

EXAMINATION AMF – 16 January 2015, 14:00-17:00

I. KNOWLEDGE OF THE COURSE (1.5 hour, no documents allowed; on 50 points, 5 points per question).

Keep answers to these questions very short (less than 4-5 lines/question, and draw schemas wherever useful).

1. Draw on a sphere the node lines of the spherical harmonic wavefunction for a d-state with $m = 0$.
2. Magnesium (Mg) has the electronic configuration $[\text{Ne}] 3s^2$. Consider the singly charged Magnesium ion Mg^+ . Determine its terms (including total angular momentum j) in its ground state and in the excited configuration $[\text{Ne}] 3d^1$.
3. Give the configuration and the spectroscopic notation for the ground states of the following elements: Be ($Z=4$), C ($Z=6$), F ($Z=9$). Hint: For a p^2 configuration, the only allowed terms are 1S , 3P , and 1D .
Give the total angular momentum of these states applying Hund's rules.
4. Briefly explain the difference between the normal and the anomalous Zeeman effects.
5. Molecular Oxygen (O_2) possesses unpaired electrons in its ground state. Explain in a few sentences how this can be understood on the basis of its molecular orbitals.
Hint: The molecular orbitals resulting from the linear combination of the 2p orbitals are, in order of increasing energy: π , σ , π^* , σ^* .
6. Rotational transitions of HCl appear in an infrared absorption spectrum at the following frequencies in cm^{-1} :
83, 104, 124, 145, 166, 186. Indicate between which levels these transitions take place and explain how to deduce the moment of inertia of the molecule from these energies.
7. In interstellar space and some planetary atmospheres, a proton can bind to molecular hydrogen to form a H_3^+ ion. Its chemical structure is an equilateral triangle with a proton at each tip. Which electronic structure do you expect for this ion?
How many vibration modes does such a molecule present? Consider the three-fold symmetry of the molecule to sketch its vibration modes and discuss their degeneracy.
How many lines do you expect to see in a pure vibrational IR absorption spectrum?
Hint: Don't forget selection rules.
8. With a photon echo experiment, one can determine the transverse (or coherence) relaxation time T_2 of an optical two-level system. Which pulse sequence should one use? Qualitatively indicate on a sketch the pulse durations and amplitudes, the waiting time(s), and the time at which the echo appears.
9. In a magnetic resonance experiment, the signal is proportional to the population difference between spin-up and spin-down states. Calculate this difference for a

proton in a magnetic field of 1 T (resonance frequency 42.6 MHz) at room temperature (300 K).

Boltzmann constant = 1.38×10^{-23} J/K, Planck constant = 6.6×10^{-34} J.s

10. 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:

- an optical two-level system in its ground state;
- the same optical two-level system directly after applying a $\pi/2$ pulse;
- the optical two-level system of b) after a waiting time T , for which $T_2 \ll T \ll T_1$;

II. Problems (1.5 hour, no documents allowed; on 50 points).

Problem A: Dioxygen (O_2) molecule (on 30 points)

- The molecular term of dioxygen, characterizing its ground state electronic structure, is $^3\Sigma_g^-$. Explain the meaning of this notation.
- The two first excited states of the dioxygen molecule are singlets and have the following terms: $^1\Delta_g$ and $^1\Sigma_g^+$. Use Hund's rules to decide which one is the lowest excited state.
- Is it possible to perform pure rotational spectroscopy on dioxygen? The molecule presents a single vibrational mode at 1550 cm^{-1} . Is it infrared active? Is it Raman active?

It turns out that, for homonuclear diatomic molecules with identical isotopes, not all rotational levels are allowed. The only allowed rotational levels are those obeying the correct nuclear spin statistics.

For a dioxygen molecule formed of two identical ^{16}O nuclei, these nuclei are **bosons** (^{16}O is a doubly magic nucleus and therefore has zero nuclear spin). Hereafter we will deduce which rotational states are allowed for this molecule.

- Express the total wavefunction of the molecule in its ground state as a product of four terms (electronic orbital, electronic spin, nuclear orbital, nuclear spin). What is the symmetry of the nuclear spin wavefunction in the exchange of the nuclei?
- We will now write the exchange of nuclei as a product of operations acting on the whole molecule, on the electrons only, and on the nuclei only. First note that the state of the whole molecule does not change upon a rotation of 180° around the Oy axis (this is a consequence of Born-Oppenheimer's approximation and of the free rotation of the molecule).

We first consider the transformation of the electronic wavefunction under this 180° rotation around Oy . Show that this rotation is the product of parity and of reflection in the Oxz plane. Deduce the transformation of the orbital electronic wavefunction in the rotation. Explain why the electron spin wavefunction doesn't change in this rotation.

6. The rotational wavefunction of the nuclei with rotational number K changes as $(-1)^K$ in the 180° rotation. Deduce the change of the total wavefunction of the molecule upon this rotation and conclude that only one parity of K is allowed. Which one is it?

7. Plot a rotational energy diagram in the ground and first excited vibrational states (zero and one quantum of the 1550 cm^{-1} mode). What is the spacing of rotational lines observed in the ro-vibrational Raman spectrum of $(^{16}\text{O})_2$? Sketch the spectrum at room temperature ($B = 3.2\text{ cm}^{-1}$ for dioxygen).

Hint: remember the selection rule for Raman transitions.

Problem B: Optical Bloch equations (on 20 points)

One gives the optical Bloch equations as:

$$\dot{u} = -\gamma u + \delta v$$

$$\dot{v} = -\delta u - \gamma v - \Omega w$$

$$\dot{w} = \Omega v - \Gamma w - \Gamma / 2$$

1. Weak field and pure dephasing: For the special case of $\Omega \ll \Gamma$ and $\gamma = \Gamma / 2$, the solution to Bloch equations with initial conditions $(0, 0, -1/2)$ has the following form:

$$w(t) = A \left[1 + e^{-\Gamma t} - B \cos(\delta t) e^{-\Gamma t / 2} \right] - \frac{1}{2}$$

Find out coefficients A and B up to the second order in Ω by considering the two limits of $t \rightarrow 0$ and $t \rightarrow \infty$. *Hint:* write first the steady-state solution at the second order in Ω .

2. What does this solution for $w(t)$ reduce to in the limit of an infinitely narrow linewidth ($\Gamma \rightarrow 0$)? Plot this result qualitatively as a function of time.

3. Short time limit: Show that for $\Omega t \ll 1$ (with the same initial condition as in 1) the solution will be

$$w(t) = -\frac{1}{2} + \frac{1}{4} \Omega^2 t^2$$

irrespective of the values of Γ and δ .

4. Qualitatively plot the excited state population as a function of time for the short time limit $\Omega t \ll 1$.