

## 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,

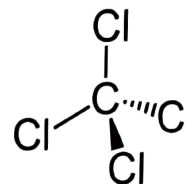
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- 1) The Born-Oppenheimer approach
  - a) (3p) Write down the Hamiltonian for a molecular system and underline those terms which form the electronic part e.g. in a Hartree-Fock calculation. Which term is the most complicated to be handled in such a calculation and why?
  - b) (3p) What is the Born-Oppenheimer approach? Illustrate its breakdown in the case of two electronically excited PES (potential energy surface) of a diatomic molecule. How is the BO approach related to the concept of a PES?
  - c) (2p) When deriving the coupling elements  $\Lambda_{ij}$ , how did our initial ansatz for the total wavefunction of a molecule as a function of electron coordinates  $r$  and nuclear coordinates  $R$  look like? (In other words, which basis functions did we choose for this expansion?) What are the values of  $\Lambda_{ij}$  within the BO approach?
  - d) (1p) How is the BO-approach related to a common approximation used for the prediction of intensities between vibrational states of different electronic states? What is the name of this technique?
  - e) (1p) What is a transition state on the PES? Why are these extremal points so important in chemistry?
- 2) Photo Electron Spectroscopy
  - a) (3p) Describe the basic principle of photo electron spectroscopy (PES) and distinguish between the techniques UPS, XPS and ESCA.
  - b) (3p) How does ZEKE (Zero Kinetic Energy) -PES work? What is its advantage compared to normal PES?
  - c) (2p) In a ZEKE setup we assume radial symmetry and a detection zone with a radius of  $r = 2$  mm. How large is the maximum kinetic energy of the electrons which will still be detected in a measurement delayed by  $\tau = 1$  ms?
  - d) (2p) Draw the following figure: Assume an arbitrary diatomic molecule consisting of atoms A and B and draw its potential energy surface in its electronic ground state with asymptotic energy  $A+B$ . Now add another potential energy surface for an ionized state of the same system with asymptote  $A+B^+$ . For a given ionization energy  $E_{\text{ion}}$ , draw the expected kinetic electron energies.
- 3) From Hund-Mulliken-Bloch to Hartree-Fock
  - a) (3p) What is our ansatz for the total electron wavefunction of  $H_2$  (not for the Hamiltonian) 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, and compare it to a triplet state with  $M_S=1$ .
  - b) (2p) The concept of Slater-Determinants extends this approach towards  $N$ -electron systems. How?
  - c) (3p) The Hartree-Fock method is based on the same ansatz for the wave function. Characterize this fundamental method of electronic structure theory in a few keywords. What kind of method is it? What is minimized, and how is this achieved?
  - d) (2p) Which dependence enforces the HF method to be iterative? Do the Lagrange multipliers we introduced have a physical meaning? Does HF retrieve the exact electronic energy?

PLEASE TURN OVER

4) Rotation and vibration of molecules

- a) (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?
- b) (2p) What is the reason for the typical intensity profile of rotational lines (wings) in a rovibrational spectrum?
- c) (2p) What do the terms “effective potential” and “rotational barrier” mean in cases of high  $J$  values?
- d) (1p) How many vibrational degrees of freedom does carbon tetrachloride ( $\text{CCl}_4$ , see picture) have?
- e) (1p) How and why are rotation and vibration actually coupled? Which extensions need to be made in the energy formulae with respect to their dependence on  $\nu$  and  $J$ ?
- f) (2p)  $\text{CCl}_4$  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). Determine, in the absence of vibrations, the rotational constant  $B$  of this molecule ( $m_{\text{C}} = 12\text{u}$ ,  $m_{\text{Cl}} = 35\text{u}$ , C-Cl bond length  $b = 175\text{ pm}$ ) and convert it into units of inverse centimeters.

5) Laser absorption and Doppler cooling

- a) (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?
- b) (1p) What is the reason for the natural linewidth of a molecular transition?
- c) (2p) Describe the principle of Doppler-cooling in detail. What is the Doppler temperature?
- d) (2p) Often, Doppler-cooling is combined with magnetic trapping forces. Describe a typical experimental setup (sketch) and explain the principle.
- e) (3p) A laser beam ( $\lambda = 500\text{ nm}$ ) with 100 mW power runs through an absorption cell with absorption coefficient  $\alpha = 10^{-6}\text{ cm}^{-1}$ . 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  $10^6$ ?

## 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	$u = 1.660 \times 10^{-27}\text{ kg}$