

## Chemical Physics (化学物理学)

1. Three problems are given below. Answer all of them.
2. Prepare your report by using A4 papers. On the first page, please put your name, student ID, and course (physics, astronomy, and so on). Language should be Japanese or English.
3. Submit your report to the administration office for students (Kyomu) by **17:00 (JST) on Feb. 12 (Tue), 2013**. If you send your report by ordinary mail, it should be delivered to the administration office by the above deadline.
4. Submission by e-mail or by fax is NOT accepted.
5. Please add your comment and suggestion on the lecture, if any.

### Problem 1

Let us compute the s-p electron static energy separation for the outer electron in an alkali atom. Consider the Li atom, as an example. Assume the inner two electrons are at  $r = a_1 = a_0/3$ , where  $a_0$  is the Bohr radius. Therefore, the potential for the outer electron can be approximated by  $V = -e^2/r$  outside  $a_1$  and  $V = -3e^2/r$  inside  $a_1$ . This is equivalent to complete shielding of two charges on the Li nucleus by the inner two electrons. The Hamiltonian for the outer single electron is, therefore,

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} - \frac{2e^2}{r} \quad (0 \leq r \leq a_1).$$

The first two terms on the right hand side corresponds to the Hamiltonian for the H atom. The third term can be treated as perturbation theory.

- (1) Summarize the eigenfunctions and eigenvalues of the  $n = 2$  level of the H atom (the first two terms of the Hamiltonian). (Note: It is not necessary to present their derivations.)
- (2) The outer electron necessarily resides in the  $n = 2$  level in the ground state of the Li atom. Using the four degenerate  $n = 2$  eigenfunctions as the basis set, calculate the Hamiltonian matrix.
- (3) Calculate the energy separation between 2s and 2p levels, and compare it with the observed value,  $14906 \text{ cm}^{-1}$ .
- (4) Propose a practical way to improve your result.

### Problem 2

Boron trifluoride ( $\text{BF}_3$ ) is a planer molecule with  $D_{3h}$  symmetry (Figure 1).

- (1) The local Cartesian coordinates for the four atoms are taken as a basis set. Calculate a trace of the representation matrix for each symmetry operation (class).
- (2) Reduce the above representation into the irreducible representations by using the character table of  $D_{3h}$  (Table 1).
- (3) What symmetry species do translational motions and rotational motions belong to?
- (4) What symmetry species do the vibrational modes of  $\text{BF}_3$  belong to? For each vibrational mode, examine whether it is infrared active or not.

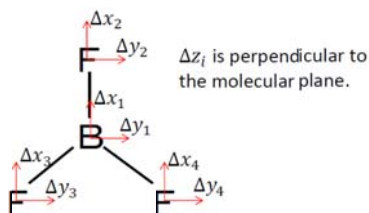


Figure 1

$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$
$A_1'$	1	1	1	1	1	1
$A_2'$	1	1	-1	1	1	-1
$E'$	2	-1	0	2	-1	0
$A_1''$	1	1	1	-1	-1	-1
$A_2''$	1	1	-1	-1	-1	1
$E''$	2	-1	0	-2	1	0

Table 1: Character Table for  $D_{3h}$

### Problem 3

The  $\pi$  electron system of cyclopropenyl cation (Figure 2a) is treated by the Huckel method. The two  $\pi$  electrons are delocalized over the three carbon atoms. The molecular orbitals for the  $\pi$  electrons are formed as linear combinations of the  $p_\pi$  orbitals of the carbon atoms ( $\chi_i$ ,  $i = 1 - 3$ ). Here, the Coulomb integral and the resonance integral are defined as,

$$\alpha = \int \chi_i h \chi_i d\tau$$

$$\beta = \int \chi_i h \chi_j d\tau \quad (i \neq j),$$

where  $h$  is the effective (one-electron) Hamiltonian. Note that  $\alpha < 0$  and  $\beta < 0$ .

- (1) Calculate the energies of three molecular orbitals by using the Huckel method.
- (2) Represent the molecular orbitals as the linear combination of  $\chi_i$  ( $i = 1 - 3$ ), and sketch them.
- (3) Obtain the total electronic energy of the two  $\pi$  electrons.
- (4) If the two  $\pi$  electrons of cyclopropenyl cation were localized in the two carbon atoms, as shown in Figure 2b, obtain the total electronic energy of the two electrons. Compare the result with that of (3).  
(Hint: Just consider for the two  $p_\pi$  orbitals of the two carbon atoms ( $\chi_i$ ,  $i = 1, 2$ ) and ignore the  $p_\pi$  orbital of the third carbon atom.)

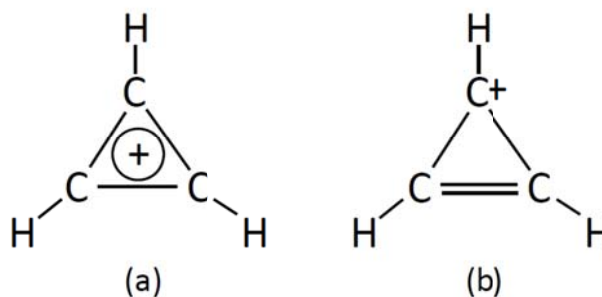


Figure 2