

Quantum Chemistry

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2004

Chapter 4

Methods for many-atom systems and their applications

If atoms are solid balls, they do not bind with each other. Real atoms can produce chemical bonds, and they can transfer electrons to yield ions. Ions can also bind with atoms. These binding processes give complexes, clusters, polymers, and crystals. Combined systems of atoms and ions are composed of nuclei and electrons, which interacts with each other by Coulomb forces.

In this chapter, we will study how nuclei and electrons form molecules, on the basis of quantum mechanical treatments for diatomic and polyatomic systems.

4.1 Motion of electrons and nuclei

4.1.1 The Hamiltonian operator for nuclei and electrons

Let us consider systems of nuclei and electrons. Such systems include molecules, ions, complexes, polymers, and crystals, and all materials. In order to make quantum mechanical treatments, some symbols need to be introduced. For systematic treatments, Z_A and Z_B denote atomic numbers for the atoms A and B, and their distance is denoted by R_{AB} , as shown in Fig.4.1. r_{ij} denotes the distance between the electrons i and j , and R_{Ai} denotes the distance between the atom A and the electron i . The Laplacian operators and masses for the atom A and the electron i are expressed by Δ_A , Δ_i , M_A , and m , respectively. Using these notations, the Hamiltonian operator can be expressed as a summation of the following five terms.

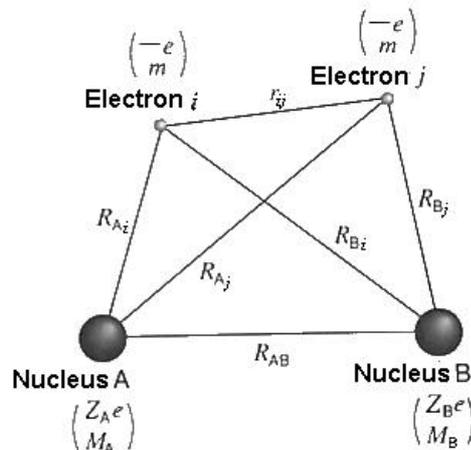


Figure 4.1: A system of nuclei and electrons

$$\hat{H} = K_n + K_e + U_{nn} + U_{ne} + U_{ee} \quad (4.1)$$

$$\text{(Kinetic energies of the nuclei)} K_n = \sum_A \left(-\frac{\hbar^2}{2M_A} \right) \Delta_A \quad (4.2)$$

$$\text{(Kinetic energies of the electrons)} K_e = \sum_i \left(-\frac{\hbar^2}{2m} \right) \Delta_i \quad (4.3)$$

(Potential energies of interactions between the nuclei)

$$U_{nn} = \sum_{A>B} \left(\frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} \right) \quad (4.4)$$

(Potential energies of interactions between the nuclei and the electrons)

$$U_{ne} = \sum_A \sum_i \left(-\frac{Z_A e^2}{4\pi\epsilon_0 R_{Ai}} \right) \quad (4.5)$$

(Potential energies of interaction between the electrons)

$$U_{ee} = \sum_{i>j} \left(\frac{e^2}{4\pi\epsilon_0 r_{ij}} \right) \quad (4.6)$$

The symbols A and i under Σ indicate that the summation should be taken for all atoms or all electrons, respectively. The symbols $A > B$ and $i > j$ under Σ denote that the summations should be taken for only one pair of nuclei or electrons without duplication.

The Hamiltonian operator given above can be applied to special systems such as a system of only one nucleus as well as a system of only one electron. If there is only one nucleus, U_{nn} is omitted, and the summation for A has only one contribution of the nucleus. For only one electron, U_{ee} is omitted, and summations for i includes only one contribution due to the electron. Furthermore, for no electrons K_e, U_{ne}, U_{ee} are omitted, and for no nuclei K_n, U_{nn}, U_{ne} are omitted. It follows that \hat{H} given above in eq.(4.1) can be applied to any system composed of arbitrary numbers of nuclei and electrons.

When we do not care for the difference between nuclei and electrons, the Hamiltonian operator \hat{H} for a system including particles with masses M_I, M_J and electric charges Q_I, Q_J can be expressed much more simply by the following formula.

$$\hat{H} = \sum_I \left(-\frac{\hbar^2}{2M_I} \right) \Delta_I + \sum_{I>J} \left(\frac{Q_I Q_J}{4\pi\epsilon_0 R_{IJ}} \right) \quad (4.7)$$

There are some reasons why in the above treatments we note the difference between nuclei and electrons, as discussed below.

4.1.2 Separation of nuclear and electronic motions

When a force F acts on a body with a mass of M , the body undergoes an acceleration of $a = F/M$. This is clear from Newton's equation of motion, $F = Ma$. Now let us suppose that forces of F act independently on two bodies with different masses of M and m . Magnitudes of accelerations on these bodies are F/M and F/m , and their ratio becomes $(F/M)/(F/m) = m/M$. If M is very large in comparison with m , this ratio becomes to be vanishing. Thus, the acceleration on the heavy body (M) can be neglected with respect to that for the light body (m). When owing to the law of action and reaction a pair of forces of the same magnitude act on each of two bodies with a very large mass ratio, the heavy body scarcely moves, whereas the light body significantly moves. Thus, the motion of a heavy particle can be neglected in comparison with the motion of a light particle. In other words, as long as the motion of light particles is concerned, heavy particles can be fixed to the rest positions.

M. Born and J.B. Oppenheimer applied such an idea based on large mass ratios to systems of nuclei and electrons, and in 1927 they introduced the adiabatic approximation or the Born-Oppenheimer approximation in which nuclei are fixed when the electronic motion is considered.

Under this approximation, we omit K_n from the complete \hat{H} in the above expression, and the following Hamiltonian \hat{H}_e , called electronic Hamiltonian, is used instead.

$$\hat{H}_e = K_e + U_{nn} + U_{ne} + U_{ee} \quad (4.8)$$

Here, U_{nn} may be omitted for problems dealing with the electronic motion, since it does not contain electron coordinates. In order to discuss the stability of the system or forces acting on nuclei, however, U_{nn} would better be included in \hat{H}_e .

Let us suppose that the eigen equation of \hat{H}_e , that is the eigen equation for electrons $\hat{H}_e\psi = u\psi$, has been solved. In order to specify meanings of the coordinates clearly, nuclear and electronic coordinates are represented by R and r , respectively. With these notations, the eigen equation for electrons is expressed by

$$\hat{H}_e(R, r)\psi(R, r) = u(R)\psi(R, r) \quad (4.9)$$

We should note here that R represents parameters of the fixed nuclear coordinates. If R is displaced, then \hat{H}_e changes accordingly to yield modified eigen functions ψ and eigen values u . Once $\psi(R, r)$ is obtained, then we know probability distributions of finding electrons around the fixed nuclei. Once $u(R)$ is determined, we know the energy at the fixed nuclear configuration. The functional values of $u(R)$ depend on R . A decrease of u results in an energetically more stable situation, and an increase of u brings the system unstable. It follows that $u(R)$ is the potential energy of nuclear motion, which changes depending on the relative positions of nuclei. This can be seen from the meaning of the complete Hamiltonian \hat{H} , which is expressed by $\hat{H} = K_n + \hat{H}_e$, and also from the meaning of the following Hamiltonian \hat{H}_n , which can be derived from \hat{H} with an replacement of \hat{H}_e by its eigen value $u(R)$.

$$\hat{H}_n = K_n + u(R) \quad (4.10)$$

\hat{H}_n is the Hamiltonian for nuclear motion in the adiabatic approximation, K_n is the kinetic energy, and $u(R)$ represents the potential energy. In this sense, $u(R)$ is called the adiabatic potential. As discussed below, from $u(R)$ we can obtain information on stable nuclear configurations (molecular structures for molecules), heats of reactions (binding energies for diatomic molecules), and strengths of chemical bonds.

Let us solve the eigen equation of \hat{H} in eq.(4.1).

$$\hat{H}\Psi = E\Psi \quad (4.11)$$

The eigen value E is for the total energy including both nuclear and electronic motion. Noting that the eigen function $\psi(R, r)$ in eq.(4.9) for electronic motion describes electronic behavior with nuclei almost resting, we assume the following form of the wave function Ψ .

$$\Psi(R, r) = \phi(R)\psi(R, r) \quad (4.12)$$

Insertion of eq.(4.12) into eq.(4.11) followed by use of eq.(4.9) as well as an approximation of $\Delta_A\psi(R, r) = 0$ based on consideration of slowly changing $\psi(R, r)$ with respect to R leads to the following equation.

$$\hat{H}_n\phi(R) = E\phi(R) \quad (4.13)$$

By solving this equation, we obtain energy levels including both nuclear and electronic motion. Namely, energies obtained from eq.(4.13) contain energies for translational, rotational, and vibrational motion in addition to electronic motion. Methods for separating translational, rotational, and vibrational motions have been studied in Section 1.12 for two-particle systems (diatomic molecules).

4.1.3 The adiabatic potentials for diatomic molecules

When the adiabatic potential is given for a polyatomic system, various properties can be determined. Let us study these characteristics of diatomic systems as examples. $u(R)$ for a diatomic molecule is in general a curve as shown in Fig.4.2. R is the distance between the nuclei, and two separated atoms correspond to the dissociation limit of $R \rightarrow \infty$. In the figure, $u(R)$ decreases on going from $R = \infty$ to the shorter distance between the two nuclei. The nuclei mutually undergo

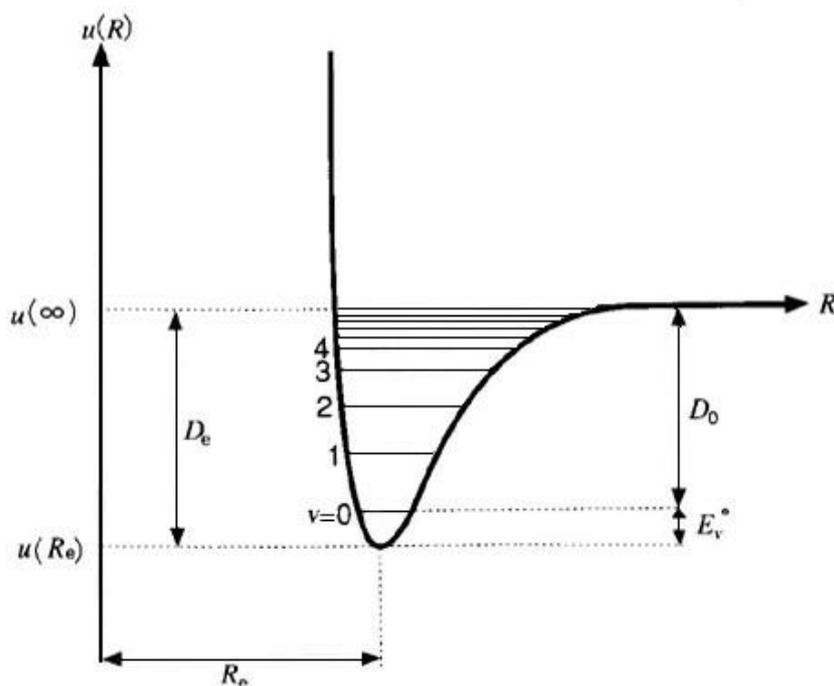


Figure 4.2: The potential energy curve for a diatomic molecule

attractive forces associated with the decrease of the energy. This means that binding forces exist. The further decrease of R leads to the minimum of $u(R)$ at a distance of R_e , and for the shorter distances $u(R)$ increases rapidly. This indicates that for $R < R_e$ atoms strongly repel each other. The force F may be defined as $F = -du/dR$, which formally represents a force expanding the interatomic distance R . For $R < R_e$ F becomes positive, which leads to a repulsion between the nuclei. For $R > R_e$ F becomes negative, which leads to an attraction between the nuclei. R_e is called the equilibrium internuclear distance, which means the bond-length or the interatomic distance, one of the most important constant determining the molecular structure.

The magnitude of the stabilization energy associated with the formation of a molecule is called the bond energy and is defined by the following quantity D_e .

$$D_e = u(\infty) - u(R_e) \quad (4.14)$$

The bond energy is roughly equal to the dissociation energy, though some corrections for thermal energies and zero-point energies need to be made for a rigorous comparison with the heat of reaction actually measured. If the bond energy is small, corrections of thermal energies are especially important. When temperature is so high that the thermal energy exceeds the bond energy, molecules tend to dissociate and become unstable.

Around the equilibrium point of $R = R_e$ in the adiabatic potential curve $u(R)$, a restoring force arises with a magnitude proportional to $\Delta R = R - R_e$. According to Hooke's law ($F = -k\Delta R$), stretched bonds tend to shrink, and conversely shrunk bonds tend to stretch. The force constant indicating the magnitude of the spring can be obtained from the second derivative of $u(R)$ as follows.

$$k = \frac{d^2u}{dR^2} \quad (\text{differentiation should be made at } R = R_e) \quad (4.15)$$

This formula can be derived from a power series expansion of $u(R)$ in terms of $\Delta R = R - R_e$ around $R = R_e$. A differentiation yielding the force F followed by a comparison with Hooke's law, neglecting the higher order terms, leads to the expression for k .

When the force constant k for the bond spring together with the reduced mass are given, the vibrational frequency in the harmonic approximation is given by the following equation.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (4.16)$$

The zero-point energy E_v° of the harmonic oscillator is given by

$$E_v^\circ = \frac{1}{2} h\nu = \frac{h}{4\pi} \sqrt{\frac{k}{\mu}} \quad (4.17)$$

The ground-state energy of a diatomic molecule cannot become the minimum energy of the adiabatic potential. This is clearly related with the explanation of the zero-point energy in section 1.10. Therefore, the net energy required for dissociation (the dissociation energy) D_0 is smaller than the bond energy D_e by the zero-point vibration energy E_v° (see Fig.4.2).

$$D_0 = D_e - E_v^\circ \quad (4.18)$$

As can be seen from the above, the adiabatic potential energy curve leads to the following very important quantities.

- (1) The bond length (The equilibrium internuclear distance) R_e
- (2) The bond energy D_e
- (3) The spring constant of the bond (The force constant) k
- (4) The vibrational frequency ν
- (5) The zero-point vibration energy E_v°
- (6) The dissociation energy D_0

Example 4.1 P. M. Morse proposed an experimental formula of the adiabatic potential curve for diatomic molecules, which is given by

$$M(R) = D[e^{-2(R-R_0)/a} - 2e^{-(R-R_0)/a}]$$

This is called the Morse potential. Using this potential, obtain (1) The equilibrium internuclear distance R_e , (2) The bond energy D_e , (3) The force constant k , and (4) The vibrational frequency ν . In the calculation of ν , assume a harmonic oscillator with a reduced mass of μ .

(Solution) In this problem we may write $u(R) = M(R)$, and we obtain

$$\begin{aligned} \frac{du}{dR} &= D \left[-\frac{2}{a} e^{-2(R-R_0)/a} - 2 \left(-\frac{1}{a} \right) e^{-(R-R_0)/a} \right] \\ &= D \left(-\frac{2}{a} \right) \left[e^{-(R-R_0)/a} - 1 \right] e^{-(R-R_0)/a} \end{aligned}$$

In order to satisfy the equilibrium condition, the value of this equation should be vanishing. Thus the parenthesis in the right side needs to be zero, and we obtain the condition to be $R = R_0$. Therefore,

$$R_e = R_0 \quad (1)$$

Next, we calculate $D_e = u(\infty) - u(R_e)$.

$$D_e = M(\infty) - M(R_0) = 0 - D[1 - 2] = D \quad (2)$$

Then, we calculate $k = d^2u/dR^2$.

$$\begin{aligned} k &= \frac{d^2M}{dR^2} \\ &= D \left[\left(-\frac{2}{a} \right)^2 e^{-2(R-R_0)/a} - 2 \left(-\frac{1}{a} \right)^2 e^{-(R-R_0)/a} \right] \end{aligned}$$

Inserting the equilibrium condition $R = R_e = R_0$, we obtain

$$k = D \left[\left(\frac{2}{a} \right)^2 - 2 \left(\frac{1}{a} \right)^2 \right] = \frac{2D}{a^2} \quad (3)$$

Assuming a harmonic oscillator,

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Inserting the above equation (3) for k into this expression, we obtain

$$\nu = \frac{1}{2\pi a} \sqrt{\frac{2D}{\mu}} \quad (4)$$

4.2 The binding force and the electron density

In the previous section we studied the relationship between the slope of the adiabatic potential and the binding force. In this section we will study how the binding forces connecting nuclei are related with the quantum mechanical behavior of electrons and elucidate the causes of chemical bonds.

4.2.1 Forces acting on nuclei and Feynman's electrostatic theorem

Forces acting on individual atoms can be calculated by differentiation of the adiabatic potential u with respect to the respective nuclear coordinates. For example, the force acting on the nucleus A $(F_A)_x$ along the x -coordinate (x_A) is given by the following equation.

$$(F_A)_x = -\frac{du}{dx_A} \quad (4.19)$$

R. P. Feynman presented a theory in 1939 that the right side of eq.(4.19) is related to the spatial distribution of electrons based on the adiabatic approximation. $\rho(x, y, z)dxdydz$ is introduced as a quantity indicating how many electrons are contained in the volume element of $dxdydz$. ρ is a quantity depending on the spatial coordinates and is called the electron density. This density is related with all electrons involved in the system, and thus it is sometimes called the total electron density. It should be noted that ρ is the number density rather than the probability density. It follows that the integration of ρ over the whole space gives the total number of electrons N .

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(x, y, z)dxdydz = N \quad (4.20)$$

The electron density ρ can be calculated from the following equation, provided that functions of occupied orbitals ϕ_i as well as their occupation numbers n_i are known.

$$\rho = \sum_i n_i |\phi_i|^2 \quad (4.21)$$

From the Pauli principle occupation numbers n_i are either 0, 1, or 2, depending on the electron configuration. When ρ is obtained by quantum mechanics, the spatial distribution of negative charges due to electrons is given by $-e\rho(x, y, z)dxdydz$.

Forces acting on nuclei are expressed with the electron density as follows.

[Feynman's electrostatic theorem]

The force acting on a nucleus is a resultant force of all sums of the electrostatic repulsion due to all other nuclei and the electrostatic attraction due to the whole electron densities.

This is called Feynman's electrostatic theorem. Since the resultant force is a vector quantity, the summation should be made, considering the directions. As studied in chapter 1, the electrostatic force on atom A at a position vector \mathbf{R}_A with an atomic number Z_A and an electric charge $Q_A = Z_A e$ caused by an electric charge Q placed at a position vector \mathbf{r} is given by

$$F = \frac{QQ_A}{4\pi\epsilon_0|\mathbf{r} - \mathbf{R}_A|^2} \quad (F < 0 \text{ for attraction, } F > 0 \text{ for repulsion})$$

In this expression, the direction of the vector is not specified. The force vector is in the opposite direction against the position of the other charge, when the force is repulsive between charges with the same sign. The unit vector of this direction is expressed as $-(\mathbf{r} - \mathbf{R}_A)/|\mathbf{r} - \mathbf{R}_A|$. Using this relation, the force vector \mathbf{F} on the atom A caused by an electric charge Q placed at \mathbf{r} is given by

$$\mathbf{F} = -\frac{QQ_A(\mathbf{r} - \mathbf{R}_A)}{4\pi\epsilon_0|\mathbf{r} - \mathbf{R}_A|^3} = -Q\mathbf{E}_A(\mathbf{r}) \quad (4.22)$$

Here,

$$\mathbf{E}_A(\mathbf{r}) = \frac{Q_A(\mathbf{r} - \mathbf{R}_A)}{4\pi\epsilon_0|\mathbf{r} - \mathbf{R}_A|^3} \quad (4.23)$$

\mathbf{E}_A represents the force on a unit charge at \mathbf{r} caused by the charge of the nucleus A, and this is called the electric field. It follows that eq.(4.22) stands for the reaction, that is the same magnitude force to the opposite direction with respect to the force on an electric charge Q at \mathbf{r} under the electric field caused by the nucleus A.

The above arguments lead to the following theorem.

[Theorem] The electrostatic force acting on a charged particle is equal to the resultant force of all reactions against the forces to other charged particles caused by the particle itself.

Using this theorem together with the formula for the electric field, a mathematical expression for the force vector \mathbf{F}_A acting on the nucleus A is given as Feynman's electrostatic theorem as follows.

$$\mathbf{F}_A = \int e\rho(\mathbf{r})\mathbf{E}_A(\mathbf{r})d\mathbf{r} - \sum_{B(B \neq A)} eZ_B\mathbf{E}_A(\mathbf{R}_B) \quad (4.24)$$

In this formula, the three dimensional volume element $dx dy dz$ is written as $d\mathbf{r}$. The integral of the first term in the right side of eq.(4.24) is the resultant force of attraction due to electron densities distributed spatially, and the second terms are the resultant force of repulsion due to other nuclei of the atomic number Z_B . Since the direction of \mathbf{E}_A is defined toward the other charge, the attraction is positive and the repulsion is negative in eq.(2.24).

4.2.2 The binding region and the antibinding region

Whether electron densities give attraction or repulsion between nuclei depends simply on where electron densities are placed spatially. In order to understand this, let us study two cases shown in Fig.4.3, (a) an electron inserted in the midpoint of two protons, and (b) an electron is placed outside at a half of the distance between the protons.

In the case of (a), the distance between the electron in the midpoint and a proton is a half of the distance between the protons, and thus attractive forces on the protons caused by the electron is four times larger than the repulsion between the protons (cf. Example 1.2). In the situation of (a), the two protons approach each other, since the attractive forces due to the electron exceeds the repulsion between the protons. In the case of (b), the proton near the electron attracted outward by the electron with the same magnitude of a force of the case (a), whereas another proton in the long distance is pulled to the same direction but very weakly with a magnitude of $(1/3)^2$ times of the force acting on the proton in the short distance. Although in this case the electron attracts both of the protons to the right side, the nearer proton is attracted much more strongly to cause a relative separation of the protons. This effect in (b) accelerate the repulsion between the protons.

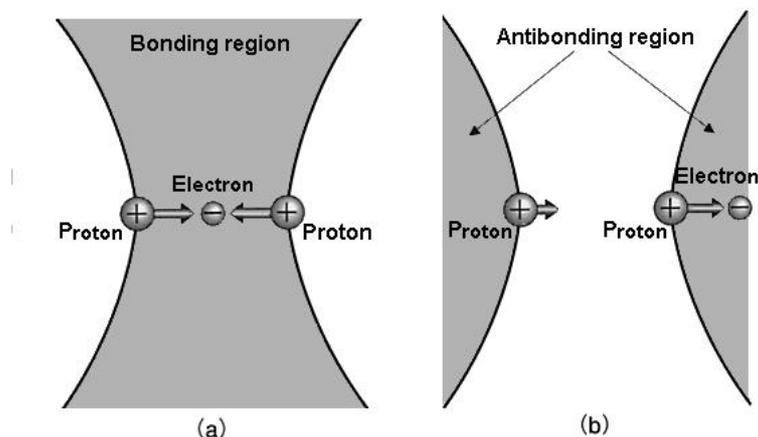


Figure 4.3: The binding region and the antibinding region

Based on the features in Fig.4.3, forces on a pair of unit positive charges by a unit negative charge can be classified into the following cases.

- (1) The force due to the unit negative charge binds two nuclei relatively.
- (2) The force due to the unit negative charge repels two nuclei relatively.

This classification divides each spatial point into either the binding region (the bonding region), the antibinding region (the antibonding region), or the boundary between the binding and antibonding regions.

When a pair of nuclei are attracted by forces due to electron densities in the binding region which cancels out the repulsion between them, the nuclei are mutually bound to make a bond. This is the mechanism of producing a chemical bond by the action of electron densities. When a chemical bond is already produced, donation-reception by oxidation-reduction, light absorption, or variation of electron distributions on the access of other atoms or molecules may cause a change of the balance between the binding force and the antibinding force. Depending on the situations, the bond may be strengthened to become short, and conversely the bond may be weakened to become lengthened or even to dissociate. In this way, depending on how electron densities distribute over the bonding and antibonding regions, chemical bonds are produced or broken.

4.2.3 The virial theorem

We have studied that binding forces originate from the action due to electron densities. The Feynman's electrostatic theorem, however, lose its significance if the electron densities are not accurately obtained. Accurate electron densities need accurate wave functions. In order to test the accuracy of wave functions, the following virial theorem is often used.

The virial theorem is expressed with using the internuclear distance R as follows.

$$2\langle K \rangle + \langle U \rangle + R \frac{du(R)}{dR} = 0 \quad (4.25)$$

$u(R)$ is the adiabatic potential in the Born-Oppenheimer approximation, and $\langle K \rangle$ and $\langle U \rangle$ are the expectation values for the kinetic energy and the potential energy, respectively. At the equilibrium internuclear distance, the last term in eq.(4.25) is vanishing, and thus the following quantity becomes equal to 2.

$$-\frac{\langle U \rangle}{\langle K \rangle} = 2 \quad (4.26)$$

A calculated value of the left side becomes different from 2, if the wave function is not accurate, and this ratio called the virial ratio in eq.(4.26) has a significance to test the quality of wave functions. The eq.(4.26) can also be applied to an atom. The relation in eq.(4.26) generally holds for a system of a potential energy with an inverse power of the distance as the Coulombic force.

4.3 The molecular orbital method

An orbital function representing the electronic motion is called an atomic orbital (AO) for an atom and a molecular orbital (MO) for a molecule. An approach using molecular orbitals for various problems in chemistry is called the molecular orbital method. A fundamental technique to obtain molecular orbitals is the SCF method based on the Hartree-Fock equation studied in Section 3.3. In this section, we will study an SCF method using linear combinations as a most powerful technique in quantum chemistry as well as its application to the molecular orbital method.

Until ca. 1980 this field has been a holy ground limited to specialists of quantum chemistry. However, recent developments of both hardwares and softwares for computers made it possible for many people even with no special trainings in chemistry to use the molecular orbital method easily. After 1990, this tendency has been accelerated. Thus we will study some basic ideas and techniques for actual calculations in quantum chemistry.

4.3.1 The SCF method using linear combinations

Although the Hartree-Fock method studied in Section 3.3 is a general method determining orbital functions based on the variation principle, its direct application is almost impossible except for atoms or simple diatomic molecules. If we use linear combinations of some known functions called basis functions or the basis set, problems to determine orbital functions reduce to feasible numerical calculations, as studied for Ritz's variation method in Section 3.2(b). It follows that we can obtain the best orbital functions that can be expressed in terms of linear combinations of the basis set.

Orbital functions $\{\phi_i\}$ to be determined are expanded in terms of linear combinations of basis functions $\chi_1, \chi_2, \dots, \chi_N$.

$$\phi_i = \sum_{p=1}^N C_{pi} \chi_p \quad (4.27)$$

C. C. Roothaan derived a set of simultaneous equations to determine the best orbital functions within the limitation of the basis set by adjusting the coefficients $\{C_{pi}\}$ in 1951. We will not describe details of the equations. The important features are as follows. For a basis set composed of N linearly independent functions, the problem reduces to solving the secular equations with the order N , as in the case of Ritz's variation method. The SCF technique is used for solving the secular equation in an iterative way until a set of SCF solutions are obtained, as in the Hartree-Fock method. Consequently, we can obtain coefficients $\{C_{pi}\}$ determining shapes of orbitals as well as their orbital energies $\{\varepsilon_i\}$. In addition, the total energy of the system, which may be called as the SCF energy, can be obtained as an approximation of the ground-state energy. For molecules, some special structures with fixed nuclear positions are assumed in the adiabatic approximation. Consecutive SCF procedures changing the molecular structures will yield approximate adiabatic potentials. The SCF method using linear combinations proposed by Roothaan crucially depends on the choice of basis functions $\{\chi_p\}$.

The following inequalities hold among the Hartree-Fock SCF energy E_{HF} , the SCF energy in the linear combination approximation E_{LC} , and the true ground-state energy E_{G} .

$$E_{\text{G}} \leq E_{\text{HF}} \leq E_{\text{LC}} \quad (4.28)$$

The equality is only possible for one electron system. For many electron systems, the equality does not hold, and the electron correlation energy, $E_{\text{HF}} - E_{\text{G}} = E_{\text{CORR}}$, is always positive. In addition, $E_{\text{LC}} - E_{\text{HF}}$ is also positive for many electron systems, which is due to the incompleteness of the basis set, since finite numbers of basis functions do not constitute a complete system.

4.3.2 The basis functions

In order to obtain molecular orbitals in the linear combination approximation, atomic orbital functions such as $1s, 2s, 2p_x, 2p_y, 2p_z$ for atoms composing a molecule are used as basis functions. This idea comes from the traditional chemical concept that a molecule is composed of atoms. From a physical point of view, molecular orbitals are considered as a superposition of electron

waves of atomic orbitals, since an electron in the proximity of a particular atom is expected to behave very similarly with the respective atomic orbitals.

Although various ways of constructing a basis set are proposed, one of the standard choice for an individual atom is to use all atomic orbitals from the inner shell to the valence electrons, which are concerned with the atomic ground-state. For example for a nitrogen atom, five types of orbitals, $1s, 2s, 2p_x, 2p_y, 2p_z$, are used for atomic orbital functions. For an alkali atom or an alkaline earth atom, np orbitals are included in addition to the ns orbitals. Such a basis set is called the minimal basis. The minimal basis is the standard basis for obtaining molecular orbitals, and we may assume this basis set if no special explanation is made.

For detailed quantum chemical calculations, we need to care for the choice of basis functions. If we use a number of basis functions to improve accuracies of calculations, the size of the computation (the computation time and the memory size) inevitably increases. In order to avoid unnecessary expansion of the computation size, carefully selected basis functions should be supplemented depending on the required accuracy of the calculations. For the better description of valence electrons, valence atomic orbital functions with different spatial expansion are used doubly or triply in addition to the standard functions. This kind of basis set is called the split valence basis. Atomic orbital functions with the higher azimuthal quantum number are often augmented for adjusting the shape of electron waves of individual atoms under the circumstance in the molecule. This type of augmented functions are called the polarization functions. For example, a basis set including only s and p type functions is augmented by d type functions as polarization functions. Furthermore, loosely bound electrons such as the additional electron in a negative ion require diffuse functions which supplement the remote area to which the additional electron may be distributed.

Atomic orbital functions for basis functions need not necessarily to be exact atomic orbital functions. In actual computations, approximate forms of atomic orbital functions have been used in general owing to the convenience dealing with various types of integrals. For such approximate functions, orbital functions proportional to $e^{-\zeta r}$, which are proposed by Slater and are called the Slater type orbitals (STO), have been used, and in recent years their analogues expanded in terms of several numbers of Gaussian functions (Gaussian) with a factor of $e^{-\alpha r^2}$, called STO- nG if the number of Gaussians is n , are widely employed. Some other basis sets composed of several Gaussians such as 4-31G and 6-31G developed by J. A. Pople and his colleagues are extensively used. The detailed descriptions of basis functions should be referred to books for the molecular orbital method and quantum chemical calculations. The SCF method with the linear combination approximation is used not only for molecular orbital calculations but also for obtaining precise atomic orbitals.

Conventions for signs and directions of atomic orbitals should be noted for practical use. In principle, any atomic orbital function can be multiplied by -1 or varied its sign, and the sign may be chosen arbitrarily for each atom within the mathematical freedom. However, in order to understand calculated results the arbitrariness of the choice of signs for employed atomic orbitals would result in confusion. For orbitals with directions such as p orbitals, coordinate axes may be chosen arbitrarily for each atom, though analyses and interpretation would become difficult. It follows that a systematic choice of signs and directions is recommended; usually, the same coordinate axes are assumed for all atoms, and signs for the same types of orbitals such as $1s, 2p$ are commonly chosen. For example, the sign for an $2p_x$ orbital is set positive at the outer region along the commonly chosen x -axis. In many programs for quantum chemical calculations, such a systematic choice has been utilized. However, usually no descriptions have been made in computation programs or their manuals, and no explanations have been included in textbooks. Thus, for students conventions for atomic orbitals are often the cause of confusion. We should also be careful about the choice of the coordinate system and signs, since a different convention may be used for a necessity such as symmetry. A different choice may be encountered when looking up some references.

Example 4.2 Write down all members of the minimal basis for a water molecule, and answer the total number of basis functions.

(Solution) Five basis functions $1s, 2s, 2p_x, 2p_y, 2p_z$ are used for an oxygen atom. There are two

hydrogen atoms, and each of them uses a 1s orbital. Thus, the total numbers of basis functions are $5 + 1 + 1 = 7$. It follows that molecular orbitals of a water molecule in the minimal basis are obtained as linear combinations of these seven basis functions.

4.3.3 The non-empirical method and the semi-empirical method

A theoretical approach with no empirical information except for the atomic numbers, geometrical coordinates of the nuclei, and numbers of electrons in the system to be studied is called the *ab initio* (from the beginning) method or the nonempirical method. In the *ab initio* method, orbital functions and their energies are determined by the SCF method in the linear combination approximation, and then the total energy of the system, the wave function, electron densities, and other properties are calculated. The nonempirical molecular orbital method in general requires calculations of a huge numbers of integrals, which amount to the fourth power of the number of basis functions. From this reason, nonempirical calculations of large molecules often encounter considerable difficulties on account of the limited system of the computation facilities.

An approach considerably reducing the computation time and the amount of the data to be disposed by estimating integral values with some equations involving empirical parameters is called the semiempirical method. Empirical parameters in the semiempirical method are adjusted so as to produce better results as far as possible. In the semiempirical molecular method, only valence electrons are treated, and the nucleus charge are often combined with the inner shell electrons to be handled as the effective core with a positive charge of (atomic number)-(the number of the inner electrons). As for planar molecules with unsaturated bonds such as benzene, electrons (π electrons) in p orbitals with a direction vertical to the molecular plane are often only dealt with, and such an approach is called the π electron approximation. In a simple molecular orbital method by E. Hückel, which will be introduced in the following Chapter, the eigen equation to obtain molecular orbitals is simplified, and only one procedure solving the secular equation gives molecular orbital functions and their orbital energies, provided that required integrals are evaluated beforehand by a given procedure.

4.3.4 Electron configuration and HOMO/LUMO

After orbital functions $\{\phi_i\}$ and orbital energies $\{\varepsilon_i\}$ are obtained by SCF methods or some other methods, we can construct determinant wave functions Φ corresponding to various electron configurations such as those shown in Fig.4.4 (cf. Ground-state and excited states of a helium atom in Section2.7).

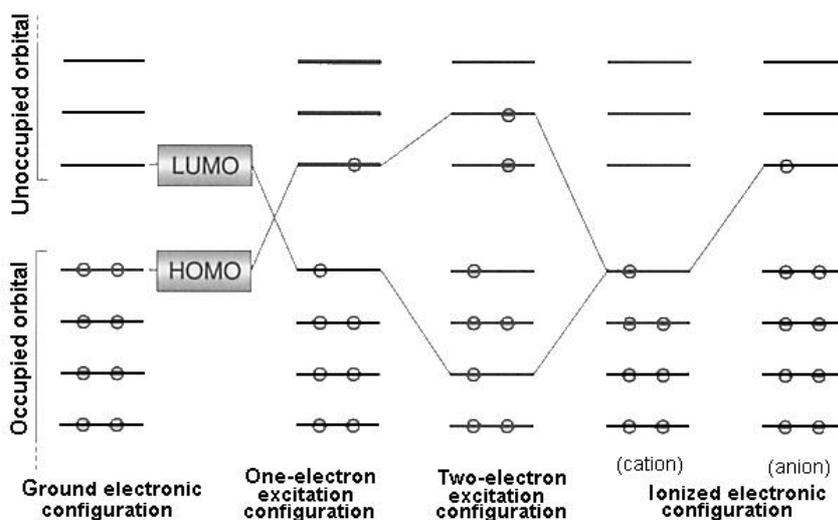


Figure 4.4: HOMO/LUMO and various electron configurations

The occupation number of electrons n_i for an orbital ϕ_i without spin is either 0, 1, or 2 owing to Pauli principle. An orbital containing one or two electrons is called an occupied orbital. An orbital of $n_i = 0$ is called a vacant orbital. An occupied orbital of $n_i = 1$ is called a singly occupied molecular orbital (SOMO) or an unpaired electron. An occupied orbital of $n_i = 2$ is called a fully occupied orbital, a pair of electrons, or an electron-pair. Among occupied orbitals, the highest occupied molecular orbital is called HOMO, and the lowest unoccupied molecular orbital is called LUMO. HOMO, LUMO, and SOMO are called the frontier orbitals, because these orbitals are especially related with the chemical reactivity as will be studied in Chapter 6.

An electron configuration with no unpaired electrons is called a closed shell, whereas an electron configuration with some unpaired electrons is called an open shell. Among all electron configurations produced with the same number of orbital functions from $\{\phi\}$, a special electron configuration with the lowest expectation value by the determinant wave function Φ is called the ground electronic configuration. The ground electronic configuration, which usually gives the minimum sum of the orbital energies, $\sum_i n_i \varepsilon_i$, may be considered to represent the ground state. In the ground electronic configuration for an even-number electron system, orbitals from the lowest to HOMO are occupied by a pair of electrons. Exceptionally, some systems with degenerate or nearly degenerate HOMO and LUMO prefer to have a configuration of two unpaired electrons with parallel spins, which can be deduced from Hund's rule. Electron configurations produced by electron excitation to unoccupied orbitals are called excited electronic configurations. Excited electronic configurations are classified into one-electron excitation configurations, two-electron excitation configurations and so forth depending on the number of excited electrons.

When addition or extraction of some electrons is made for an electrically neutral N -electron system, we can construct a configuration of an $N + z$ electron system. The system becomes a negative ion if $z > 0$, and it becomes a positive ion if $z < 0$. Electron configurations for ions are called ionic (or ionized) configurations.

4.3.5 Orbital energies and ionization energies

In connection with a mono positive ion, the difference between the energy E_i of an ionic configuration Φ_i constructed with the SCF orbitals of the neutral system and the energy E_g of the ground electronic configuration Φ_g , $E_i - E_g$, is simply equated with a -1 times value of the orbital energy ε_i for the orbital ϕ_i from which an electron is removed.

$$E_i - E_g = -\varepsilon_i \quad (4.29)$$

This equation presented in 1934 is called Koopmans' theorem. If we assume that $E_i - E_g$ equals to the ionization energy, we may suppose that -1 times of SCF occupied orbital energies correspond to ionization energies for removing an electron from the respective orbitals. Thus the following equation holds.

$$I_i = -\varepsilon_i \quad (4.30)$$

This is called Koopmans' formula. Similar treatment for a mono negative ion leads to an analogous equation including the orbital energy ε_k for the additional electron and the energy E_k for the configuration of the negative ion.

$$E_g - E_k = -\varepsilon_k \quad (4.31)$$

If we assume that the left side of this equation represents the electron affinity A_k , we obtain

$$A_k = -\varepsilon_k \quad (4.32)$$

As clearly be seen from definitions of HOMO and LUMO, the electron affinity becomes the maximum at LUMO, and the ionization energy becomes the minimum at HOMO, provided that the electronic configuration represents to the ground state.

$$A_k \leq A_{\text{LUMO}} \leq I_{\text{HOMO}} \leq I_i \quad (4.33)$$

The middle equation is limited to a special system in which an orbital is HOMO as well as LUMO.

4.3.6 Methods including the electron correlation

As mentioned in Section 3.3, the SCF method does not include the electron correlation. In order to include electron correlation effects, the configuration interaction (CI) method based on the variation approach and Møller-Plesset's (MP) method based on the perturbation approach are extensively used.

In the CI method, linear combinations of various electron configurations $\{\Phi_i\}$ as many as possible are used to solve $\hat{H}\Psi = E\Psi$.

$$\Psi = \sum_j C_j \Phi_j \quad (4.34)$$

Mathematical treatments for this problem is the same as mentioned for Ritz's variation method. Inclusion of electron configurations as many as possible for obtaining the better accuracy and reliability is incompatible with saving the computation time and the computer memory for reducing the cost of calculations. A compromise between the conflicting demands needs to be made. The CI method often requires special knowledge to choose reasonable selections of electron configurations to be included. The CI method has an advantage to obtain excited-state energies and wave functions in addition to the ground-state properties owing to the characteristics of Ritz's variation method.

In the MP method, an unperturbed Hamiltonian operator \hat{H}_0 is defined so that it may have eigen functions constructed as determinant wave functions $\{\Phi_j\}$ using the SCF orbitals. Thus the perturbation for the MP method \hat{H}' is introduced as $\hat{H}' = \hat{H} - \hat{H}_0$, which is the difference between the exact Hamiltonian \hat{H} and \hat{H}_0 . Treatments to the second order have already been mentioned in Section 3.1. Energy corrections by the MP method starts from the second order, which is denoted as MP2. In general the n -th order treatment in the MP method is denoted as MP n . Although it is possible to include the higher order terms such as MP3 or MP4, the higher terms need considerably long computation time. Since there is no difficulties except for the choice of the order n , the MP method is conveniently used for the correction of the ground-state energy.

4.4 Quantum chemical calculations

In this section quantum chemical calculations by the nonempirical molecular orbital method are compared with the experiments.

4.4.1 Molecular structures

By finding out the minimum point on the potential energy surface depending on the nuclear coordinates (geometry optimization), we can determine the molecular structure. Table 4.1 lists calculated molecular structures in comparison with the experiments. Molecular structures are determined by experimental methods, such as electron diffraction and microwave spectroscopy. Theoretically obtained molecular structures can be used to predict microwave spectra and other experiments.

4.4.2 Molecular vibrations

Vibrational frequencies ν can be calculated with the curvatures (the second derivatives) around the minimum of the potential energy surface. Table 4.2 lists calculated vibrational frequencies in the harmonic approximation in comparison with experimental harmonic frequencies deduced from the experiments assuming the Morse potential with unit of the wave number (cm^{-1}). Although we will not describe details to avoid stepping outside the range of this book, calculations of molecular vibrations are useful for prediction of infrared (IR) absorption spectra as well as Raman scattering spectra. Furthermore, knowledge of molecular vibrations can be used to obtain important thermodynamic quantities such as heat capacities and entropies.

Table 4.1: Molecular structure (Bond length $R/\text{\AA}$ and bond angle $\theta/^\circ$)

Molecule	Structure constant	SCF method	MP2 method	CI method	Experiment
H ₂	$R(\text{H} - \text{H})$	0.730	0.738	0.746	0.742
CH ₄	$R(\text{C} - \text{H})$	1.084	1.090	1.091	1.092
	$\theta(\text{HCH})$	109.47	109.47	109.47	109.47
H ₂ O	$R(\text{O} - \text{H})$	0.947	0.969	0.966	0.958
	$\theta(\text{HOH})$	105.5	104.0	104.3	104.5
HCN	$R(\text{C} - \text{N})$	1.133	1.177	1.154	1.153
	$R(\text{C} - \text{H})$	1.509	1.070	1.067	1.065
HNC	$R(\text{C} - \text{N})$	1.154	1.187	1.171	1.169
	$R(\text{N} - \text{H})$	0.985	1.002	0.997	0.994
HCHO	$R(\text{C} - \text{O})$	1.184	1.221	1.205	1.208
	$R(\text{C} - \text{H})$	1.092	1.104	1.101	1.116
	$\theta(\text{HCH})$	115.7	115.6	115.8	116.5

Table 4.2: Molecular vibration of diatomic molecules in harmonic approximation/ cm^{-1} . Experimental harmonic frequencies are obtained from observed data assuming the Morse potential.

Molecule	SCF method	MP2 method	Experiment
H ₂	4647	4528	4401
HF	4358	4038	4139
LiH	1415	1393	1406
LiF	1033	998	914
Li ₂	339	368	351
CO	2438	2113	2170
N ₂	2763	2173	2360

4.4.3 Heats of reaction

Quantum chemical calculations of reactants and products lead to the heat of reaction, which can be obtained from the energy change on the reaction. For a reaction of $\text{A} + \text{B} \rightarrow 2\text{C}$, we need to calculate the energies $E(\text{A})$, $E(\text{B})$, $E(\text{C})$ by a molecular orbital method, and the heat of reaction can be obtained as $\Delta E = 2E(\text{C}) - E(\text{A}) - E(\text{B})$. For endothermic reactions $\Delta E > 0$, and for exothermic reactions $\Delta E < 0$. Table 4.3 shows calculated results for heats of reaction in comparison with the experiments. Although experimental values of heats of reaction are conventionally shown for the standard state at a pressure of 1 atm and a temperature of 298 K, listed values in Table 4.3 are those at 0 K corrected with zero-point energies so that they may correspond to theoretically obtained values.

4.4.4 Electron distribution and the electric dipole moment

We can obtain the electron density distribution by molecular orbital calculations. Figure 4.5 demonstrates electron densities in some molecules. Contour lines in the figure are shown in a geometric series with a ratio of 2. $\text{HC}\equiv\text{CH}$, $\text{HC}\equiv\text{N}$, and $\text{N}\equiv\text{N}$ are called an isoelectronic series, since they have the same number of electrons, similar electron configurations, and similar orbital shapes. The third and the fourth orbitals from the bottom are inner shell orbitals, whose electron densities are concentrated around the nuclei with extremely narrow spacings. The bottom maps are contours of the total electron densities, and these maps represent the shapes of the molecules.

The electron distribution of a molecule is related to its electric polarization. The electric polarization of a molecule is represented by the electric dipole moment. When an electric charge Q_i is located at \mathbf{R}_i in a group of electric charges, the electric dipole moment μ of this system is given

Table 4.3: Heats of reaction including zero-point energies at 0 K (the unit is kJ mol⁻¹)

Reaction	SCF method	Experiment
Li ₂ + H ₂ → 2LiH	92	84
F ₂ + H ₂ → 2HF	-561	-556
Cl ₂ + H ₂ → 2HCl	-230	-192
O ₂ + 2H ₂ → 2H ₂ O	-439	-523
N ₂ + 3H ₂ → 2NH ₃	-138	-155
HC ≡ CH + H ₂ → CH ₂ = CH ₂	-226	-201
CH ₂ = CH ₂ + 2H ₂ → 2CH ₄	-268	-238
CO + 3H ₂ → CH ₄ + H ₂ O	-247	-264
HOOH + H ₂ → 2H ₂ O	-364	-360
HCN → HNC	52	61
CH ₃ CN → CH ₃ NC	87	87

Table 4.4: Molecular electric dipole moments (in the unit of 10⁻³⁰ Cm)

Molecule	SCF method	Experiment
H ₂	0.0	0.0
HF	6.6	6.1
HCl	5.0	3.6
LiH	19.3	19.4
LiF	20.2	21.0
LiCl	24.8	23.8
NaF	26.7	27.2
NaCl	31.3	30.0
HCN	10.8	10.0
C ₂ H ₂	0.0	0.0
NH ₃	6.5	4.9
PH ₃	2.6	1.9
H ₂ O	7.4	6.2
H ₂ S	4.6	3.2
HCHO	9.2	7.8

by the following formula.

$$\boldsymbol{\mu} = \sum_i Q_i \mathbf{R}_i \quad (4.35)$$

Within the adiabatic approximation, we may treat electrons as electron densities and nuclei resting, and it follows that the electric dipole moment based on the quantum theory is given by the following equation.

$$\boldsymbol{\mu} = - \int e\rho(\mathbf{r})\mathbf{r}d\mathbf{r} + \sum_A eZ_A \mathbf{R}_A \quad (4.36)$$

Table 4.4 lists some examples of theoretically calculated electric dipole moments in comparison with the experiments. Experimental values of molecular electric dipole moments are obtained by the following experiments.

- (1) Measurements of dielectric constants or refractive indexes for gases and solutions.
- (2) Measurements of changes of microwave spectra under the applied electric fields (the Stark effect).
- (3) Measurements of changes in directions under the action of the applied electric fields for molecular beams ejected through a nozzle into vacuum.

As unit for dipole moments, 1 D(debye) = 3.3356 × 10⁻³⁰ Cm is sometimes used.

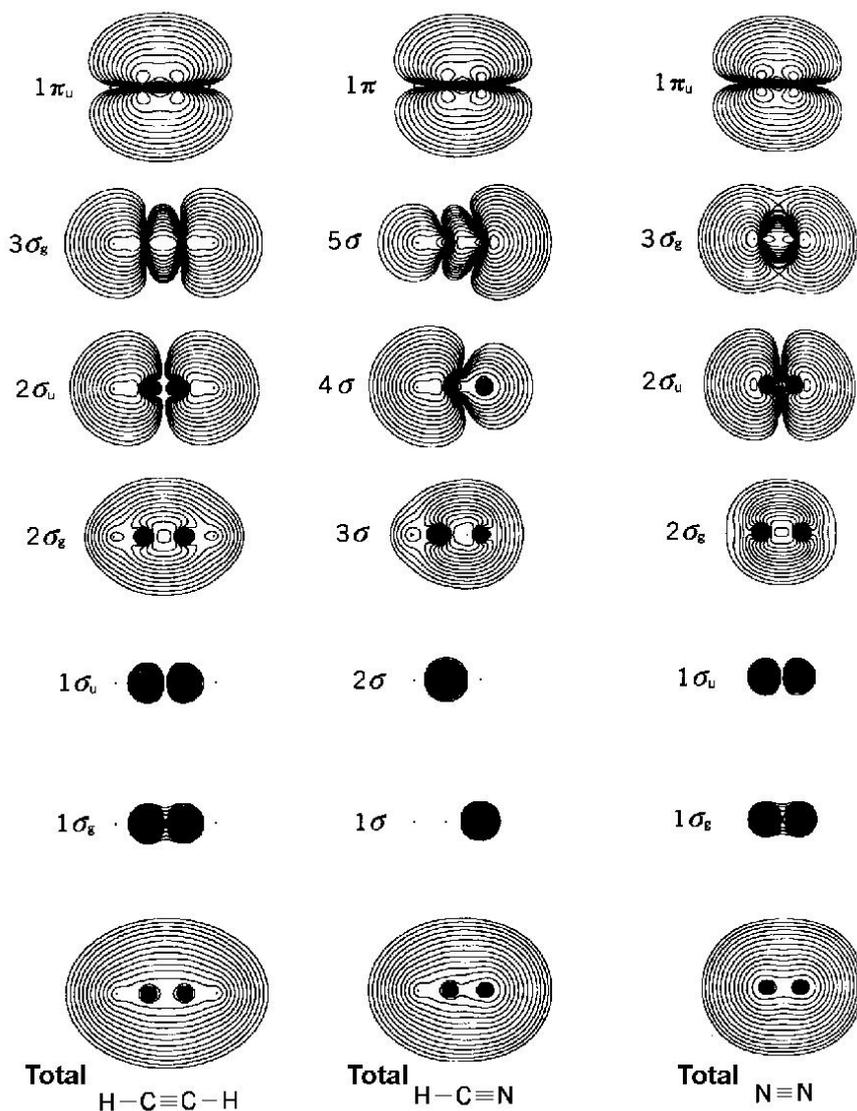


Figure 4.5: Contour maps of electron densities

4.4.5 Ionization energy

Ionization energies can easily be obtained from molecular orbital energies via Koopmans' formula (4.30). Table 4.5 lists examples of calculated ionization energies via Koopmans' formula in comparison with experimental values. This table only shows the lowest ionization energies corresponding to the energy required to remove an electron from HOMO. Improved results by the configuration interaction (CI) method are also listed for some molecules. Ionization energies can be measured by the following experiments.

- (1) Measurements of photoelectron spectra.
- (2) Measurements of the minimum energies required to ionize the sample molecule by impact of electron beams, which can be made by means of a mass spectrometer.
- (3) Observation and analysis of spectral line series called Rydberg series which is similar to spectral line series of the hydrogen atom.

Photoelectron spectroscopy gives not only the lowest ionization energy but also other ionization energies, corresponding to removal of an electron from various molecular orbitals (cf. Section 5.8).

Table 4.5: The lowest ionization energies for molecules (eV)

Molecule	SCF method	CI method	Experiment
F ₂	18.20	15.48	15.83
N ₂	17.13	16.62	15.60
H ₂ O	13.64	11.70	12.62
H ₂ S	10.43	9.61	10.48
NH ₃	11.29	9.68	10.85
HF	17.09	15.14	16.05
HCN	13.56	13.28	13.60
HCHO	11.96	10.32	10.88
CO ₂	14.63	13.01	13.78
CS ₂	9.94	9.23	10.06
CH ₂ = CH ₂	12.12	10.22	10.51
CH≡CH	11.02	10.75	11.40
CH ₃ CN	12.56	12.10	12.21
CH ₃ Cl	11.68	10.70	11.29
CH ₃ OCH ₃	11.38	9.62	10.04
CH ₃ OH	12.16	10.37	10.94
C ₂ H ₅ OH	11.89		10.64
C ₂ H ₅ SH	9.58		9.36
C ₂ H ₅ NH ₂	10.19		9.50
C ₂ H ₅ Cl	11.54		11.06
C ₆ H ₆	9.03		9.25
C ₆ H ₅ NH ₂	7.95		8.00
C ₆ H ₅ OH	8.55		8.70
B ₂ H ₆	12.75	11.86	11.89

Exercises

4.1 J. E. Lennard-Jones proposed an experimental formula representing intermolecular potential energy curves, which includes integers n and m (usually $n = 12$, $m = 6$) and constants D and σ .

$$U(R) = D \left[\frac{m}{n-m} \left(\frac{\sigma}{R} \right)^n - \frac{n}{n-m} \left(\frac{\sigma}{R} \right)^m \right]$$

Using this equation, obtain the equilibrium internuclear distance R_e and the bond energy D_e .

4.2 Calculate expectation values of the potential energy $\langle U \rangle$, the kinetic energy $\langle K \rangle$, and their ratio (the virial ratio) = $-\langle U \rangle / \langle K \rangle$ for the 1s wave function of the hydrogen atom.

4.3 List up the minimal basis set for molecular orbital calculations of a formaldehyde molecule, and answer the number of basis functions.