each case.
- ²(d) Without doing any calculation, explain why the excited triplet wavefunction $1\sigma_g^1 1\sigma_u^1$ is expected to give a lower energy than the excited singlet wavefunction $1\sigma_g^1 1\sigma_u^1$.