

Advanced Atomic and Molecular Physics

Final Exam

Dear Students, please aim for short and economic answers. In many cases, a single sentence will be sufficient to answer the extra questions. When discussing experimental setups, please also provide labelled sketches.

All the best,

Andreas Hauser

1) Infrared spectroscopy

- (3p) Describe the setup of a Michelson interferometer and its relation to the Fabry-Pérot interferometer. Draw a sketch showing the transmission and reflection of all relevant rays.
- (2p) Why are the interference patterns in transmission and in reflection inverted to each other? How can this be explained by reflection properties at the air-to-glass interface?
- (1p) At 600 nm wavelength, what is the distance of travel for one mirror between two maxima in transmission?
- (3p) How can this interferometer be used for infrared spectroscopy on molecules?
- (1p) What limits the resolution of this interferometer?

2) Laser absorption and Doppler cooling

- (2p) What is the reason for Doppler-broadening of spectral lines? What is the typical shape of such a profile and how is it different from natural broadening?
- (1p) What is the reason for the natural linewidth of a molecular transition?
- (2p) Describe the principle of Doppler-cooling in detail. What is the Doppler temperature?
- (2p) Often, Doppler-cooling is combined with magnetic trapping forces. Describe a typical experimental setup (sketch) and explain the principle.
- (3p) A laser beam ($\lambda = 500$ nm) with 100 mW power runs through an absorption cell with absorption coefficient $\alpha = 10^{-6}$ cm $^{-1}$. How many fluorescence photons are emitted per cm path length if every absorbed laser photon yields a fluorescence photon? How large is the output current of a photo detector if it catches the fluorescence emitted into a solid angle of 0.2 sterad, its cathode has a conversion efficiency of 20%, and the current amplification of the detector is 10^6 ?

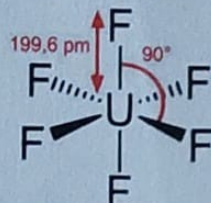
3) From Hund-Mulliken-Bloch to Hartree-Fock

- (3p) What is our ansatz for the total electron wavefunction of H_2 in the Hund-Mulliken-Bloch approach? How do we build molecular orbitals? Write down the wave function for the electronic ground state, a "singlet" state.
- (2p) The concept of Slater-Determinants extends this approach towards N-electron systems. How?
- (3p) The Hartree-Fock method is based on the same ansatz for the wf. Characterize this fundamental method of electronic structure theory in a few sentences. What kind of method is it? Does it retrieve the exact electronic energy?
- (2p) What is a potential energy surface or PES in this context, and how is the Hartree-Fock method related to the solution of the nuclear part of the total molecular Hamiltonian?

PLEASE TURN OVER

4) Rotation of molecules

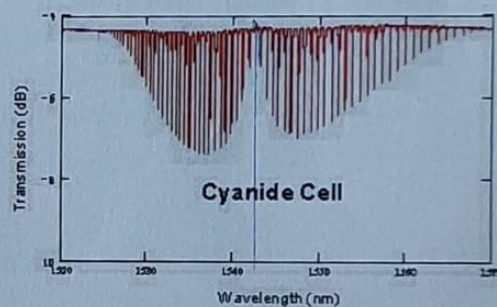
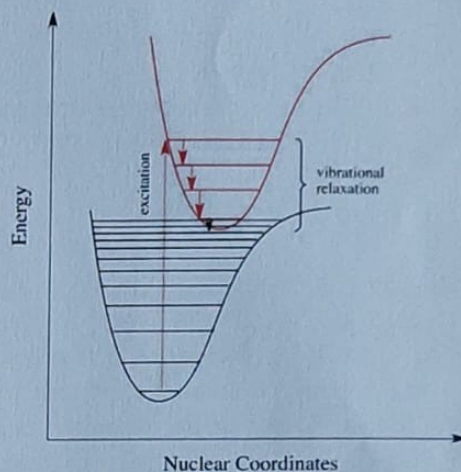
- (2p) A certain diatomic molecule absorbs energy by rotating. The first excited rotational state is at an energy of 0.10 eV above the ground state. What is the energy of the second excited rotational state above the ground state?
- (2p) What is the reason for the typical intensity profile of rotational lines (wings) in a rovibrational spectrum (see e.g. the small figure of question 5)?
- (2p) What do the terms "effective potential" and "rotational barrier" mean in cases of high J values?
- (1p) How many vibrational degrees of freedom does uranium hexafluoride (UF_6 , see picture) have?
- (3p) UF_6 is a "spherical top" molecule. Therefore, its rotational energies are dependent on a single quantum number and are calculated exactly by the same formula as diatomics (note that the moment of inertia has to be calculated differently though). Use the information from the picture to determine, in the absence of vibrations, the rotational constant B of this molecule ($m_{\text{U}} = 238\text{u}$, $m_{\text{F}} = 19\text{u}$) and convert it into units of inverse centimeters.



5) PES comparison

The figure to the right shows the potential energy surface of a diatomic molecule in its electronic ground state (black) and first excited state (red).

- (4p) Focus on the ground state at first, i.e. on the black curve. Indicate how the following characteristics can be derived from the picture: equilibrium distance, dissociation energy, rotational constant B , rotational moment of inertia, vibrational energy spacing, zero-point energy. Why are the vibrational spacings not equidistant?
- (2p) There are no general selection rules for combined electronic-vibrational transitions. Which principle can be used instead to calculate the intensities of vibronic spectra? Write down the quantum mechanical expectation value which defines the transition probability in this case.
- (2p) Draw the approximate nuclear wavefunctions or probabilities for the levels at the beginning and at the end of the large red arrow. Interpret this situation as fluorescence, and explain why the fluorescence light will be emitted at larger wavelength than the pump light.
- (2p) The smaller picture to the right shows the adsorption spectrum of HCN, a standard gas cell often used for laser calibration. Estimate the wavelength of the vibrational transition and convert into a frequency ω_e in units of inverse centimeters.



Universal Constants

Speed of light	$c = 2.998 \times 10^8 \text{ m/s}$
Planck's constant	$h = 6.626 \times 10^{-34} \text{ Js}$
Electron charge	$e = 1.602 \times 10^{-19} \text{ C}$
Electron mass	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Atomic mass unit	$u = 1.660 \times 10^{-27} \text{ kg}$