

EXAMINATION AMP – 15 January 2016 14:00-17:00

$1/2$	1	$1/2$	0
$1/2$	-1	$1/2$	-1
$1/2$	0	$1/2$	0
$-1/2$	1		
$-1/2$	0		
$-1/2$	-1		

I. KNOWLEDGE OF THE COURSE (about 1 hour 30 minutes, no documents allowed; on 50 points, 5 points per question)

1. i) Give the complete spectroscopic notation for the ground state and the first 2 singlet and 2 triplet excited states of the Helium atom, based on the configurations $1s^2$, $1s 2s$, and $1s 2p$.
 ii) Draw an energy diagram and indicate with arrows all the dipole-allowed optical transitions between these levels.

Singlet $1s^2$
 $\rightarrow (1s)^2 : 1s^0$
 Singlet $1s 2s$
 $1p_{1/2} \quad 1p_{3/2} \quad 1p_1$
 Triplet:
 $3p_{1/2} \quad 3p_{3/2}$
 $3s_1 \quad 3p_0$

2. Give the configuration and the spectroscopic notation for the ground states of the following elements: Be ($Z=4$), O ($Z=8$), F ($Z=9$), including total angular momentum. Hint: For a p^2 configuration, the only allowed terms are $1S$, $3P$, and $1D$.

3. The atomic number of aluminium is 13. What is the electronic configuration of this atom in its ground state?

4. Of the following 3 combinations of configurations and terms, only one can exist in hydrogen: $(4f) 2F_{3/2}$, $(3p) 2P_{3/2}$, $(2d) 2D_{3/2}$. Which one and why?

5. i) What is the central-field approximation?
 ii) How does the energy diagram of a one-electron atom with a central field differ from that of hydrogen? *spin-orbit coupling?*

6. i) Which property (-ies) must a diatomic molecule possess in order to make pure rotational spectroscopy possible?
 ii) In which spectral region do these pure rotational lines appear? *IR*

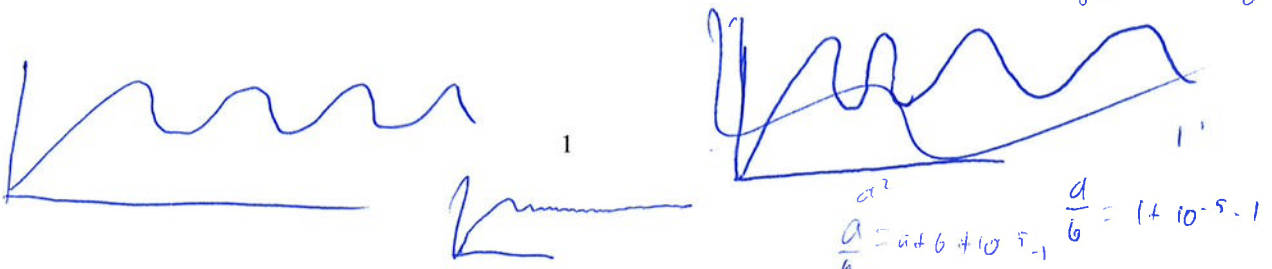
7. i) The acetylene molecule ($H-C\equiv C-H$) is linear. Three of its vibrational modes are infrared-active. How many Raman-active vibrational modes do you expect? *3*
 ii) The hydrogen peroxide molecule ($H-O-O-H$) is non-linear and non-planar due to free electron pairs on the oxygen atoms. It has 6 Raman-active modes. How many infrared-active modes do you expect? *3N-6: 0*

8. Give the three components of the Bloch vector (with modulus normalized to 1 for a pure state) in the rotating frame for the following situations:

- i) an optical two-level system in its ground state;
 ii) the same optical two-level system directly after a $\pi/2$ pulse has been applied;
 iii) the same optical two-level system after a waiting time T , for which $T_2 \ll T \ll T_1$;
 iv) a proton in a magnetic field B at room temperature (the ratio of the Larmor energy to the thermal energy is $\epsilon = \frac{\mu_p B}{k_B T} \approx 10^{-5}$).

$\begin{pmatrix} 0 \\ 1 \end{pmatrix}$
 $\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$
 none!
 system is relaxed.

- 9) In an optical nutation experiment, a resonant wave with constant amplitude is applied suddenly at time zero on a two-level system in its ground state.



Sketch the variations of the population of the excited state for positive times, both in the absence and in the presence of population relaxation from the excited to the ground state. (Neglect adiabatic coherence relaxation).

10. Using a photon echo experiment, one can determine the transverse relaxation time T_2 . Which pulse sequence should one use for this experiment? Indicate on a sketch the pulse durations and intensities, the waiting time(s), and the time at which the echo appears.

II. PROBLEM (1 hour and 30 minutes, no documents allowed; on 50 points)

Warning: The text of this problem looks very long, but its difficulty consists more in *understanding* the questions than answering them. Therefore, read the text carefully and only answer questions indicated in **bold characters**.

Λ -Doubling in the boron monohydride molecule BH

1. The Boron atom (B) has $Z = 5$.

i) Give the configuration of the ground state and the atomic spectroscopic term associated.

We form the heteronuclear molecule BH out of two ground state atoms. In the molecular ground state, the two atoms are bound by a sigma bond built on the $1s$ orbital of hydrogen and the $2p_z$ orbital of boron.

ii) What is the molecular term (angular momentum, spin multiplicity, symmetry with respect to the Oxz plane), corresponding to the ground state of BH?

iii) Qualitatively sketch the electron density in the Oxz plane as a two-dimensional plot with contour lines (lines with equal electronic density).

2. We now also consider excited states of this molecule built on the $1s$ orbital of hydrogen and all $2p$ orbitals of boron with $m = -1, 0, +1$, which are eigenstates of L_z .

i) Note that the $m = 0$ orbital is the same as $2p_z$. **How do the $m = -1, +1$ orbitals relate to p_x and p_y orbitals?**

ii) To find all states built on such orbitals, we have to distribute the two binding electrons on 6 spin-orbitals ($\sigma \uparrow, \sigma \downarrow, \pi_x \uparrow, \pi_x \downarrow, \pi_y \uparrow, \pi_y \downarrow$), taking Pauli's principle into account. **How many such states are there?**

Find the number of singlet states and of triplet states.

In the following we consider only the two $^1\Pi$ states with lowest energy.

iii) If a small perturbation breaks the symmetry between π_x and π_y , the molecular wavefunction should be built from the $1s$ orbital of hydrogen and, for example, the

$2p_x$ orbital of boron. Based on a linear combination of atomic orbitals, **qualitatively sketch the electron density in the Oxz plane as a two-dimensional plot**, as done in question 1.iii). Notice that the charge distribution of this orbital has no longer axial symmetry, but “bulges” on one side of the molecular axis.

For a molecule with *fixed* nuclei in an electronic state with axial angular momentum $\Lambda \neq 0$, the energies of the two eigenstates of L_z are obviously degenerate and uncoupled. This is no longer true, however, when the molecule is allowed to rotate. Coriolis and centrifugal effective forces appear in the non-inertial molecular frame. They couple the two eigenstates, and split the energies by an amount ΔE_Λ called Λ -doubling (or Λ -type doubling), which we wish to calculate.

3. Neglecting electronic and nuclear spins, neglecting the change in internuclear distance between ground state and excited state, the rotational energy of the molecule is $BK(K+1)$. K is the quantum number corresponding to the *total* angular momentum, including electronic and nuclear orbital contributions.

i) Express the rotational constant B of boron hydride as a function of the atomic masses M_H , M_B and of the internuclear distance d_{BH} .

$$B = \frac{1}{2\mu d_{BH}^2} \quad \text{met } \mu = \frac{M_H M_B}{M_H + M_B}$$

More precisely, the classical rotational kinetic energy can be expressed by means of the nuclear angular momentum \vec{N} in the molecular frame (necessarily perpendicular to the molecular axis Oz) as:

$$H_{rot} = B(N_x^2 + N_y^2).$$

When this quantity is considered as a quantum-mechanical operator, it does not commute with the total Hamiltonian of the rotating molecule, because only the total angular momentum $\vec{K} = \vec{N} + \vec{L}$ does. We express the rotational energy as a function of the total angular momentum \vec{K} and the electronic angular momentum \vec{L} as:

$$H_{rot} = B[(K_x - L_x)^2 + (K_y - L_y)^2]$$

ii) Express $K_x^2 + K_y^2$ in operators \vec{K}^2 , K_z .

$$\vec{K}^2 - K_z^2$$

We disregard the terms in L_x^2 and L_y^2 , which do not involve molecular rotation. The Hamiltonian can thus be written as:

$$H_{rot} = H^{(0)} + V_C,$$

where the $H^{(0)}$ part leads to rotational levels at energies:

$$E_{rot} = B[K(K+1) - \Lambda^2], \quad \text{with } K = \Lambda, \Lambda+1, \Lambda+2, \dots$$

$$K_+ L_- = K_x L_x + 2i k_y L_y - i k_x L_y + i k_y L_x$$

$$K_- L_+ = K_x L_x + K_y L_y + i k_x L_y - i k_y L_x$$

and the other part $V_C = -2B(K_x L_x + K_y L_y)$ corresponds to Coriolis and centrifugal actions in the molecular rotating frame.

iii) Express V_C in operators $K_{\pm} = K_x \pm iK_y$, and $L_{\pm} = L_x \pm iL_y$.

$$2(K_x L_x + K_y L_y) = K_+ L_- + K_- L_+$$

4. i) Explain why V_C couples electronic states with different values of Λ , and give the associated selection rule on $\Delta\Lambda$ (Hint: notice that L_{\pm} are the raising and lowering ladder operators of the electronic angular momentum).

$$V_C = B(K_+ L_- + K_- L_+) \\ \Delta\Lambda = ?$$

We consider the Π -states ($M_{\Lambda} = \pm 1$) of boron hydride. Second-order perturbation leads to a splitting between the two states $|M_{\Lambda} = 1; K\rangle$ and $|M_{\Lambda} = -1; K\rangle$ if one introduces coupling to a Σ -state $|M_{\Lambda} = 0; K\rangle$.

Second-order perturbation theory gives the matrix of corrections and couplings between two degenerate states Φ_i and Φ_j ($i=1,2, j=1,2$) according to:

$$\langle \Phi_i | \Delta H^{(2)} | \Phi_j \rangle = \sum_{\Phi_3} \frac{\langle \Phi_i | V_C | \Phi_3 \rangle \langle \Phi_3 | V_C | \Phi_j \rangle}{E_i - E_3}$$

and can be written as a 2×2 matrix in the basis of $|M_{\Lambda} = 1, K\rangle$ and $|M_{\Lambda} = -1, K\rangle$:

$$\Delta H^{(2)} = A \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}, \text{ with } A = B^2 K(K+1) \frac{|\langle \Pi | L_{\pm} | \Sigma \rangle|^2}{E_{\Pi} - E_{\Sigma}} \text{ (demonstration not required).}$$

ii) What are the eigenvalues and eigenvectors of this matrix?

$$2A?, \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

iii) What is the nature and symmetry of the eigenstates (e.g., consider their reflection in the Oxz plane)?

iv) Obtain the expression of the Λ -doubling ΔE_{Λ} as a function of the rotational constant and of $\Delta = E_{\Pi} - E_{\Sigma}$, the energy difference between electronic states.

5. Experimentally, the Λ -doubling of a Π -state is observable only when Δ is small enough and B large enough. For boron hydride, $B \approx 10 \text{ cm}^{-1}$, whereas $\Delta \approx 1000 \text{ cm}^{-1}$.

i) Estimate the Λ -doubling energy and compare it to the rotational energy itself (approximate the matrix element $\langle \Pi | L_{\pm} | \Sigma \rangle$ as 1 in units of \hbar).

ii) Notice that the Λ -doubling appears as a change of moment of inertia. How large is the relative change $\Delta I / I$, and how does this observation relate to the last remark of question 2.iii)?

iii) What do you think of the Λ -doubling of a Δ -state?