UNIVERSITY OF AMSTERDAM

Faculty of Science

Exam

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

Hertentamen
Date: 9 January 2017
Time: 18-21 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 (grafisch), Rekenmachine (niet-grafisch), Studieboek of reader, Group theory hand outs. Other tools are not allowed.

PRACTICAL MATTERS

- The first 30 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!

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

$$\psi(r, \vartheta, \varphi) = R_{21}(r)(2Y_{10}(\vartheta, \varphi) + i\, Y_{1-1}(\vartheta, \varphi))$$

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 the wavefunction normalized? If not, normalize it.

For the following questions, consider the normalized wavefunction:

[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.

[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.

Consider the raising angular momentum operator
$$\ell_+ = \ell_x + i\ell_y$$

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

[1](b) What is the effect of ℓ_+ when is applied to the states $|3\,1\rangle$ 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 $\ell = 3$ and spin angular momentum $s = \frac{1}{2}$. Write all the microstates of the system in the uncoupled representation $|\ell\,m_l\,s\,m_s\rangle$ and in the coupled representation $|\ell\,s\,j\,m_j\rangle$.

$$\ell_x \ell_z + i\ell_y \ell_z - \ell_z \ell_x + \ell_z i\ell_y + |\ell_z \ell_x + \ell_z \ell_y$$
$$\hbar \ell_y + i\ell_x -$$
$$\ell_z(\ell_x - \ell_x) + i2\ell_y) \qquad - \ell_z \ell_x$$

$$(\ell_x + i\ell_y)\ell_z$$
$$\ell_x \ell_z + i\ell_y \ell_z + \ell_z \ell_x + i\ell_z \ell_y$$
$$\ell_z(\ell_x - \ell_x) + i2\ell_y \,\#$$

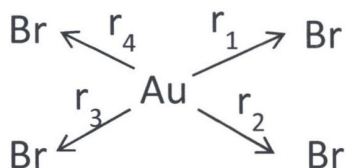[8](a) Detemine the point group to which the following molecules belong:
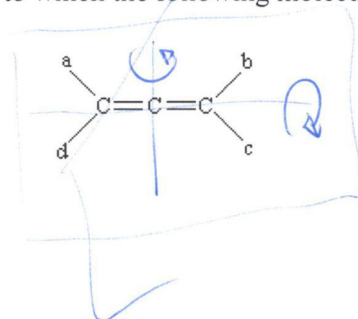
(1) $a = b = c = d$
(2) $a = b$ and $c = d$, but $a \neq c$
(3) $a = d$ and $b = c$, but $a \neq b$
(4) $a \neq b \neq c \neq d$

[2](b) It is known that molecule AB_3 has a C_3 axis and its dipole moment is zero. Which point group does it belong to? Explain your answer.

Exercise 4 (15 points)

$AuBr_4^-$, of which the structure is shown below, belongs to D_{4h} point group:

Use r_1, r_2, r_3 and r_4 as generating coordinator and find out the symmetry-adapted linear combination (SALC) for A_1 and B_1.

* Character table for D_{4h} point group

	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linears, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

2

Exercise 5 (7 points)

In the following we consider a ground-state harmonic oscillator with frequency ω for which the ground state is given by the wavefunction

$$\psi_0(x) = \left(\frac{\alpha}{\pi^{1/2}}\right)^{1/2} e^{-\alpha^2 x^2/2}$$

Suppose that this ground-state harmonic oscillator experiences a constant perturbation a during expansion ($x \geq 0$). Determine the second-order correction to its energy due to the $v = 1$ state for which the wavefunction is given by

$$\psi_1(x) = \left(\frac{2\alpha^3}{\pi^{1/2}}\right)^{1/2} x e^{-\alpha^2 x^2/2}$$

Exercise 6 (18 points)

According to the variation of constants technique, the coefficient of a state f that was initially unoccupied is given by:

$$c_f(t) = -\frac{i}{\hbar} \int_0^t H_{fi}^{(1)}(t) e^{i\omega_{fi} t} dt$$

Suppose a time-dependent perturbation $H^{(1)}(t)$ is applied which is 0 for $t < 0$ and $t > T$, and a constant V_0 for $0 \leq t \leq T$.

[4](a) Explain why in this case the expression for $c_f(t)$ can be written as

$$c_f(t) = -\frac{i}{\hbar} H_{fi}^{(1)} \int_0^t e^{i\omega_{fi} t} dt$$

in which $H_{fi}^{(1)} = \langle f|V_0|i \rangle$.

[4](b) Show that working out the integral leads to an expression for $c_f(t)$ that reads

$$c_f(t) = -\frac{H_{fi}^{(1)}}{(E_f - E_i)} e^{\frac{i(E_f - E_i)t}{2\hbar}} 2i \sin\left(\frac{E_f - E_i}{2\hbar} t\right)$$

Hints: (1) $\hbar\omega_{fi} = E_f - E_i$; (2) $\sin x = \frac{e^{ix} - e^{-ix}}{2i}$

3

Now consider a particle of mass m that <u>initially</u> is in the ground state ($n = 1$) of a one-dimensional infinite square well of length a. At time $t = 0$ the potential is changed into

$$V(x) = \begin{cases} V_0 & 0 \leq x \leq a/2 \\ 0 & a/2 \leq x \leq a \\ \infty & \text{otherwise} \end{cases} \qquad \text{with } V_0 \ll E_1$$

After a time T the potential is changed back to that of the one-dimensional infinite square well of length a. We are going to consider the probability that after time T the particle is in the first excited state ($n = 2$).

[5](c) Show that $H_{21}^{(1)} = \dfrac{4V_0}{3\pi}$

Hint: $\sin ax \sin bx = \dfrac{1}{2}(\cos(a - b)x - \cos(a + b)x)$

[5](d) Show that the probability that the particle is in the first excited state ($n = 2$) after time T is given by

$$\left[\frac{16ma^2 V_0}{9\pi^3 \hbar^2} \sin\left(\frac{3\pi^2 \hbar T}{4ma^2} \right) \right]^2$$

4

Exercise 7 (20 points)

Consider a lead (Pb) atom in the excited configuration $[Xe]6s^2 4f^{14} 5d^{10} 6p5f$

[4](a) Give the terms (and their degeneracy) that arise from this configuration.

[4](b) Give the levels that are obtained when we consider spin-orbit coupling. Which one has the lowest energy?

[6](c) The ground-state configuration of the same atom is $[Xe]6s^2 4f^{14} 5d^{10} 6p^2$. How do the answers to (a) and (b) change in this case?

[6](d) Give the ground state configurations and terms of the molecules C_2^- and C_2^+, and give their bond orders.

Exercise 8 (15 points)

Consider an approximation for the Na atom (ground-state configuration: $[Ne]3s^1$) in which the effect of the electrons in the closed shells is modeled with an effective central potential, so that only the 3s electron needs to be treated explicitly. Study the molecules Na_2^+ and Na_2 within this approximation:

[5](a) Denoting $a(\mathbf{r})$ and $b(\mathbf{r})$ the (approximate) 3s orbitals centered in the two atoms, write the bonding ($1\sigma_g$) and antibonding ($1\sigma_u$) wavefunctions for Na_2^+. Explain why the bonding wavefunction gives a lower electronic energy.

[6](b) Write in terms of the $1\sigma_g$ and $1\sigma_u$ orbitals of question a) the four possible LCAO wavefunctions for the molecule Na_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. Which one is the ground state around the internuclear equilibrium distance?

[4](c) Which one of the four wave functions of question b) gives the lowest energy at dissociation (internuclear distance going to infinity)? Explain your answer.