Quantum Chemistry

Molecular Orbital Theory: Computational Exercise

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Brief Overview: Students learn basic concepts of the molecular orbital method, perform *ab initio* calculations based on the molecular orbital theory using a computer server, and discuss electronic structures, chemical properties, reactivity, etc. on the obtained results. In addition, by understanding the programs to be used and making programs by themselves, students learn how to put computers to practical use for research in chemistry. Specifically, the following two subjects are addressed:

1. Computational Chemistry A "Simple Hückel theory: practice and computing"
2. Computational Chemistry B "Non-empirical (*ab initio*) molecular orbital theory: usage and computing"

- Classes will be held at the PC room in the General Media Center (COM-D in Building 2).
- Windows 10 operating system is used on the terminal (PC). Students may bring their personal notebook PCs instead. (Note that PCs with poor graphics card are likely to be inappropriate.)
- Following software is used: Gaussian 16 and GaussView 6 (license owned by Sophia University), TeraTerm (Free), and WinSCP (Free). GaussView 6 can be installed in a personal notebook PC if desired. (Unfortunately, no Macintosh version is available for GaussView 6. It is compatible with Windows 10, 8, and 7.)
- Multiple nodes on the computing cluster owned by Nanbu, Kuze, and Sebastian groups of the Department of Materials and Life Sciences, Faculty of Science and Technology will be used as computing server. Refrain from reckless use because fourth-year, master-course, and doctoral students from Nanbu, Kuze, and Sebastian laboratories are using it daily for research.
- This computational exercise takes four days over two weeks. Since students are likely to use the computer server for the first time, they should listen carefully to what TAs and teachers say before conducting the actual exercise.
- At the end of this text, the pages of the tasks on the preparatory report and the report after the experiment were posted. At the respective time of submissions of the preparation report and the report after performing the experiment, print each page and paste it on the submitted report as a cover.

Introduction

Natural sciences are an ongoing development seeking out true understanding of nature and natural processes. Typical examples would be the various material sciences, trying to explain the constitution of matter; the formation and evolution of universe; or the evolution of life as we know it. Among these questions, the role of chemistry is amidst physics and biology. In other words, the role of chemistry is investigation of molecules and molecular structures, understanding the natural laws behind them and explore how they can be used for the benefit of humanity.

In quantum chemistry, the knowledge of chemistry, most of which has been learned experimentally is explained theoretically based on the quantum theory established in physics. The aim is to explain the essence of chemical bonding, understand the physical and chemical properties and the chemical reactivity of molecules, and use the results for understanding and application of various phenomena.

1. Schrödinger equation

In order to understand the properties of molecules, we have to investigate the behavior of electrons surrounding a nucleus and connecting different atoms. Because electrons are moving in a very small space at a very high speed, they remarkably exhibit the duality of being a particle and a wave, like light. For this reason, it is impossible to observe the position and momentum of an electron (uncertainty principle). It can be said only that an electron is present at a point *x* and time *t* with a certain probability $P(x,t) = \Psi(x,t)^2$.

The motion of such electrons is described by the following Schrödinger equation, which has combined the wave equation and the equation of motion in classical mechanics:

$$\hat{\mathrm{H}}\Psi = E\Psi . \qquad (1)$$

Since electrons with negative charges move around nuclei with positive charges, the Hamiltonian can be expressed by the kinetic energy (T) of electrons and the sum of potential energy (V) due to attractive interaction with the nuclei and mutual repulsive interaction between the electrons. Solving eq. (1), the eigenvalue *E* is obtained as the total energy and the corresponding eigenfunction (Ψ) is a wave function describing the state of the electrons. Once these quantities are obtained, we can learn about the various properties of the molecule.

When electrons are bound by nuclei, they have discrete negative energies $E_1, E_2, \cdots$ and a wave function $\Psi_1, \Psi_2, \cdots$ exists, which corresponds to each of these electronic states. The energy becomes discrete instead of taking an arbitrary value continuously. This corresponds to the fact that steady resonance waves can exist only at certain frequencies like the vibration of strings and membranes.

The Schrödinger equation (1) is the second order partial differential equation and can be solved analytically and exactly only in the case of a hydrogen atom and hydrogen-like atoms. In the case of multi-electron systems, it cannot be solved exactly due to interaction between electrons and an approximate method must be used. The more accurately we try to solve it, the more difficult the actual calculation becomes. With the development of computers, *ab initio* methods have become widely used.

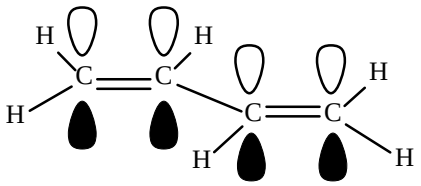
$\Psi \cdots$

2. Computational Chemistry A: “Simple Hückel theory: practice and computing”

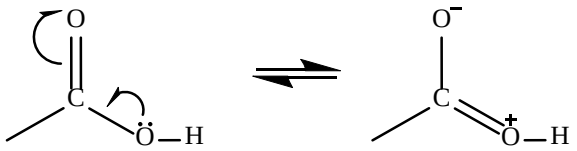
2.1. About the π electron system

In order to understand the electronic states of a molecule, we should first understand its molecular structure. In unsaturated compounds, there are σ (sigma) electrons forming a molecular skeleton and π (pi) electrons capable of forming a more reactive conjugated system. Because the π orbital has a node on the molecular plane and does not overlap with the σ orbitals, π electrons can be regarded as moving independently of σ electrons in the mean field created by the σ framework. The simple Hückel method is used to calculate the molecular orbitals for such conjugated π bonds.

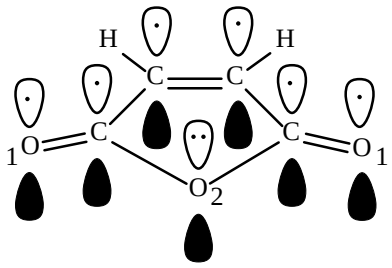
For example, the π orbital of butadiene (see figure below) consists of four p orbitals perpendicular to the molecular plane and accommodates four electrons in it.



Benzene consists of a 6π orbital and 6π electron system. In unsaturated hydrocarbons, the number of π orbitals and the number of π electrons often match. However, when heteroatoms other than carbon are contained, the number of electrons participating in π bonding does not coincide with the number of orbitals. For example, the number of orbitals is different in pyridine and pyrrole, but both are 6π electron systems. Furthermore, the carboxyl group is written as the resonance shown below. This is because one of the orbitals for two unshared electron pair (lone pair), present in the oxygen of the –OH group, consists of a π orbital.

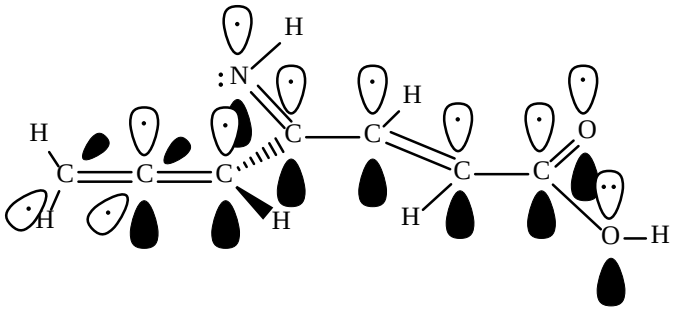


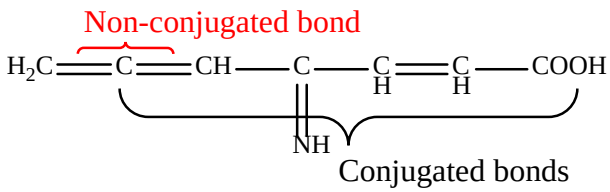
Similarly, in maleic anhydride, often used in the Diels-Alder reaction, one π electron in O1 and two π electrons (lone pair electrons) in O2, shown in the figure below, are involved in the conjugation and form a 7π orbital and 8π electron system.



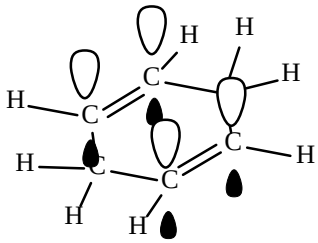
Also, in the case of molecules with triple bonds and allenes, there are two orthogonal π bonds and

care must be taken as to which π bond is being considered.



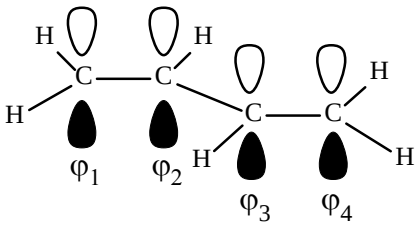


In addition, when π bonds are separated by a σ bond like in 1,4-cyclohexadiene, there is no conjugation between the π bonds and the system is regarded as two ethylene units existing independently.



2.2. Solution of butadiene

Let us find the molecular orbital of butadiene, as an example, by using simple Hückel method. Butadiene contains four electrons in the p orbitals on the four sp^2 hybridized carbons.



Let these four p orbitals be φ_1, φ_2, φ_3, and φ_4 from the end. Then, the π molecular orbital is written in an LCAO approximation as follows:

$$\psi = C_1\varphi_1 + C_2\varphi_2 + C_3\varphi_3 + C_4\varphi_4 . \qquad (2)$$

In the Hückel method, electrons in a molecule are regarded as moving independently and the total electron Hamiltonian H is approximated by the sum of one-electron operators. Furthermore, based

on the variational principle, a secular equation for each of coefficients C_1, C_2, C_3, and C_4 is obtained as follows:

$$\begin{cases} C_1(h_{11}-ES_{11})+C_2(h_{12}-ES_{12})+C_3(h_{13}-ES_{13})+C_4(h_{14}-ES_{14})=0 \\ C_1(h_{21}-ES_{21})+C_2(h_{22}-ES_{22})+C_3(h_{23}-ES_{23})+C_4(h_{24}-ES_{24})=0 \\ C_1(h_{31}-ES_{31})+C_2(h_{32}-ES_{32})+C_3(h_{33}-ES_{33})+C_4(h_{34}-ES_{34})=0 \\ C_1(h_{41}-ES_{41})+C_2(h_{42}-ES_{42})+C_3(h_{43}-ES_{43})+C_4(h_{44}-ES_{44})=0 \end{cases} \quad (3)$$

Here, the simple Hückel method is based on the following four assumptions:

(1) Neglect the overlap integral (S) between different atomic orbitals.

$$S_{ij}=\begin{cases} 1 & \cdots \quad i=j \\ 0 & \cdots \quad i\neq j \end{cases} \quad (4)$$

(2) If the *i* th atom and the *j* th atom are not bonded, the resonance integral (β) between them is assumed to be zero.

(3) Let α be the orbital energy of the p orbital of a carbon atom.

(4) Let β be the resonance integral between the C-C bonds of benzene. Usually, the same value can be chosen for the resonance integral as benzene even for the C-C bond of a conjugated system of non-aromatic unsaturated hydrocarbons. This simplification gives qualitatively correct results.

In the case of butadiene, we can set

$$h_{11}=h_{22}=h_{33}=h_{44}=\alpha \quad \text{(Coulomb integral)}, \quad (5)$$

$$\left.\begin{array}{l} h_{12}=h_{23}=h_{34}=h_{21}=h_{32}=h_{43}=\beta \\ h_{13}=h_{24}=h_{14}=h_{31}=h_{42}=h_{41}=0 \end{array}\right\} \text{(resonance integral)}. \quad (6)$$

Then, the above equation becomes

$$\begin{cases} C_1(\alpha-E)+ & C_2\beta & + & 0 & + & 0 & =0 \\ C_1\beta & +C_2(\alpha-E)+ & C_3\beta & + & 0 & & =0 \\ 0 & + & C_2\beta & +C_3(\alpha-E)+ & C_4\beta & & =0 \\ 0 & + & 0 & + & C_3\beta & +C_4(\alpha-E) & =0 \end{cases} \quad (7)$$

or

$$\begin{pmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{pmatrix}=0 \quad (8)$$

In order to obtain a nontrivial solution (the trivial solution is $C_1=C_2=C_3=C_4=0$), we set the

determinant of equation (8) to zero.

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 . \qquad (9)$$

By dividing both sides by β, and by setting

$$\frac{\alpha - E}{\beta} = x , \qquad (10)$$

we have

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 . \qquad (11)$$

Decomposing the determinant, we have the quartic equation of x

$$x^4 - 3x^2 + 1 = 0 . \qquad (12)$$

The solutions are

$$x = \pm \frac{\sqrt{5} \pm 1}{2} . \qquad (13)$$

The orbital energy E is given as follows by setting $E = \alpha - x\beta$

$$\left.\begin{aligned} E_1 &= \alpha + (\sqrt{5} + 1)\beta/2 \\ E_2 &= \alpha + (\sqrt{5} - 1)\beta/2 \\ E_3 &= \alpha - (\sqrt{5} - 1)\beta/2 \\ E_4 &= \alpha - (\sqrt{5} + 1)\beta/2 \end{aligned}\right\} \qquad (14)$$

For each orbital energy E, corresponding x is inserted into the secular equation or into the following equation

$$\begin{pmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{pmatrix} = 0 \quad \text{or} \quad \begin{cases} C_1 x + C_2 = 0 \\ C_1 + C_2 x + C_3 = 0 \\ C_2 + C_3 x + C_4 = 0 \\ C_3 + C_4 x = 0 \end{cases} \qquad (15)$$

and coefficients Cs of the molecular orbital are obtained. It should be noted here that because the secular equations or equation (15) is not a simultaneous equation, the coefficients are not uniquely determined, that is, only the ratio of each coefficient is determined.

From the orthonormality of the molecular orbital constituting another condition, we have

$$\int \psi^* \psi d\tau = 1. \qquad (16)$$

Substituting $\psi = C_1\varphi_1 + C_2\varphi_2 + C_3\varphi_3 + C_4\varphi_4$ into equation (16) and using the orthogonality of atomic orbitals

$$\int \varphi_i^* \varphi_j d\tau = \delta_{ij},$$

we have

$$C_1^2 + C_2^2 + C_3^2 + C_4^2 = 1. \qquad (17)$$

Using this condition, the coefficients are determined apart from a common sign.

Namely, for $x = \frac{1 \pm \sqrt{5}}{2}$, that is, for E_2 and E_4, we have $C_1 = -C_4$, $C_2 = -C_3$ and for $x = -\frac{1 \pm \sqrt{5}}{2}$, that is, for E_1 and E_3, we have $C_1 = C_4$, $C_2 = C_3$. Therefore, from $C_2 = -xC_1$ and equation (17), the molecular orbital is obtained for E_1 as

$$\psi_1 = \frac{1}{\sqrt{5+\sqrt{5}}}(\varphi_1 + \varphi_4) + \frac{1}{\sqrt{5-\sqrt{5}}}(\varphi_2 + \varphi_3), \qquad (18a)$$

for E_2 as

$$\psi_2 = \frac{1}{\sqrt{5-\sqrt{5}}}(\varphi_1 - \varphi_4) + \frac{1}{\sqrt{5+\sqrt{5}}}(\varphi_2 - \varphi_3), \qquad (18b)$$

for E_3 as

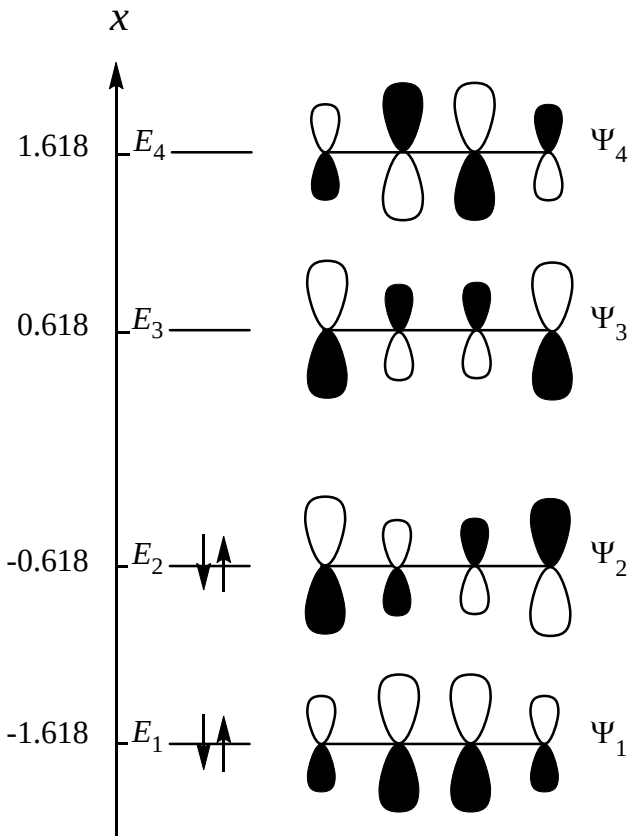
$$\psi_3 = \frac{1}{\sqrt{5-\sqrt{5}}}(\varphi_1 + \varphi_4) - \frac{1}{\sqrt{5+\sqrt{5}}}(\varphi_2 + \varphi_3), \qquad (18c)$$

and for E_4 as

$$\psi_4 = \frac{1}{\sqrt{5+\sqrt{5}}}(\varphi_1 - \varphi_4) - \frac{1}{\sqrt{5-\sqrt{5}}}(\varphi_2 - \varphi_3). \qquad (18d)$$

(The results are the same even if the entire molecular orbitals are multiplied by a minus sign.)

Because both α and β are negative, the energy level (molecular orbital energy) is higher for a larger x.



Relationship between energy level and corresponding π molecular orbital of butadiene

According to Pauli's principle, up to two electrons can occupy each molecular orbital. In the case of butadiene, there are two electrons in Ψ_1 and two electrons in Ψ_2. Therefore, Ψ_2 is the highest energy orbital occupied by electrons, HOMO (highest occupied molecular orbital), and Ψ_3 is the lowest unoccupied molecular orbital (LUMO) with no electron. These HOMO and LUMO are called frontier orbitals and play a very important role in the reactivity.

In butadiene, both Ψ_2 and Ψ_3 have large coefficients on carbons at the end. It can be understood that both the nucleophilic reaction and the electrophilic reaction occur at the end. The same is true for the Diels-Alder reaction.

The total electron energy is obtained by summing up the number of electrons times the orbital energy for all occupied orbitals, i.e.,

$$\begin{aligned} E_{total} &= 2E_1 + 2E_2 \\ &= 4\alpha + 2\sqrt{5}\beta \end{aligned} \tag{19}$$

Because the energy when the carbon atoms are completely unbound is 4α [sometimes chosen as 4(α+β)], the energy ΔE stabilized by the resonance, when the molecule is formed, becomes

$$\begin{aligned}\Delta E &= E_{molecule} - E_{atoms} \\ &= \left(4\alpha + 2\sqrt{5}\beta\right) - 4\alpha = 2\sqrt{5}\beta < 0\end{aligned} \tag{20a}$$

$$\begin{aligned}\Delta E &= E_{molecule} - E_{atoms} \\ &= \left(4\alpha + 2\sqrt{5}\beta\right) - 4\left(\alpha + \beta\right) = 2\sqrt{5}\beta - 4\beta < 0\end{aligned} \tag{20b}$$

These show that ΔE is negative, indicating that the π bond of the butadiene molecule is stable. Furthermore, by assuming that butadiene is composed of two ethylene units, we can understand how much their connection by the double bonds makes butadiene stable.

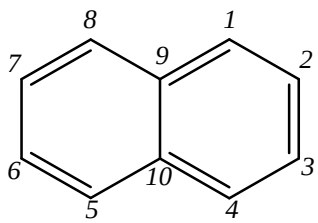
2.3. Hückel matrix

When the number of atoms related to the π bond is small, the determinant can be calculated analytically by hand. It becomes difficult to obtain the analytical results of molecular orbitals for large molecules. Then, we use a computer to calculate the molecular orbitals by numerically solving eigenvalue problems. Equation (15) is modified into the following form:

$$\begin{pmatrix} 0 & -1 & 0 & 0 \\ -1 & 0 & -1 & 0 \\ 0 & -1 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix}\begin{pmatrix} \mathrm{C}_1 \\ \mathrm{C}_2 \\ \mathrm{C}_3 \\ \mathrm{C}_4 \end{pmatrix} = \begin{pmatrix} x & 0 & 0 & 0 \\ 0 & x & 0 & 0 \\ 0 & 0 & x & 0 \\ 0 & 0 & 0 & x \end{pmatrix}\begin{pmatrix} \mathrm{C}_1 \\ \mathrm{C}_2 \\ \mathrm{C}_3 \\ \mathrm{C}_4 \end{pmatrix} \tag{21}$$

This is an eigenvalue equation in which we obtain the eigenvalue x and the eigenvector (C_1 C_2 C_3 C_4) by diagonalizing the 4×4 matrix on the left side into that on the right side. Therefore, the input information consists of the number of dimensions of the eigenvalue problem to be solved, that is, the number of atoms participating in the π bond (4 in butadiene), and the matrix on the left side of equation (21). Matrix elements are simply given by −1 for a pair of atoms connected by bonding.

For example, in the case of naphthalene, we put numbers as shown below:



Then, the matrix is given by equation (22).

$$\begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \end{array} \begin{array}{c} \begin{array}{cccccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \end{array} \\ \begin{pmatrix} 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & -1 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & -1 \\ 0 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & -1 & 0 \end{pmatrix} \end{array} \tag{22}$$

Now, we just ask the computer to solve the eigenvalue problem.

2.4. The case containing heteronuclear atoms

In the case of unsaturated hydrocarbons, all Coulomb integrals can be set to α and resonance integrals to β, and therefore the elements of the Hückel matrix only take 0 or -1. What should we do if we want to find Hückel MO for the π electron system containing atoms other than carbon atoms?

Because the Coulomb integral corresponds to the orbital energy of each atom, it takes a different value depending on the atom, and the resonance integral also varies depending on the combination of atoms to be bonded. Therefore, the following parameters are introduced.

$$\alpha_{\mathrm{X}} = \alpha_{\mathrm{C}} + l_{\mathrm{X}} \times \beta_{\mathrm{CC}}, \qquad (23)$$

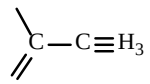
$$\beta_{\mathrm{XY}} = k_{\mathrm{XY}} \times \beta_{\mathrm{CC}}. \qquad (24)$$

They will be measured in units of orbital energy α_C (about −11.2 eV) of the p orbital of carbon and the resonance integral β_{CC} (about −2.0 eV at R_{CC} = 1.40 Å) between atom C and neighboring C of benzene. The deviation of the Coulomb integral of atom X from α_C is measured in units of β_{CC}, and the resonance integral between X and Y atoms is measured in units of β_{CC} of benzene. Values for these parameters are provided in Table 1.

Table 1. Parameters for heteroatoms in the simple Hückel method (l_X and k_{XY} are written with negative signs rather than the values themselves). This is due to a consideration that each value can be used as an element of the Hückel matrix itself.

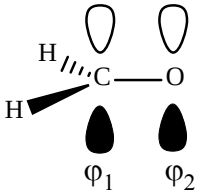
Coulomb integral		Resonance integral			
Atom X	$-l_X$	Between atoms X and Y	$-k_{XY}$	Between atoms X and Y	$-k_{XY}$
C・	0.0	C=C	-1.0	C−F	-0.95
=N・	-0.5	(C=C)	-1.1	C−Cl	-0.7
−N:	-0.8	(C−C)	-0.9	C−Br	-0.6
=O・	-1.1	C=N	-1.1	C−I	-0.5
−O・	-1.5	C≡N	-1.3	N=N	-1.2
−F	-2.0	C−N:	-0.9	N=O	-1.1
−Cl	-1.7	C=O	-1.2		
−Br	-1.3	C−O:	-0.7	C≡H_3 [(a)]	-2.5
−I	-1.15	C=S	-1.0	C−CH_3 [(a)]	-0.6
=S・	-0.3	C−S:	-0.5		
−S:	-1.0				
C (C≡H_3) [(a)]	+0.1				
H_3 (C≡H_3) [(a)]	+0.5				

(a) The methyl group does not have π electrons, but when it is desired to take into account a super conjugation like that in toluene, H3 can be treated like a single p orbital.



Let us try to solve formaldehyde as an example. When the molecular orbital is expressed as

$\psi = C_1\varphi_1 + C_2\varphi_2$, the secular equation to be solved is



$$\begin{cases} C_1(\alpha_1 - E) + \quad C_2\beta_{12} \quad = 0 \\ \quad C_1\beta_{12} \quad + C_2(\alpha_2 - E) = 0 \end{cases} \tag{25}$$

where index 1 denotes a carbon and index 2, an oxygen. Then, we can set as follows:

$$\begin{aligned} \alpha_1 &= \alpha_C \\ \alpha_2 &= \alpha_C + l_O \times \beta_{CC} \\ \beta_{12} &= k_{CO} \times \beta_{CC} \end{aligned} \tag{26}$$

Dividing both sides by β_{CC} and setting $\dfrac{\alpha_C - E}{\beta_{CC}} = x$, equation (25) becomes as follows:

$$\begin{cases} C_1 x \ + \quad C_2 k_{CO} \quad = 0 \\ C_1 k_{CO} + C_2(x + l_O) = 0 \end{cases} \tag{27}$$

Therefore, the secular equation of formaldehyde becomes,

$$\begin{vmatrix} x & k_{CO} \\ k_{CO} & x + l_O \end{vmatrix} = 0 . \tag{28}$$

Using the values of $-k_{CO}$ and $-l_O$ listed in Table 1, equation (28) becomes the following quadratic equation:

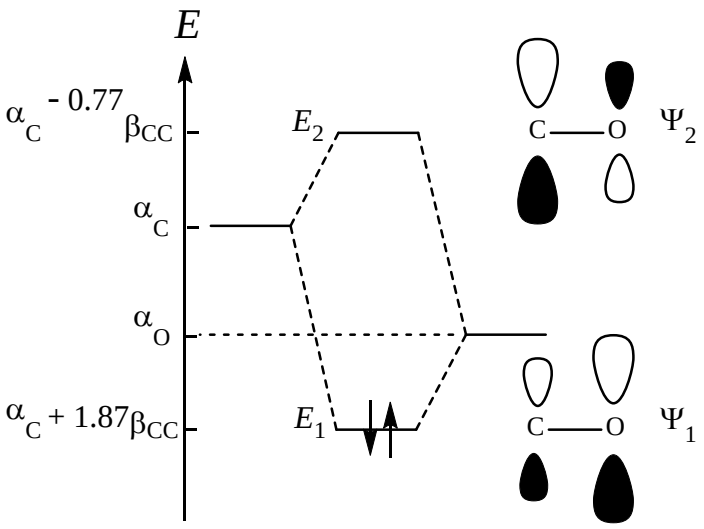
$$x^2 + 1.1x - 1.44 = 0 . \tag{29}$$

$$\therefore \quad x = 0.770, \quad -1.870 . \tag{30}$$

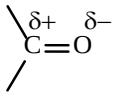
Using $C_1^2 + C_2^2 = 1$ and $C_2 = -\dfrac{x}{1.2} C_1$, the solutions are obtained as

$$\text{for} \quad x = 0.770 , \quad C_1 = 0.842, \ C_2 = -0.540 , \tag{31a}$$

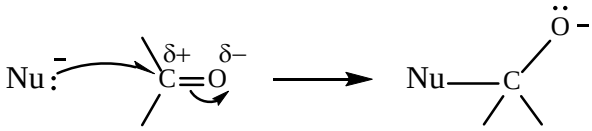
$$\text{for} \quad x = -1.870 , \quad C_1 = 0.540, \ C_2 = 0.842 . \tag{31b}$$



From this result, it is clear that the HOMO of formaldehyde is concentrated on the oxygen atom, as shown in the following figure.



This explains that electrophilic reagents such as proton tend to attack the oxygen atom. Also, LUMO spreads widely on carbon atoms, explaining the phenomenon that nucleophilic attack occurs on the carbon. In addition, it means that the C-O bond is extended.



2.5. Practice of simple Hückel method

(1) Choose molecules with unsaturated compounds or conjugated systems to be calculated and determine the number of atoms and π electrons involved in π bonds.

(2) Numbers are attached to atoms and a matrix element is obtained using a table. (Because the upper right and the lower left are the same in the matrix (symmetric matrix), only one of them can be input.)

(3) Create necessary data and execute the Hückel program using a computer. The program name is huckel and the command name is the same. (The operation procedure is on the next page.)

(4) Based on the coefficients and the orbital energies of the output molecular orbitals, investigate the properties of MO, the properties of molecules, the reactivity, etc.

(5) If you have time, analyze the Fortran source program huckel.f of the Hückel method and find out what algorithm is being used. Then, add a program to calculate electron density and the order of bonding, and examine the nature of the π bond.

(6) In addition, improve the Hückel program and develop your own programs for various purposes. (For the Fortran language, search web pages and study by yourself.)

(7) By compiling the Fortran source program huckel.f and linking the libraries, using command ifort, you can create your own command huckel. The source files are stored under the directory /usr/local/Explab/huckel and are freely available for students interested in them.

2.6. Advice on reports

It is better to display each MO, to look at the chemical reactivity from the shape of the HOMO and the LUMO orbitals, which are considered to be involved in the reaction, to compare them for various groups of molecules, and to correlate them with the properties of the molecule. In addition, compare the result calculated analytically for a small molecule with the result actually obtained by using a computer, and confirm whether they are correct or not.

- The Hückel MO and the orbital energy of unsaturated hydrocarbons exhibit various interesting properties that can also be proved mathematically. It is better to compare linear and cyclic compounds when the number of conjugated hydrocarbons is even and odd.
- In addition, apply the Hückel method to various phenomena, such as substituent effects, the strength of a cation-anion bond, and the prediction of reaction route.
- Focus on what you should investigate by the calculation, why you chose the molecular system, what you understood from the results obtained, what you could apply the method to, etc.

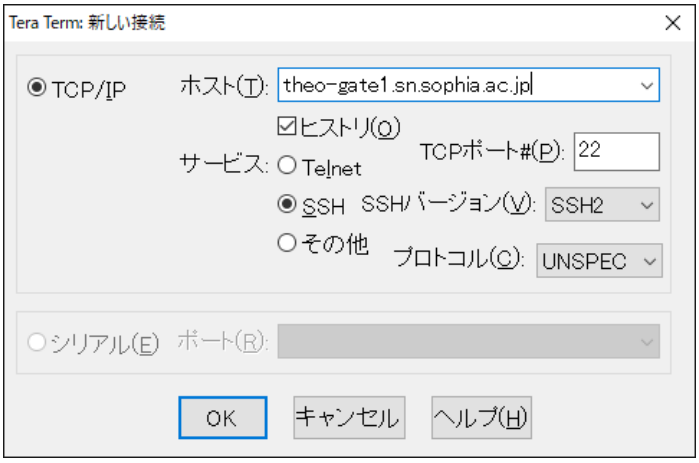
2.7. Terminal operation in the computer room

Start using (using software TeraTerm)

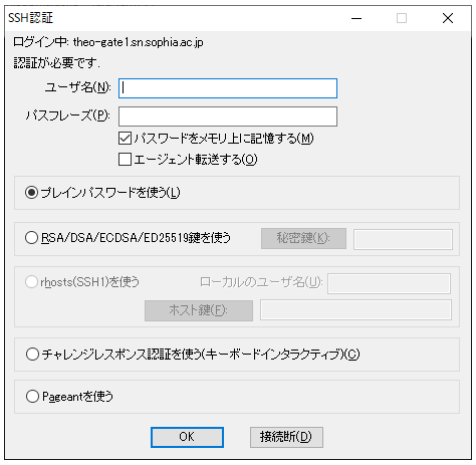
(1) Start Windows 10 PC and start software TeraTerm.

(2) All input commands consist of half-width alphanumeric characters. Entering double-byte characters may cause garbled characters. Be careful.

(3) Enter “theo-gate1.sn.sophia.ac.jp” with single byte alphabet numerals for the host name and connect to the computer (Linux CentOS) to be used by SSH2. (It is also possible to enter “133.12.47.21” with single byte numerals)



(4) Input the login name and password. (Login name and password will be notified in class)



(5) After a message such as “Last login: Fri Mar 2 11:33:52 2018 from rikou96.cc.sophia.ac.jp”, prompt `[jikken1@gate1 ~]$` appears on the screen, waiting for command input.

(6) Enter command `pwd` and check if the end is `jikken1`. In case of uncertainty, please inform the person in charge.

(7) When you come to this stage, it has reached the executable state.

(8) [Note] If you change the window size of `TeraTerm` to, for example, `80 columns x 73 lines`, execute command `resize` and tell the size of the window to the computer server. (The default size is `80 columns x 24 lines`)

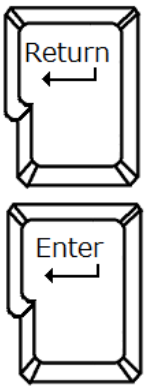
End of use

(1) When you enter command logout, the terminal automatically disappears.

Example of execution

An example of executing the simple Hückel method is described below.

- The part denotes input and the return key should be pushed down at the end of the line.
- Because lowercase letters should be used in standard, make sure that the CAPS key is unlocked.
- If you want to output a result not only to the screen but also to the printer, output the result to the file instead of the screen, execute the data transfer shown on page 23, use software "WordPad" on Windows 10 on PC to open the transferred file, and then output it to the printer in the computer room. Of course, you can make a copy into a private USB memory and output it at home.
- It is easier for you to understand the computer if you think that it is written in English.



Return keys

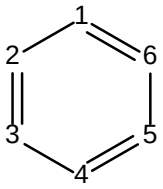
Input on screen

```
 [jikken1@gate1 ~]$ huckel[return]
 Enter TITLE
C6H6 benzene[return]
 Enter the number of dimension
6[return]
 Enter indices of i,j and the element :
1 2 -1[return]
2 3 -1[return]
3 4 -1[return]
4 5 -1[return]
5 6 -1[return]
6 1 -1[return]
0 0 0[return]
```

☞ "Execution of the Hückel program

☞ "Here, enter your favorite title freely

☞Enter the "Hückel" matrix elements. Only upper triangular elements should be inputted because of the symmetric matrix.



```
Your TITLE : C6H6 benzene
--- Your Huckel matrix ---

          1            2            3            4            5
    -------------  -------------  -------------  -------------  -------------
 1     0.0000000    -1.0000000     0.0000000     0.0000000     0.0000000
 2    -1.0000000     0.0000000    -1.0000000     0.0000000     0.0000000
 3     0.0000000    -1.0000000     0.0000000    -1.0000000     0.0000000
 4     0.0000000     0.0000000    -1.0000000     0.0000000    -1.0000000
 5     0.0000000     0.0000000     0.0000000    -1.0000000     0.0000000
 6    -1.0000000     0.0000000     0.0000000     0.0000000    -1.0000000

          6
    -------------
 1    -1.0000000
 2     0.0000000
 3     0.0000000
 4     0.0000000
 5    -1.0000000
 6     0.0000000
```

"The above shows the inputted Hückel matrix"

"In the case of zero, the eigenvalue problem normally ended"

```
Status on your diagonalization : 0
(If your status showing non-zero, your input has something wrong!)

-- Wavefunctions(Eigen functions),Psi_i and Orbital energy(Eigen values),x_i --

    1  -2.0000000  2  -1.0000000  3  -1.0000000  4   1.0000000  5   1.0000000
    -------------  -------------  -------------  -------------  -------------
 1    -0.4082483    -0.5000000     0.2886751     0.5042217    -0.2812362
 2    -0.4082483    -0.5000000    -0.2886751    -0.4956686    -0.2960507
 3    -0.4082483     0.0000000    -0.5773503    -0.0085531     0.5772869
 4    -0.4082483     0.5000000    -0.2886751     0.5042217    -0.2812362
 5    -0.4082483     0.5000000     0.2886751    -0.4956686    -0.2960507
 6    -0.4082483    -0.0000000     0.5773503    -0.0085531     0.5772869

    6   2.0000000
    -------------
 1    -0.4082483
 2     0.4082483
 3    -0.4082483
 4     0.4082483
 5    -0.4082483
 6     0.4082483
```

- The Column vector corresponds to the coefficient (C_1 C_2 C_3 C_4 C_5 C_6) of the wave function (number 1 corresponds to atom number 1 and see the benzene structure shown on the previous page).
- The first line "1 –2.0000000 2 –1.0000000 ..." shows the orbital energies. The energy (the value of *x*) of the first orbital is –2.0000000, the second is –1.0000000, and so on. There are six orbital energies in benzene.
- The second and third are found to have the same orbital energy (–1.0 or α+β) and are degenerate. (1.0 or α–β also for Nos. 4 and 5)
- HOMO consists of Nos. 2 and 3 and LUMO 4 and 5 (see pages 6.10 to 6.12 of reference 1). MO with energy close to HOMO or LUMO has similar properties.

Execution using input file

Next, a method of execution using file `input` without directly inputting data on screen will be explained below. The necessary input data should be stored in a file before execution. The file name can be chosen freely. Do not forget what you wrote in a file, however.

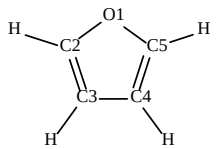
```
[jikken1@gate1 ~]$ vi input [return]
```

```
~
~
~
~
~
~
~
~
"input" [New File]   0,0-1
```

```
C4H4O furan
□
~
~
~
~
~
-- INSERT --          3,1
```

```
C4H4O furan
5
1 1 -1.5
1 2 -0.7
2 3 -1
3 4 -1
4 5 -1
5 1 -0.7
0 0 0
:wq
```

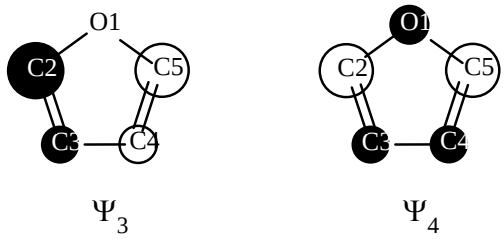
- Edit mode and command mode are switched by key `Esc`. Entering key "a" puts you in the edit mode, where you can enter letters and numbers. Push the key `Esc` to stop the edit mode.
- Immediately after opening a file, the screen will look like one on the left.



- When "a" is entered, -- INSERT -- is displayed in the lower left, entering into the edit mode, and write C4H4O furan. Further, by entering `[return]` twice, two blank lines are created.
- When pushing key `Esc`, -- INSERT – disappears, showing now in the command mode.
- Use the arrow keys to move the position of the pointer indicated by the square box under the line of C4H4O furan.
- - By entering "a", going into the edit mode, where -- INSERT -- is again displayed in the lower left corner, enter 5, push `[return]` once for a line feed.
- Keep the edit mode, continue input as shown on the left, and finally push `Esc` to exit the edit mode.
- Finally enter ":" (colon) and enter "wq" and `[return]`. Then, you can save the contents and exit.

For details on the subcommands of the text editor `vi` (commands to be entered after ":" (colon)), refer to "https://www.linux.com/learn/vim-101-beginners-guide-vim" or see "O'Reilly Book". You can also see the function by entering ": help subcommand-name" in the `vi` command mode. The input file written and saved by editor `vi` can be found by using command `ls`.

Furthermore, by looking at the molecular orbital, both HOMO and LUMO have larger values at the oxygen atom. It is expected, therefore, that the reactivity of the carbon atom adjacent to the oxygen will be high.



Next we show how to use obtained file `input` and execute program `huckel` without input on the screen.

Enter `[jikken1@gate1 ~]$ huckel < input [return]`.

```
Enter TITLE
Enter the number of dimension
Enter indices of i,j and the element :

Your TITLE : C4H4O

--- Your Huckel matrix ---

          1            2            3            4            5
    -------------  -------------  -------------  -------------  -------------
  1    -1.5000000    -0.7000000     0.0000000     0.0000000    -0.7000000
  2    -0.7000000     0.0000000    -1.0000000     0.0000000     0.0000000
  3     0.0000000    -1.0000000     0.0000000    -1.0000000     0.0000000
  4     0.0000000     0.0000000    -1.0000000     0.0000000    -1.0000000
  5    -0.7000000     0.0000000     0.0000000    -1.0000000     0.0000000

Status on your diagonalization : 0
(If your status showing non-zero, your input has something wrong!)

-- Wavefunctions(Eigen functions),Psi_i and Orbital energy(Eigen values),x_i --

    1  -2.2090986  2  -1.2149299  3  -0.6180340  4   0.9240285  5   1.6180340
    -------------  -------------  -------------  -------------  -------------
  1    -0.7324391    -0.5894600    -0.0000000    -0.3406903    -0.0000000
  2    -0.3709797     0.1200267    -0.6015010     0.5898878     0.3717480
  3    -0.3068233     0.5584461    -0.3717480    -0.3065900    -0.6015010
  4    -0.3068233     0.5584461     0.3717480    -0.3065900     0.6015010
  5    -0.3709797     0.1200267     0.6015010     0.5898878    -0.3717480
```

The above "`huckel < input [return]`" means that the `huckel` program is executed with the data contained in file `input` as input data, and the result will be outputted on the screen. If you specify the output file as a file called `output` below, the result will not be outputted on the screen but will be stored in file `output`.

```
[jikken1@gate1 ~]$ huckel < input > output [return]
[jikken1@gate1 ~]$
```

Here, to see file `output` using command `less`, execute as follows.

```
[jikken1@gate1 ~]$ less output [return]
```

```
Enter TITLE
Enter the number of dimension
Enter indices of i,j and the element :

Your TITLE : C4H4O

--- Your Huckel matrix ---

          1            2            3            4            5
    -------------  -------------  -------------  -------------  -------------
  1    -1.5000000    -0.7000000     0.0000000     0.0000000    -0.7000000
  2    -0.7000000     0.0000000    -1.0000000     0.0000000     0.0000000
  3     0.0000000    -1.0000000     0.0000000    -1.0000000     0.0000000
  4     0.0000000     0.0000000    -1.0000000     0.0000000    -1.0000000
  5    -0.7000000     0.0000000     0.0000000    -1.0000000     0.0000000

Status on your diagonalization : 0
(If your status showing non-zero, your input has something wrong!)

-- Wavefunctions(Eigen functions),Psi_i and Orbital energy(Eigen values),x_i --

    1  -2.2090986  2  -1.2149299  3  -0.6180340  4   0.9240285  5   1.6180340
    -------------  -------------  -------------  -------------  -------------
  1    -0.7324391    -0.5894600    -0.0000000    -0.3406903    -0.0000000
  2    -0.3709797     0.1200267    -0.6015010     0.5898878     0.3717480
  3    -0.3068233     0.5584461    -0.3717480    -0.3065900    -0.6015010
  4    -0.3068233     0.5584461     0.3717480    -0.3065900     0.6015010
  5    -0.3709797     0.1200267     0.6015010     0.5898878    -0.3717480


output (END)
```

The result is displayed as shown above. When there is a lot of output, the display will stop with the screen size and the space key should be pushed to show the next page. (For details, refer to the manual using command `man`, like `[jikken1@gate1 ~]$ man less`)

Summary of commands (used when prompt "$" is displayed)

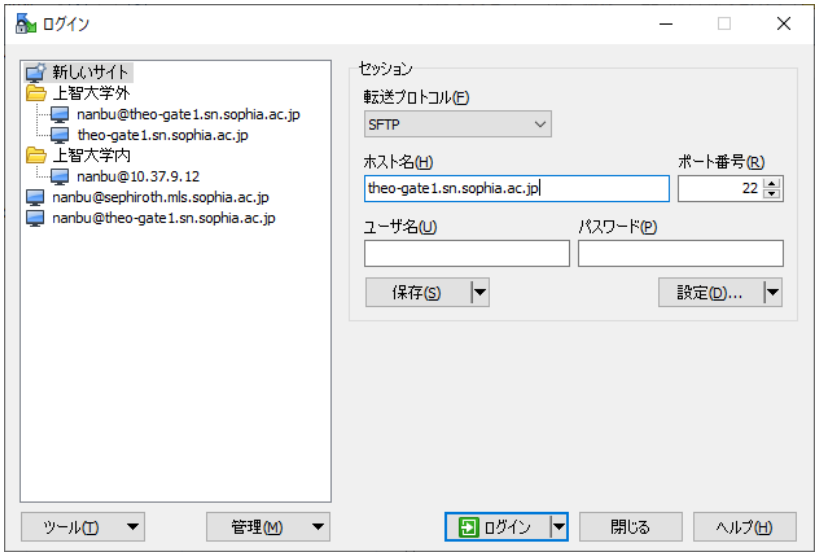
`vi filename`	A screen editor that creates and edits file `filename` (other editors: `emacs`, etc.)
`ifort filename.f90`	Compile the program contained in `filename.f90` into a machine language and then create an executable file. If you do not specify a name of the executable file, file `a.o` is created.
`ls`	List the files under the current directory.
`ls *.log`	List files whose names end with "`.log`".
`rm filename`	Delete file `filename`. Be careful about using it. If you erase all files, you need to re-compute all the results again.
`mv file1 file2`	Rename file with name "`file1`" to file with name "`file2`".
`cp file1 file2`	Copy the content of file "`file1`" into file "`file2`".
`less filename`	When listing the contents of `filename`, the listing stops at every page. To go to the next page, press the `Space` key or key "`f`" (`forward`), and to return to the previous page, press "`b`" key (`backward`). To stop, press key "`q`" (`quit`).
`tail filename`	List the last part of the contents of `filename`. By the way, attaching option "`-100f`", the last part is updated every time when the contents of `filename` is updated, which is convenient for monitoring the result during calculation.
`a.out`	When executing executable file `a.out`, the calculation starts with inputting `a.out [return]`.
`a.out < input > output`	Enter this way and `[return]`, when executing executable file `a.out`, for input file `input` and output file `output`. When the calculation is completed, prompt (`[jikken1@gate1~]$`) is displayed.

Data transfer (data transfer from using computer to computer room or vice versa)

Start using (using software WinSCP)

(1) Start Windows 10 and start software WinSCP.

(2) All input commands consist of half-width alphanumeric characters. Entering double-byte characters may cause garbled characters. Be careful.



(3) Select SFTP as connection protocol, enter “theo-gate1.sn.sophia.ac.jp” with single byte alphabet numerals for host name, and then connect to the computer to be used.

(4) Enter user name and password. (Login name and password will be notified in class)

(5) The left side shows the folder structure of the Windows 10 PC in the computer room, and the right side shows the home directory structure of the computer (Linux CentOS) which performs calculation.

(6) By dragging and dropping the file or directory on the right side to the left side, that in the computer (Linux CentOS) can be transferred to the Windows 10 PC and recognized as a file or a folder. Therefore, it appears as a file or a folder on the PC, i.e., in Explorer. In case of uncertainty, please inform the person in charge.

(7) If you open the file with WordPad, you can see the contents of the file created by the computer (Linux CentOS).

End of use

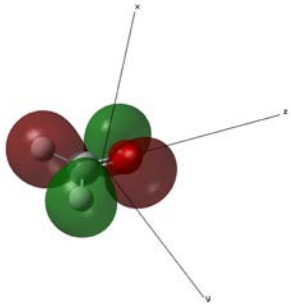
If you select × in the upper right corner of the WinSCP window, the window automatically disappears.

3. Computational Chemistry B: “Non-empirical (*ab initio*) molecular orbital method: usage and computing (*ab initio* SCF MO method)”

The term ‘*ab initio*’ means ‘from the beginning’. In an *ab initio* self-consistent-field molecular orbital method[2-4], we accurately solve SCF equations for all electrons starting from the principle of quantum mechanics without using any empirical means. Of course, the program is complicated, the process requires many steps, and it should be understood that calculations require long computation time and large storage capacity.

Again, an LCAO approximation will be used. In this practice, the atomic orbitals used to construct the molecular orbital consist of the polarized double zeta basis set including polarization basis functions (specifically, Dunning's cc-pVDZ). That is, for hydrogen atoms, five atomic orbitals consisting of two s orbitals (2s) and three p_x, p_y, p_z orbitals (1p) are used for construction of the molecular orbitals. For the second periodic atoms (Li to Ne), 14 atomic orbitals consisting of 3s, 2p, and 1d will be used. For the third periodic atoms (Na to Ar), 18 orbitals consisting of 4s, 3p, and 1d will be used.

For example, the number of orbitals of formaldehyde is 14 for C, 14 for O, and 5 for each of two H atoms, giving therefore 38 atomic orbitals in total, which corresponds to the system of 38 orbitals and 16 electrons. Therefore, HOMO of formaldehyde should be obtained as 8th MO and LUMO as 9th MO.



HOMO of formaldehyde Ψ_8

Here, without learning more about the theoretical basis of the method, let us learn various aspects of applications by actually calculating the molecular orbitals and the energies of fundamental molecules by the *ab initio* SCF method.

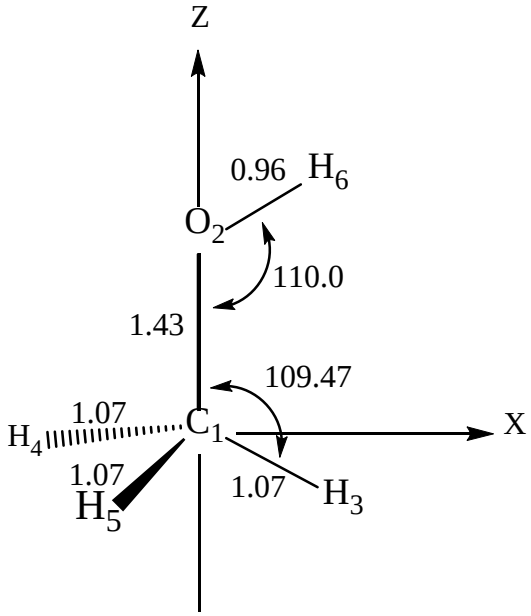
In performing calculations, the information to be inputted into the computer is only the molecular structure, that is, the positions of the nuclei. As a method of inputting this, a Z-matrix method is used. To do this, it is necessary to first study the bond length and bonding angle of the molecule to be calculated.

3.1. How to make input data by Z-matrix method

Once we know the bond length and bond angle for a molecule, we first configure the molecule in the space and put number to each atom. The followings are the rules:

The first atom is placed at the origin.
The second atom is on the Z axis.
The third atom is on the XZ plane.

Let us consider, for example, the Z-matrix for methanol configured as shown below.



Molecular structure of methanol

Below is the Z-matrix data for the above figure.

[1]	C						
[2]	O	1	B1				
[3]	H	1	B2	2	A1		
[4]	H	1	B3	2	A2	3	D1
[5]	H	1	B4	2	A3	3	D2
[6]	H	2	B5	1	A4	3	D3

B1	1.43
B2	1.07
B3	1.07
B4	1.07
B5	0.96
A1	109.47
A2	109.47
A3	109.47
A4	110.00
D1	-120.00
D2	120.00
D3	0.00

The methanol input data can be understood as follows:

The atom [1] is carbon.

The atom [2] is oxygen and is connected to [1] with distance B1 (bond distance) of 1.43 Å.

The atom [3] is hydrogen and has distance B2 of 1.07 Å from [1], and has angle A1 (bond angle) [3]-[1]-[2] of 109.47°.

The atom [4] is also hydrogen and has distance B3 of 1.07 Å from [1], angle [4]-[1]-[2] (A2) of 109.47°, and angle D1 between the plane [4]-[1]-[2] and the plane [1]-[2]-[3] (dihedral angle) of −120° (see the next page for the meaning of a negative angle). (Also called as a dihedral angle composed of [4]-[1]-[2]-[3])

The atom [5] is also hydrogen and has distance B4 of 1.07 Å from [1], angle of [5]-[1]-[2] (A3) of 109.47°, and dihedral angle [5]-[1]-[2]-[3] (D2) of 120°.

The atom [6] is also hydrogen, has distance (B5) of 0.96 Å from [2], angle [6]-[2]-[1] (A4) of 110.00°, and dihedral angle [6]-[2]-[1]-[3] (D3) of 0°, i.e., on the same plane as [6]-[2]-[1], and is located on the *cis* side of [3].

Generally for the coordinates of the [n]th atom, enter the following:

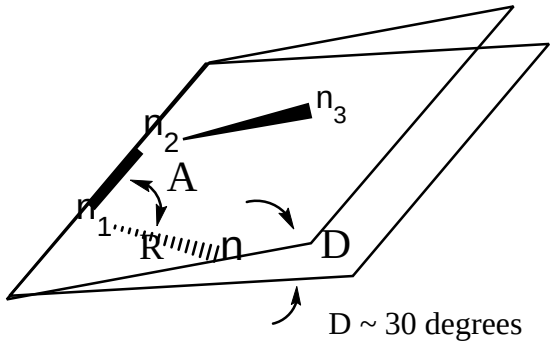
[n]	Element symbol	n1	R	n2	A	n3	D

Here, if the atomic symbol is a carbon atom, C is chosen. Also, if there are two or more of the same element and differentiation is difficult, you can put C1, C2, C3, ..., with numbers. By entering X, which does not exist as an atom in the element symbol, you can define a point to create a molecular skeleton. Such a point is called a dummy atom.

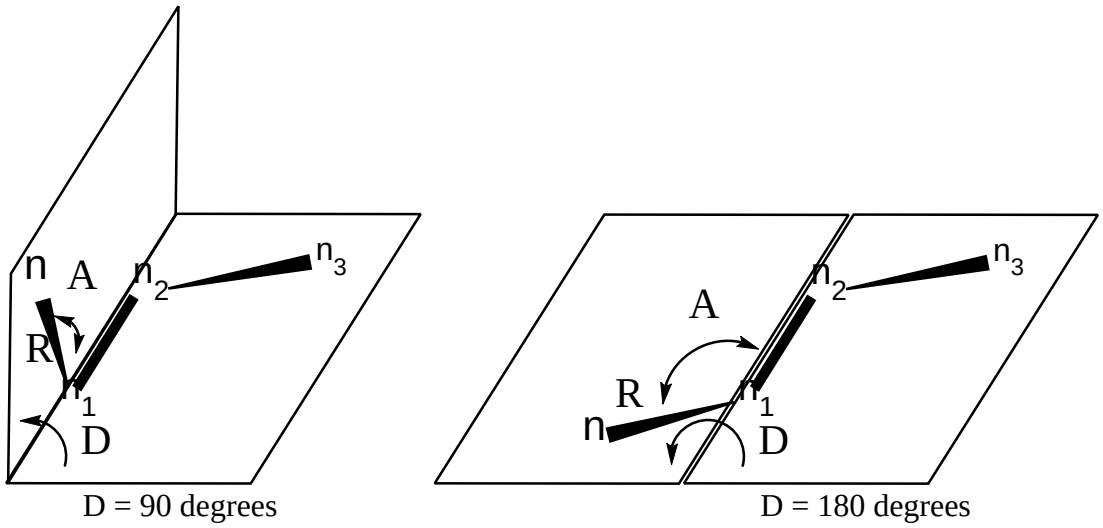
R is the distance (units of Å, default) between [n]th atom and [n1]th atom.

A is the angle (in degrees) formed by atoms [n]-[n1]-[n2].

D is the angle (in degrees) made by the plane formed by atoms [n]-[n1]-[n2] and the plane formed by atoms [n1]-[n2]-[n3], called the dihedral angle, which is defined as shown in the following figure.



Definition of dihedral angle

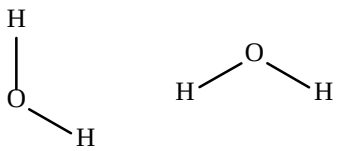


Definition of dihedral angle (positive in the counterclockwise direction and negative in the clockwise direction)

<u>Note: When the dihedral angle exceeds 180°, the angle is defined by the rotation in the opposite direction with negative sign.</u>

3.1.1. Effective use of dummy atoms

When it is difficult to define distance R, angle A, and dihedral angle D using only the atoms that actually make up the molecule, when the symmetry of the molecule collapses, or when the molecule is not easily arranged in the three-dimensional space, you can use dummy atom (X). For example, in the case of H_2O, for which there are two configurations shown below, the configuration in the right-hand side will output the molecular orbital in a form easily recognizable.

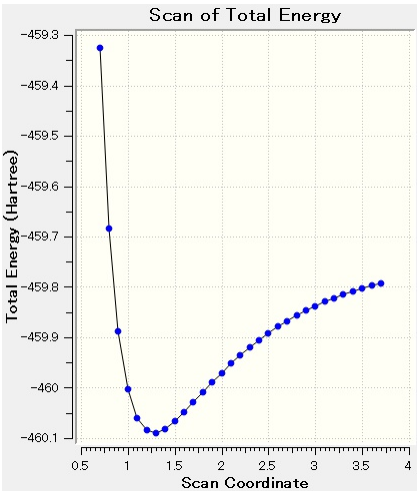


Any number of dummy atoms can be used, which are used just for the calculation of orthogonal coordinates (Cartesian coordinates) and do not appear in the resulting output.

3.2. What you can understand by the *ab initio* SCF MO method

As in the Hückel method[1-2], it is possible to understand the reactivity of a molecule from the shape of a molecular orbit. In the *ab initio* method, because all electrons are considered, it is possible to understand the shape of HOMO and LUMO of a molecule having no π electron and to understand the orbitals as a three-dimensional object.

- The energy of an orbital occupied by electrons is approximately equal to the ionization energy that is required for removing an electron in that orbit, if its sign is changed. Furthermore, the energy of a non-occupied orbital becomes a measure of the electron affinity.
- In the Hückel method[1-2], the total energy has to be obtained by summing the energies of the necessary orbitals, but in the *ab initio* method, it is different from the sum, but is automatically calculated as an absolute value. Therefore, the change in energy due to modification of the skeleton of the molecule or the change in the stableness and unstableness caused by interaction with other molecules can be directly obtained. For example, SCF MO calculations for various inter-nuclear distance R of the diatomic molecule HCl will give the total energy shown in the figure on the right-hand side. Here, the energy unit is Hartree, E_h (1 E_h = 27.211386 eV, 1 eV = 8065.544 cm^{-1}). From this, the most stable inter-nuclear distance can be estimated and the force constant (spring constant) of HCl molecule can be obtained by assuming a harmonic oscillator. Furthermore, it can be concluded, from the difference between the energy of each atom given in Table 2 and the total energy of the molecule, how stable (unstable) the molecule is in comparison with the isolated atoms.



Potential energy curve

Table 2. The energy of isolated atoms (RHF method with cc-pVDZ basis) in units of Hartree (E_h)

H	-0.49927		
Li	-7.43241	Na	-161.85302
Be	-14.57233	Mg	-199.60829
B	-24.52659	Al	-241.87013
C	-37.59598	Si	-288.78690
N	-54.24822	P	-340.61501
O	-74.66527	S	-397.41312
F	-99.37186	Cl	-459.46718

- Because the total energy of the molecule can be calculated, the potential energy barrier of internal rotation of ethane, the energy barrier of configuration inversion of ammonia, and the energy difference of various isomers can be obtained. Also, by calculating molecules HF and HF ... HF, the energy of the hydrogen bond can be estimated from $E(H_2F_2) - 2E(HF)$.
- In addition, much information about the structure and orientation of the molecule will be obtained.

3.3. Advice on reports

You can understand various properties of simple molecules in this way. Therefore, you should freely select molecules and investigate their structure, reactivity, and stability from the calculated results. When choosing the targets of calculation, you should clarify the reason and the purpose. You should also try to analyze known chemical facts and make some theoretical predictions.

- In previous practice, the Hückel MO and the orbital energies of unsaturated hydrocarbons were determined by using the Hückel method. Various interesting properties were found, and some could be proved mathematically. The method had been applied to various phenomena, such as substituent effect, bond strength of cation and anion, prediction of reaction route, etc. It is interesting to examine whether similar results can be obtained by using the *ab initio* SCF MO method. However, it will be an all-electron calculation and therefore computation time should be carefully monitored. The computation time can be predicted, for example, by choosing STO-3G basis function and performing a test calculation with the minimum basis.
- On the other hand, for the calculation, you may select a molecular system completely different from previous practice. In that case, you should emphasize which properties your computations are for, why you chose the molecular system, what you understood from the results obtained, and to what you could apply the results.

3.4. Restrictions

In this practice, the *ab initio* SCF MO method can be used only when the total number of electrons is even (radicals and excited states are not treated here). Furthermore, triplet states like those in O_2 will be excluded even in the case of even electron numbers.

(1) Because the *ab initio* SCF MO method requires a very long computation time depending on the molecule, molecules to be studied are limited in such a way that the number of atoms of the third period is two or less and the number of benzene rings is at most three, for example.

(2) Do not perform two or more calculations at the same time. Perform the next calculation after confirming that the previous calculation is over. Calculation of a system having three benzene rings may take three days or more in some cases.

<u>List of SCF related batch processing commands (used when prompt $ is displayed)</u>

For details of the basic terminal operation in the computer room, see instructions on pages 16 to 17 and page 22.

`qsub` Submit a batch job.
`qstat` Display the status of the submitted batch job.
`qdel` Stop the submitted batch job forcibly.
`qps` Display the whole batch jobs submitted.

3.5. Practice procedure

Determine the molecule to be studied and examine its structure (bond distance and bonding angle). If necessary, investigate it in the chemical handbook or in library. When structural data of the molecule of interest are not available, a partial structure of a similar molecule may be chosen.

```
%mem=4gb
%nproc=1
%chk=mol1.chk
#p test opt freq rhf/cc-pvdz population=full

Formaldehyde

0 1
C
O 1 1.2
H 1 1.08 2 120.0
H 1 1.08 2 120.0 3 180.0

```

1. Create an input file using program GaussView 6 or Z-matrix method from the data of bond distance and bond angle. In particular, you need to use editor `vi` (see pages 19 to 20 and WordPad). GaussView 6 has a help system. Refer to it when necessary. When making input with WordPad, the input file should be transferred from using PC to the server computer (see page 23).
2. The figure on the right shows an input file that performs a standard optimization of the molecular structure of formaldehyde in the electronic ground state (to find the most stable

structure) and a normal-mode analysis of the molecular vibration. In order to make it easier to understand in the display, line numbers are provided.

- `%mem=4gb` The amount of memory used is 4 GBytes (gigabytes)
- `%nproc=1` One process to use
- `%chk=mol1.chk`
  Checkpoint file `mol1.chk` (It stores the main points of the calculated result. (It contains binary data. When analyzing it with GaussView 6 on a PC, it is necessary to convert it into an ASCII text file using command formchk)
- `#p test opt freq rhf/cc-pvdz population=full`
  A line starting with # should contain the input keywords specifying the calculation method of Gaussian 16.
  - ✓ "`p test`" is fixed
  - ✓ "`opt`" for optimizing the molecular structure (computation time increases if initial molecular structure is not good)
  - ✓ "`freq`" for normal mode analysis on molecular vibration (computation time increases, and caution needed)
  - ✓ "`rhf/cc-pvdz`" for a restricted Hartree-Fock method using the cc-pVDZ function as the basis or the RHF method
  - ✓ "`population=full`" for electron distribution analysis (should always be specified for convenience)
- Blank line
- Comment '`Formaldehyde`' (enter your favorite comments, several lines are accepted)
- Blank line
- `0 1` for neutral charge and a spin-singlet state (In the RHF method used, electrons are always required to be in pairs)
- From line 9 to 12: Designation of the initial molecular structure before calculation by the Z-matrix method of formaldehyde
- Blank line, this blank line is mandatory (indicating the end of input)

3. The main program package of the quantum chemistry calculation is Gaussian 16 (see Ref.5). By choosing keywords on web page http://gaussian.com/ of Gaussian, you can find manuals of available options.
4. In this practice, the restricted Hartree-Fock (RHF) method is mainly used. If you want to use other methods, consult with your teacher or TA and select a method while referring to the above manual. If the calculation accuracy is increased, the computation time will be extremely long, and depending on the molecule, it may take more than one month. Consult with the teacher or TA on the plan of the practice.

5. Execute the *ab initio* calculation using command `g16.csh`. This calculation requires very long time and sometimes is made overnight. (Calculation can be made on a day different from that of the practice class.)
6. Confirm that the job is over and use command `less` to see output file (`*.log`) on the screen. Alternatively, use program WinSCP, transfer the output file from the computer server to your PC, and use program GaussView 6 to analyze the `log` file.
7. Use command `rm` to erase unnecessary files and `logout`.

Illustration

An example will be shown using fluoromethane molecule (CH_3F). **You should prepare Gaussian16 input file ch3f.gjf yourself.** (Here you access the computer from home, using TeraTerm found on page 16 by port# 50801). After logging in with ssh, the following message appears.

```
Last login: Sat Feb 24 20:39:58 2018 from
p2601125-ipngn17601hodogaya.kanagawa.ocn. ne.jp
[jikken1@gate1 ~]$
```

[Note] If you set `TeraTerm`'s window size to `80 columns x 73 lines`, for example, execute command `resize` and tell the size of the window to the computer server. (The default size is `80 columns x 24 lines`).

- ⬜ is input and the return key is pushed at the end of the line.
- The input file is "`ch3f.gjf`". To execute a job, execute `g16.csh` for command `qsub` and program Gaussian16 as follows:

```
[jikken1@gate1 ~]$ qsub g16.csh ch3f.gjf [return]
Your job 19816 ("g16.csh") has been submitted
[jikken1@gate1 ~]$
```

You see that job-ID 19816 has been submitted.

- You can see the job execution status by command `qps` or `qstat`.

```
[jikken1@gate1 ~]$ qps [return]
hep.q@hep1.localdomain        BIP   0/1/24       0.00    linux-x64
  19816 0.50500 g16.csh    nanbu       r    03/14/2018 10:47:26    1
--------------------------------------------------------------------------------
```

"`r`" indicates that the job is in the `running` state.

- Similarly, you can see the end of job by command `qps` or `qstat`.

```
[jikken1@gate1 ~]$ qps [return]
hep.q@hep1.localdomain        BIP   0/1/24       0.00    linux-x64
--------------------------------------------------------------------------------
```

If your job-ID disappears from the list, it means the end of the calculation. However, it is unknown whether the calculation is successful until the output file is checked.

- Check that the job is over and use command `less` to see the output on the screen. Analysis of the results can also be done here.

```
[jikken1@gate1 ~]$ less ch3f.log [return]
```

```
 Entering Gaussian System, Link 0=/usr/local/g16/g16/g16
 Input=ch3f.gjf
 Output=ch3f.log
 Initial command:
 /usr/local/g16/g16/l1.exe "/scratch/nanbu/tmp.29896/Gau-29955.inp" -scrdir="/sc
ratch/nanbu/tmp.29896/"
 Entering Link 1 = /usr/local/g16/g16/l1.exe PID=    29956.
```

The contents of the result file are displayed fully on the screen. You can jump to the last line of the result file by pushing keys shift + g (that is, capital letter G). If the following message is displayed, it indicates that the calculation is normally completed.

```
 Job cpu time:      0 days  0 hours  0 minutes  1.0 seconds.
 Elapsed time:      0 days  0 hours  0 minutes  1.4 seconds.
 File lengths (MBytes):  RWF=     6 Int=     0 D2E=     0 Chk=     1 Scr=     1
 Normal termination of Gaussian 16 at Wed Mar 14 10:47:29 2018.
(END)
```

If "`Normal termination of Gaussian 16`" is shown, the calculation has ended normally.

- By using command `gop`, it is possible to check the progress of structure optimization by the RHF method during calculation.

```
[jikken1@gate1 ~]$ gop ch3f.log [return]
     1          E(RHF) =      -138.940419837
     2          E(RHF) =      -139.027830984
     3          E(RHF) =      -139.018680344
     4          E(RHF) =      -139.042766621
     5          E(RHF) =      -139.044771395
     6          E(RHF) =      -139.045140706
     7          E(RHF) =      -139.045142823
     8          E(RHF) =      -139.045142823

   ITER   [Max Force]  [RMS Force]  [Max Disp.]  [RMS Disp.]

    1     0.534758     0.143375     0.264725     0.079484
    2     0.154178     0.041291     0.346516     0.153970
    3     0.029820     0.017609     0.191385     0.116451
    4     0.026164     0.007872     0.050160     0.016071
    5     0.004198     0.001994     0.032547     0.014716
    6     0.000866     0.000280     0.002898     0.001393
    7     0.000250     0.000080     0.000976     0.000405
    8     0.000250     0.000080     0.000879     0.000376

 thre.     0.000450     0.000300     0.001800     0.001200

 Conver ?     YES          YES          YES          YES
```

The value of `E(RHF)` is the potential energy in the optimization process of the molecular structure.

After calculations are performed eight times and the calculation proceeds in the direction that the potential energy decreases during the process, the most stable structure of the molecule may be obtained. The above results clearly show an energy decrease.

Next, the lines below `ITER` show the force on the molecular structure (~ gradient of the potential energy) and the maximum and the root mean square of the structural change in each iterative calculation. More specifically, `ITER` indicates how unstable the molecular structure is at each iteration of the `SCF` calculation. The line starting with "`thre.`" indicates the corresponding threshold. That is, if the result is smaller than the corresponding threshold, the molecule has reached its most stable structure on the potential-energy hypersurface determined by the parameters of the molecular structure. It is important to make comparison of the results with the inputted molecular coordinates. In the present calculation for a single molecule, the results should be close to the structure of the gas phase molecule observed in experiments.

Analysis of calculated results

- Execute two commands before analysis, and create a cube file and an fchk file.

```
[jikken1@gate1 ~]$ formchk ch3f.chk [return]
```

```
Read checkpoint file ch3f.chk
Write formatted file ch3f.fchk
FChkPn:  Coordinates translated and rotated.
FChkPn:  Coordinates match /B/ after translation and rotation.
```

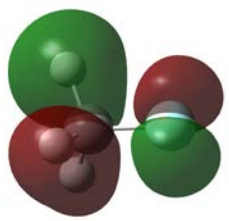
Use command formchk to convert the check file ch3f.chk to file ch3f.fchk. See pages 30 and 31 for the specification of the check file.

```
[jikken1@gate1 ~]$ cubegen 0 MO=8,9,10 ch3f.fchk ch3f.cube [return]
Top CubeGen        Wed Mar 14 14:21:05 2018
 Aft UFChkP         Wed Mar 14 14:21:05 2018       0.08 cpu,       0.08 elapsed
 Aft DecCub         Wed Mar 14 14:21:05 2018       0.00 cpu,       0.00 elapsed
 Aft Density        Wed Mar 14 14:21:05 2018       0.00 cpu,       0.00 elapsed
 Bef DoCube         Wed Mar 14 14:21:05 2018       0.01 cpu,       0.09 elapsed
 There are a total of     518003 grid points.
 ElSum from        orbitals=      1.4994881100
 Aft DoCube         Wed Mar 14 14:21:08 2018       1.36 cpu,       3.62 elapsed
```

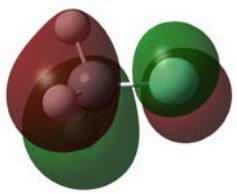
Using command `cubegen` and the previously converted file `ch3f.fchk`, create cube file `ch3f.cube` of the 8th, 9th, and 10th molecular orbitals (MOs). This process is essential to describe MO on the screen using program GaussView 6. Because the orbital energy is the same between the 8th and 9th MOs of fluoromethane, HOMO is doubly degenerate. The 10th MO is LUMO.

- Three files, `ch3f.log`, `ch3f.fchk`, and `ch3f.cube`, containing the calculated results, should be transferred from the computer server to your PC by using the program WinSCP (see page 23)
- After that, use the function of GaussView 6 and analyze three files. The file `ch3f.log` shows the main chemical properties of the molecule and the wave function is visualized by `ch3f.cube`.

In the figure on the right for the wave function of HOMO and LUMO, the values of an isosurface are chosen as 0.04 for HOMO (isovalue=0.04) and 0.06 for LUMO (isovalue=0.06).



Molecular orbital Ψ_8, HOMO

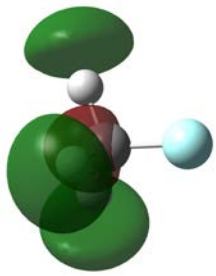


Molecular orbital Ψ_9, HOMO

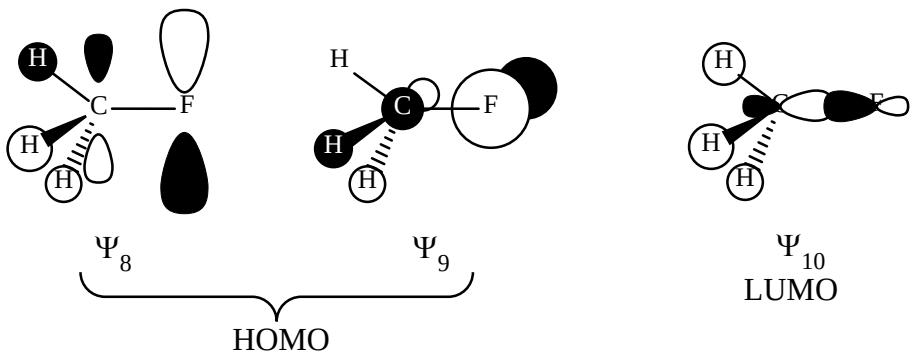
To summarize the characteristics of CH_3F, it has 18 electrons, and electrons occupy up to the 9th orbital. In this molecule, the orbital energy is the same between the 8th and 9th orbitals and,

therefore, both degenerate orbitals, Ψ_8 and Ψ_9, become HOMO. The energy is negative up to the 9th orbital and electrons occupying Ψ_8 and Ψ_9 are most easily ionized. LUMO is the 10th and is the orbital that easily accepts an extra electron from outside.

Using the pictures of HOMO and LUMO, the shapes of three MOs are illustrated as follows.

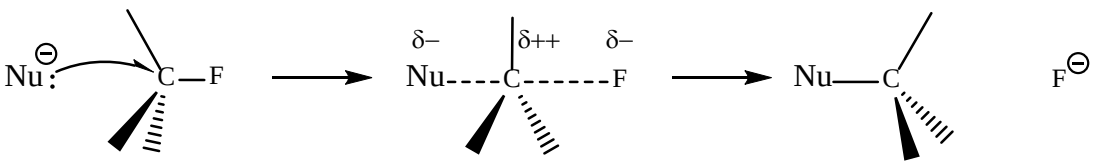


Molecular orbital Ψ_{10}, LUMO



HOMO and LUMO of methyl fluoride

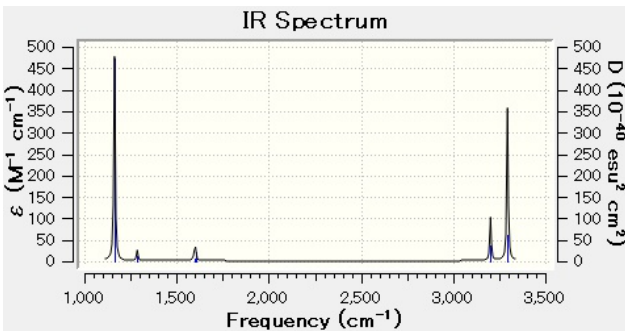
HOMO Ψ_8 and Ψ_9 are the lone pair orbitals of F, indicating that these are on halogen atoms that are susceptible to attack by electrophilic reagents. It is found that LUMO Ψ_{10} has an anti-bonding property at the part of a C-H bond and plays an important role in cutting the C-F bond by accepting electrons from the back side of carbon during an S_N2 reaction.



IR spectra can also be estimated and compared with experiments. For experimental results refer to Chemistry WebBook[6] in NIST, USA:

(https://webbook.nist.gov/chemistry/)

The position of the peaks in experimental results can be almost reproduced by the theoretical calculation. However, the experimental results vary slightly depending on conditions.



IR spectrum obtained by theoretical calculation

4. References

1. Roger Nix, “An Introduction to Molecular Orbital Theory” PDF file stored in Moodle, see the web-site of Shinkoh NANBU.
2. Christopher J. Cramer, “Essentials of Computational Chemistry: Theories and Models”, WILEY.
3. Peter Atkins, Julio de Paula and James Keeler, “Atkins' Physical Chemistry, 11th edition”, Topic 9 “Molecular structure”, OXFORD.
4. Attila Szabo and Neil S. Ostlund, “MODERN QUANTUM CHEMISTY, Introduction to Advanced Electronic Structure Theory”, DOVER.
5. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
6. NIST Chemistry WebBook (https://webbook.nist.gov/chemistry/)

4. Computational Chemistry A

Date of Prep.-Report submission：_____

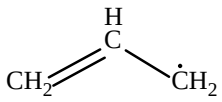
"Simple Hückel theory: practice and computing"

Experimenter	Student ID number：	Name：
Group name		

Experiment date

First time	Year	Month	Day	Day of week
Second time	Year	Month	Day	Day of week

1. The allyl radical is a conjugated π-system with a p-orbital on the carbon adjacent to a homonuclear double bond (C=C).
   (1) Construct and solve the Hückel secular determinant analytically. Estimate its π-electron energy (orbital energy) by using the Hückel approximation.



Allyl radical

2. The formaldehyde is an unsaturated hydrocarbon system containing heteronuclear diatoms. (see pages 12-14 of the text)
   (1) Construct and solve the Hückel secular determinant analytically. Estimate its π-electron energy (orbital energy) by using the Hückel approximation.

5. Computational Chemistry B

Date of Prep.-Report submission：_____

"Non-empirical (*ab initio*) molecular orbital theory: usage and computing"

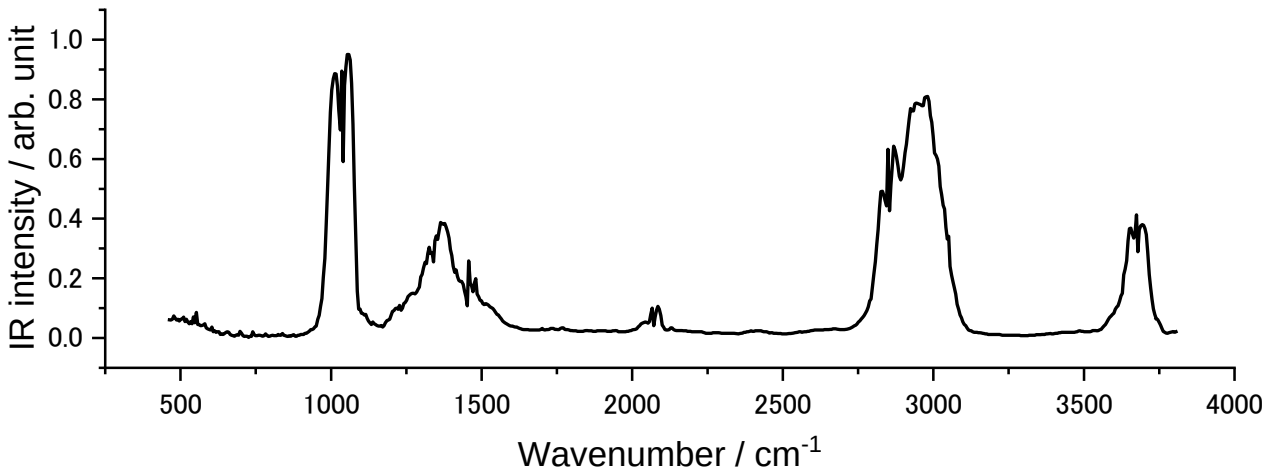
Experimenter	Student ID number：	Name：
Group name		

Experiment date

First time	Year	Month	Day	Day of week
Second time	Year	Month	Day	Day of week

1. What is the number of vibrational modes of a non-linear molecule composed of N atoms? How many normal modes are in a methanol molecule?

2. Investigate vibrational energy levels of methanol looking at Ref.7 in the text.
   (1) Perform the assignment of multiple peaks which appear in infrared absorption spectrum in gas shown in the following figure
   (2) If there is a peak that cannot be assigned, consider why.



Infrared absorption spectrum of methanol in the gas phase observed by experiment

4. Computational Chemistry A

Date of Report submission：_____

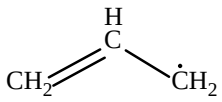
"Simple Hückel theory: practice and computing"

Experimenter	Student ID number：	Name：
Group name		

Experiment date

First time	Year	Month	Day	Day of week
Second time	Year	Month	Day	Day of week

1. The allyl radical is a conjugated π-system with a p-orbital on the carbon adjacent to a homonuclear double bond (C=C).



Allyl radical

   (1) Construct and solve the Hückel secular determinant analytically. Estimate its π-electron energy (orbital energy) by using the Hückel approximation.
   (2) For the obtained analytical orbital energies and molecular orbitals, confirm the agreement with the result obtained using the Hückel-based computational chemistry program (huckel). Furthermore, create a π-molecular orbital energy correlation diagram.

2. The formaldehyde is an unsaturated hydrocarbon system containing heteronuclear diatoms. (see pages 12-14 of the text)
   (1) Construct and solve the Hückel secular determinant analytically. Estimate its π-electron energy (orbital energy) by using the Hückel approximation.
   (2) For the obtained analytical orbital energies and molecular orbitals, confirm the agreement with the result obtained using the Hückel-based computational chemistry program (huckel). Furthermore, create a π-molecular orbital energy correlation diagram.
   (3) Discuss the reactivity of the molecule as an electron donor and its reactivity as an electron acceptor using the obtained HOMO and LUMO.

3. Following the advice in section 3.6, investigate three- and four-atom systems using the computational chemistry program (huckel). (Attach the results of all Hückel calculations.)

5. Computational Chemistry B

Date of Report submission：_____

"Non-empirical (*ab initio*) molecular orbital theory: usage and computing"

Experimenter	Student ID number：	Name：
Group name		

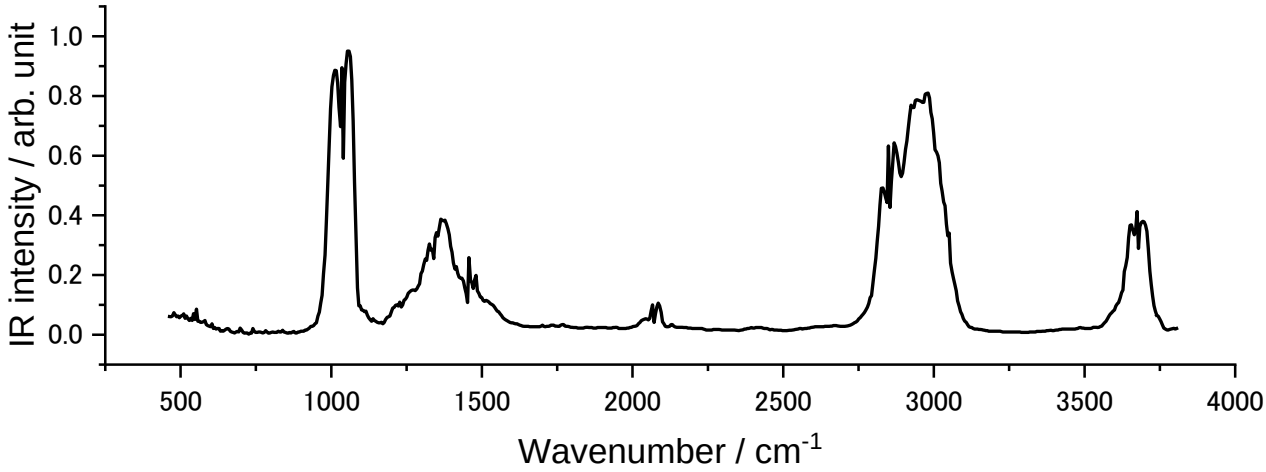
Experiment date

First time	Year	Month	Day	Day of week
Second time	Year	Month	Day	Day of week

1. The infrared absorption spectrum of methanol molecule observed experimentally is shown below.

   Perform quantum chemistry calculation (by Gaussian16) and assign multiple peaks that appear in the spectrum below to vibrational modes of the methanol molecule.

   (Boltzmann distribution is discussed in "Atkins Physical Chemistry (Bottom), 8th Edition, Chapter 16, Statistical Thermodynamics 1: Concepts.")



Infrared absorption spectrum of methanol in the gas phase observed by experiment

2. Following the advice in section 4.3, investigate three- and four-atom systems using quantum chemistry calculation (with Gaussian16). Attach the results of vibration analysis and the figures of MO.