

Quantum Chemistry

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Chapter 5

Molecular orbital and molecular structure

Various problems in chemistry can be investigated theoretically based on the molecular orbital method. Theoretical approaches can be grouped into two types; one is the quantitative approach yielding calculated values which can be compared with experimental values, and the other is the qualitative approach giving explanation and expectation of experiments. Basic descriptions for the quantitative approach have been given in the preceding chapter. In this chapter, basic methods of qualitative treatments and applications to molecular structures and molecular electronic states will be studied. In the last section of this chapter, relationships among energy levels of molecular orbitals, ionization energies, and dissociation energies will also be studied in connection with observed photoelectron spectra.

5.1 Hydrogen molecule ion and hydrogen molecule

5.1.1 Hydrogen molecule ion

A hydrogen molecule ion is composed of two protons and an electron. In Figure 5.1 \mathbf{R}_A , \mathbf{R}_B , and \mathbf{r} denote positions of two protons A, B, and the electron, respectively. Fixing the protons at the distance R , we consider the motion of the electron using the following Hamiltonian operator \hat{H} .

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \quad (5.1)$$

r_A and r_B denote distances between the electron and the protons A and B, respectively. The wave function ψ representing the motion of the electron is a function of the position of the electron \mathbf{r} , and ψ changes together with the change of the distance R between the protons.

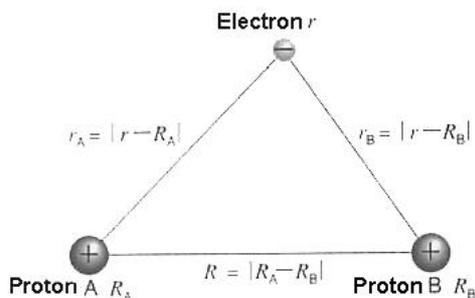


Figure 5.1: The Hydrogen molecule ion H_2^+

Since ψ represents the behavior of the electron wave of a hydrogen molecule ion, it can be expressed as a superposition of electron waves for isolated hydrogen atoms, which correspond to electron waves moving around respective protons separately. Thus, ψ of the hydrogen molecule ion can be expanded as a linear combination of atomic orbitals χ_A and χ_B for the hydrogen atoms.

$$\psi(\mathbf{r}) = C_A\chi_A(\mathbf{r}) + C_B\chi_B(\mathbf{r}) \quad (5.2)$$

C_A , C_B are coefficients representing the weights of the superposition of χ_A and χ_B . As χ_A , χ_B , the valence 1s orbital function ϕ_{1s} for the hydrogen atom is used.

$$\phi_{1s}(r) = \pi^{-1/2}a_B^{-3/2}e^{-r/a_B} \quad (5.3)$$

For χ_A and χ_B , distances r_A , r_B between the electron and the respective proton A,B should be used for the variables of ϕ_{1s} .

$$\begin{aligned} \chi_A &= \phi_{1s}(r_A) \\ \chi_B &= \phi_{1s}(r_B) \end{aligned} \quad (5.4)$$

Now, let us consider the following expectation value u of \hat{H} by ψ in eq.(5.2).

$$u = \frac{\int \psi^* \hat{H} \psi d\mathbf{r}}{\int \psi^* \psi d\mathbf{r}} \quad (5.5)$$

Conditions minimizing this u based on Ritz's variation method yield the following simultaneous equations (cf. Section 3.2).

$$\begin{aligned} (\alpha - u)C_A + (\beta - uS)C_B &= 0 \\ (\beta - uS)C_A + (\alpha - u)C_B &= 0 \end{aligned} \quad (5.6)$$

In place of the following integrals including atomic orbital functions χ_A and χ_B , symbols α , β and S are used in the above equations.

$$\int \chi_i^* \hat{H} \chi_j d\mathbf{r} = \begin{cases} \alpha & (i = j) \\ \beta & (i \neq j) \end{cases} \quad (5.7)$$

$$\int \chi_i^* \chi_j d\mathbf{r} = \begin{cases} 1 & (i = j) \\ S & (i \neq j) \end{cases} \quad (5.8)$$

In the above equations, i and j refer to protons A and B, but no specification of A and B need to be made for α , since two protons are the same particle.

Among the integrals in eqs. (5.7) and (5.8), integrated values depend on the distance R between the protons, except for the integral of the normalization condition of the 1s function. α , β and S are integrals including exponential functions, which can be calculated based on mathematical knowledge in the college level. Although the details will not be mentioned, qualitative features of these integrals are summarized as follows.

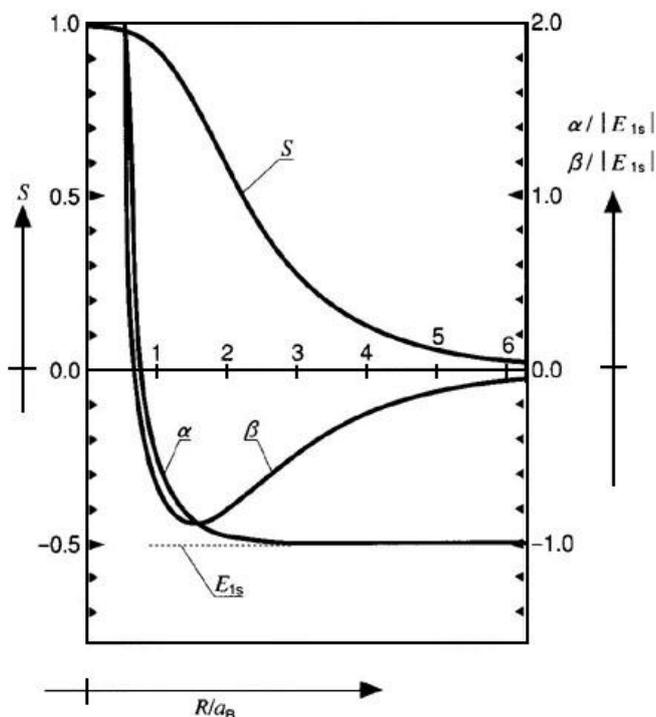
The overlap integral S satisfies the following inequalities.

$$0 < S < 1 \quad (5.9)$$

As shown in Fig.5.2, $S \rightarrow 1$ in the limit of $R \rightarrow 0$, and $S \rightarrow 0$ in the limit of $R \rightarrow \infty$. α and β approach $+\infty$ in the limit of $R \rightarrow 0$. Although the potential energy due to attractive forces between the electron and the protons becomes just twice of the case of a hydrogen atom in the limit of $R \rightarrow 0$, the potential energy for the repulsion between the protons corresponding to the last term of eq.(5.1) diverges to $+\infty$ for $R \rightarrow 0$. The value of α for $R \rightarrow \infty$ agrees with the 1s orbital energy E_{1s} of a hydrogen atom, since the interaction with the other proton may be neglected. The value of β for $R \rightarrow \infty$ results in $\beta \rightarrow 0$, because at least one of the orbital functions becomes to vanish irrespective of the location of the electron. Figure 5.2 also shows the R -dependence of u_a , u_b .

In order to obtain nontrivial solutions for the simultaneous equations (5.6) other than $C_A = C_B = 0$, the following secular equation should be satisfied.

$$\begin{vmatrix} \alpha - u & \beta - uS \\ \beta - uS & \alpha - u \end{vmatrix} = 0 \quad (5.10)$$

Figure 5.2: The R -dependence of α, β and S

We expand this equation to obtain

$$(\alpha - u)^2 - (\beta - uS)^2 = 0$$

This is a quadratic equation of u , and two solutions u_a, u_b (let $u_a > u_b$ for convenience) are given as follows.

$$\begin{aligned} u_a &= \frac{\alpha - \beta}{1 - S} \\ u_b &= \frac{\alpha + \beta}{1 + S} \end{aligned} \quad (5.11)$$

These two solutions are approximate energy levels of H_2^+ . u_a and u_b correspond to the excited state and the ground-state, respectively. Figure 5.3 shows variations of u_a, u_b as functions of the internuclear distance R .

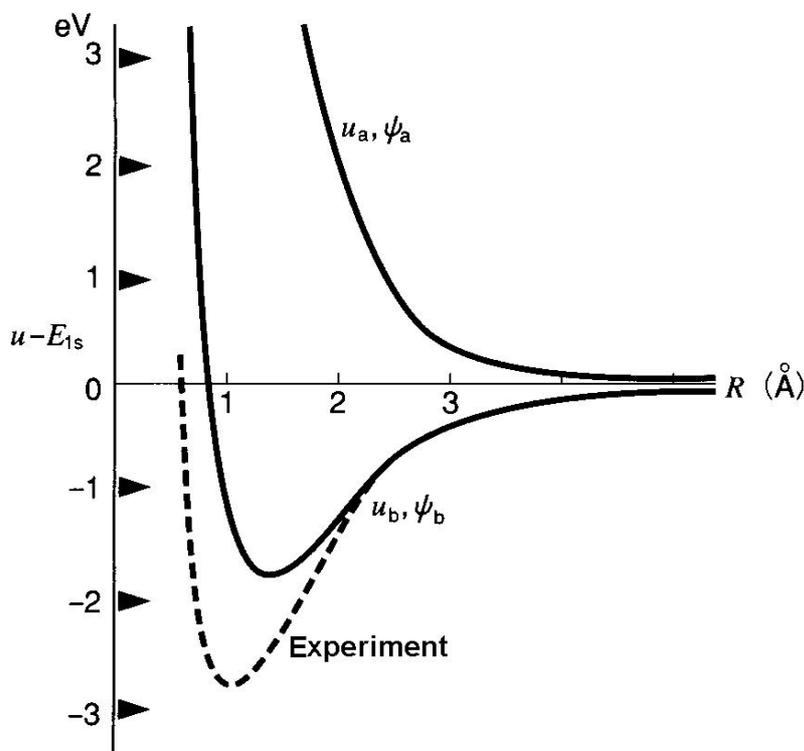
The curve for u_b has a minimum giving an internuclear distance $R_e = 1.32 \text{ \AA}$ and a binding energy $D_e = 1.77 \text{ eV}$, which means a production of a stable bond. Corresponding observed values are $R_e = 1.06 \text{ \AA}$ and $D_e = 2.78 \text{ eV}$. These results are not disappointing, since the restriction of the wave function ψ in the form of eq.(5.2) is a very crude approximation. It is significant that a brief description of the chemical bonding with R_e of 1 \AA and D_e of a few eV is given. The curve for u_a decreases with the increase of R , which gives repulsion between nuclei to lead to dissociation.

Wave functions ψ_a, ψ_b corresponding to the respective states are obtained by using relations for C_A and C_B , which are derived from insertion of u_a, u_b into eq.(5.6). The following normalization condition should also be used.

$$\int |\psi|^2 d\mathbf{r} = C_A^2 + C_B^2 + 2C_A C_B S = 1 \quad (5.12)$$

Insertion of u_a into eq.(5.6) gives

$$(C_A + C_B) \frac{\beta - \alpha S}{1 - S} = 0$$

Figure 5.3: Potential energies for H_2^+

This equation leads to $C_A = -C_B$, and by using the normalization condition we obtain for ψ_a

$$\psi_a = \frac{\chi_A - \chi_B}{\sqrt{2(1 - S)}} \quad (5.13)$$

Next, using u_b similarly we obtain

$$\psi_b = \frac{\chi_A + \chi_B}{\sqrt{2(1 + S)}} \quad (5.14)$$

Now, let us consider physical significance of these wave functions ψ_a and ψ_b . As can be seen from eq.(5.2), ψ is a new electron wave produced by interference of electron waves of atomic orbitals χ_A and χ_B with weighting factors of coefficients C_A and C_B . In ψ_a signs of two components $C_A\chi_A$ and $C_B\chi_B$ are opposite to cancel out each other (Fig.5.4). Such an orbital is called an antibonding orbital. Interference of electron waves of atomic orbitals effectively occurs at spatial regions between two nuclei where the orbitals overlap each other. For ψ_a , electron densities in the binding region decrease by interference in comparison with the case of no interference, and electron densities in the antibonding region increase to result in strong repulsion between the nuclei. On the other hand for ψ_b , two components are constructive with the same sign. Such an orbital is called a bonding orbital. In the case of ψ_b , electron densities in the binding region increase to produce binding forces between the nuclei (Fig. 5.4). The bonding in the hydrogen molecule ion is due to an electron shared in the binding region between two nuclei, and thus this kind of bond is called the one-electron bond. Although treatments here are approximate, the following two findings are important; (1) electron distribution determined by interference between electron waves lead to binding or anti binding forces, and (2) only one electron can produce a bond.

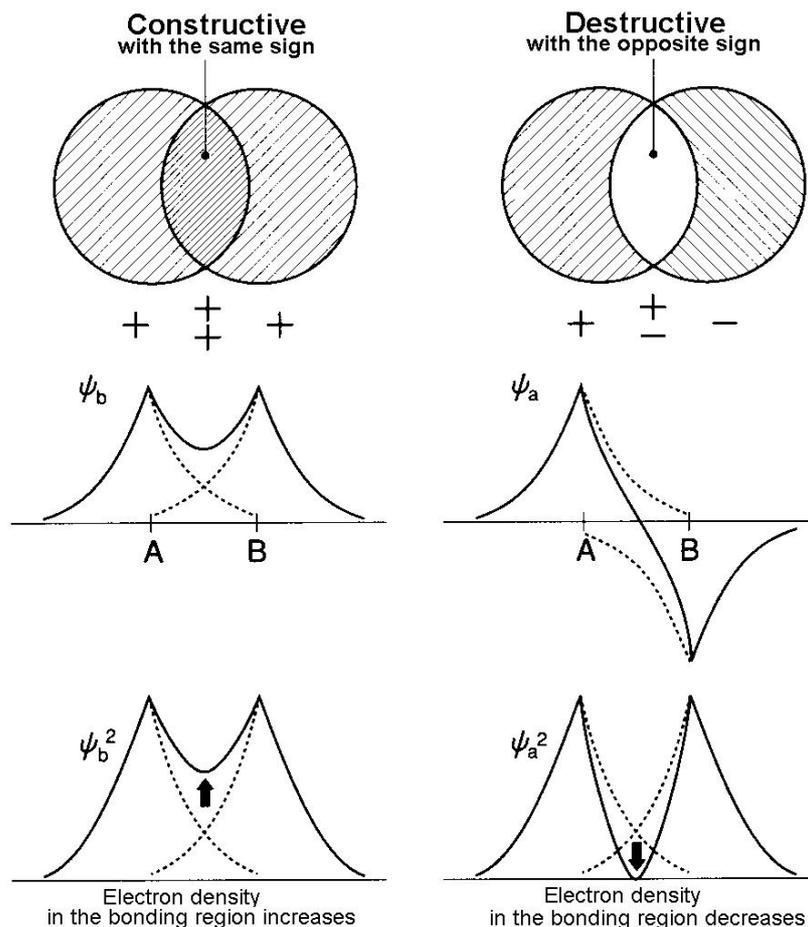


Figure 5.4: Interference of electron wave of atomic orbitals

5.1.2 The hydrogen molecule

The first explanation based on quantum mechanics was made for the mechanism of the chemical bond in a hydrogen molecule by W. Heitler and F. London in 1927. According to their valence bond method, a bond is formed by interactions between atoms approaching each other. This method is thereafter a standard version of the theory of the chemical bond in many textbooks. Long after in 1962 J. R. Reudenberg made a careful analysis of the binding energy in the valence bond method, and he disclosed that the balance of potential and kinetic energies, which is related with the virial ratio studied in Section 4.2, is incorrect in the method by Heitler and London. Recent developments of computers have considerably increased the advantage of the molecular orbital method, and thus we do not deal with the valence bond method.

The molecular orbital method mentioned in Section 4.3 gives potential energy curves for a hydrogen molecule as shown in Fig.5.5. $E(\text{H}_2)$ and $E(\text{H})$ denote energies of a hydrogen molecule and a hydrogen atom, respectively. R and a_B are the internuclear distance and the Bohr radius, and both of the ordinate and the abscissa are normalized to the atomic unit. Even in the SCF level a stable chemical bond is formed, and the configuration interaction method (CI) considering the electron correlation effects gives a much better result in comparison with the experiments. The molecular orbital method and its application to many molecules including the hydrogen molecule will be described in detail in the following Sections.

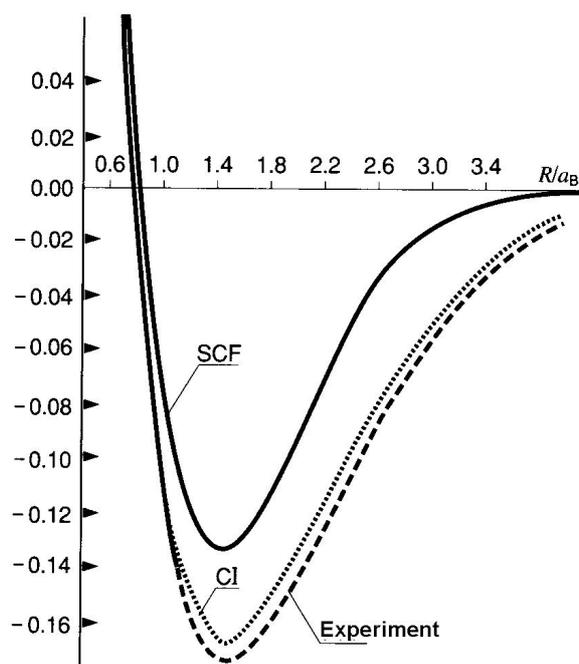


Figure 5.5: The potential energy of the hydrogen molecule H_2 . The ordinate shows $\frac{E(H_2) - 2E(H)}{2|E(H)|}$

5.2 The Hückel molecular orbital method

Precise calculations by the *ab initio* molecular orbital method produce considerable amounts of computed results due to the huge size of the calculations, which often leads to confusions in the interpretation. In general, the larger basis set in the linear combination method yields the better accuracy at the expense of the simplicity. Many basis functions inevitably make it difficult to understand obtained wave functions in terms of interference of electron waves. These difficulties in interpretation and understanding also lead to difficulties in scientific analyses and prediction without calculations.

In order to avoid such difficulties in interpretation and understanding, even specialists of molecular orbital calculations dare to perform simple calculations with the minimal basis (cf. Section 4.3) for the basis functions and carefully investigate constructions of molecular orbitals. Without numerical calculations, shape of orbitals as well as energy levels can be briefly anticipated on the basis of drastically simplified molecular orbital methods. In this section, we study the Hückel molecular orbital method, since it has been used as the most suitable method to discuss the qualitative nature of molecular orbitals.

5.2.1 Fundamental treatments in the Hückel method

In the Hückel molecular orbital method, which is sometimes called the Hückel method or the HMO method, shape and energies of orbitals are obtained without numerical integrations as far as possible. Although there are many integrals in the basic equations, various quantities included in the secular equation are replaced by parameters with characteristic values depending on the elements or bonding types.

Molecular orbitals $\{\phi_i\}$ in the Hückel method are expressed as linear combinations of atomic orbitals $\{\chi_q\}$.

$$\phi_i = \sum_q C_{qi} \chi_q \quad (5.15)$$

Here, $\{\chi_q\}$ are assumed to be normalized atomic orbital functions. Unless necessary, real functions are used for $\{\chi_q\}$, and coefficients of the linear combinations are also treated as real numbers. In

some special cases such as ring molecules with periodicity, complex numbers should be used for $\{C_{qi}\}$ exceptionally. Molecular orbitals $\{\phi_i\}$ should be normalized by the following condition.

$$\int \phi_i^2 d\mathbf{r} = \sum_p \sum_q C_{pi} C_{qi} S_{pq} = 1 \quad (5.16)$$

S_{pq} is the overlap integral between χ_p and χ_q given by the following equation.

$$S_{pq} = \int \chi_p \chi_q d\mathbf{r} \quad (5.17)$$

Since $\{\chi_q\}$ are assumed to be normalized, $\{S_{pp}\}$ are all equal to the unity. The absolute value of $\{S_{pq}\}$ for $p \neq q$, which is in general smaller than 1, becomes very small to be neglected, if the distance between p and q is very large. $\{S_{pq}\}$ represent how much extent electron waves of the atomic orbitals are overlapping, and thus they are called overlap integrals.

Molecular orbitals $\{\phi_i\}$ are determined from the following one electron eigen equation.

$$\hat{h}\phi_i = \varepsilon_i \phi_i \quad (5.18)$$

Here, \hat{h} is the one-electron Hamiltonian operator determining the electron motion. This \hat{h} includes an operator corresponding to the kinetic energy of an electron and average potentials of interactions between electrons as well as attractive potentials from nuclei. The problem to obtain $\{\phi_i\}$ and $\{\varepsilon_i\}$ begins with the condition minimizing the expectation value ε_i of \hat{h} with $\{\phi_i\}$ by changing $\{C_{qi}\}$. This is a variational problem in terms of linear combinations, which leads to the following simultaneous equations.

$$\sum_q (H_{pq} - \varepsilon_i S_{pq}) C_{qi} = 0 \quad (5.19)$$

Here, H_{pq} is given by the following equation.

$$H_{pq} = \int \chi_p \hat{h} \chi_q d\mathbf{r} \quad (5.20)$$

H_{pq} is called the Coulomb integral for $p = q$ with writing $H_{pp} = \alpha_p$ and called the resonance integral for $p \neq q$ with writing $H_{pq} = \beta_{pq}$. Resonance integrals as well as overlap integrals can be neglected, since they become very small when p and q are in a long distance.

Orbital energies ε_i are obtained from the following secular equations (cf. Section 3.2).

$$|H_{pq} - \varepsilon_i S_{pq}| = 0 \quad (5.21)$$

Inserting orbital energies ε_i from the solutions of eq.(5.21) into eq.(5.19) and using normalization conditions of eq.(5.16), $\{C_{qi}\}$ are obtained.

5.2.2 The simple Hückel method

According to the policy of the Hückel method that numerical calculations of integrals should be avoided as long as possible, the simple Hückel method adopts further simplifications with the following approximations. The traditional Hückel method is this method, which can be compared with the extended Hückel method mentioned in the next subsection and is called as the simple Hückel method. In the conventional Hückel method, the π electron approximation is usually adopted. If α and β are carefully estimated, the Hückel method can be applied to the more general cases.

(1) Neglect of overlap integrals S_{pq} ($p \neq q$)

Overlap integrals S_{pq} for $p \neq q$ are much smaller than the case of $S_{pp} = 1$, and thus they can be neglected.

$$S_{pq} = \delta_{pq} = \begin{cases} 1 & \text{for } p = q \\ 0 & \text{for } p \neq q \end{cases} \quad (5.22)$$

This approximation leads to the following equations much more simplified than eqs. (5.19) and (5.21).

$$\sum_q (H_{pq} - \varepsilon_i \delta_{pq}) C_{qi} = 0 \quad (5.23)$$

$$|H_{pq} - \varepsilon_i \delta_{pq}| = 0 \quad (5.24)$$

In addition, the normalization condition for molecular orbitals is also simplified as follows.

$$\sum_q C_{qi}^2 = 1 \quad (\text{the summation should be taken for all atomic orbitals } \chi_q) \quad (5.25)$$

Since the assumption of eq.(5.22) corresponds to the expansion in terms of the orthonormal set $\{\chi_q\}$ by eq.(5.15), the summation of coefficients of all molecular orbitals $\{\phi_i\}$ satisfies the following formula.

$$\sum_i C_{qi}^2 = 1 \quad (\text{the summation should be taken for all molecular orbitals } \phi_i) \quad (5.26)$$

(2) Neglect of resonance integrals β for non-bonded atomic pairs

β_{pq} as well as S_{pq} become very small when χ_p and χ_q become spatially far apart. However, for bonded atomic pairs β_{pq} are considered, since they are very important. β_{pq} for non-bonded atomic pairs are disregarded.

(3) Parameterization of resonance integrals β for bonded atomic pairs

Depending on combinations of atomic orbitals, β_{pq} is treated as a parameter. In many cases, numerical values for β are not necessarily given. Sometimes β is determined by experiments. Although the sign of β is important, it depends on the type of bonds (cf. Section 5.3).

(4) Parameterization of Coulomb integrals α

Depending on the type of atomic orbitals, Coulomb integrals are treated as parameters. α equals approximately to the atomic orbital energy, and its sign is always negative. $|\alpha|$ is equal to the energy required to remove an electron from the atomic orbital, which is approximately the ionization energy. Although α can often be used with no value, the relative magnitude as well as its sign are very important.

5.2.3 The Extended Hückel method

Although the simple Hückel method is a convenient method, it cannot be applied to a system in which positions of chemical bonds are not clear. For example, metal complexes as well as organic compounds having complex structures are not suitable for the simple Hückel method. Thus, the extended Hückel method exceptionally evaluating overlap integrals was proposed, and it has been extensively used as an improved approach, though such a treatment is clearly against the policy avoiding numerical integrations as far as possible. The extended Hückel method is based on the fundamental formula of eqs. (5.15)~(5.21) as well, and some further approximations used are summarized as follows.

(1) Overlap integrals S_{pq} are evaluated by direct integration using atomic orbitals functions $\{\chi_q\}$. In many cases, STOs mentioned in Section 4.3 are used.

(2) Resonance integrals $H_{pq} = \beta_{pq}$ ($p \neq q$) are estimated by the following approximate formula.

$$\beta_{pq} = K S_{pq} \frac{\alpha_p + \alpha_q}{2} \quad (5.27)$$

Here, α_q is a Coulomb integral involving an atomic orbital χ_q , and the constant K is set as $K = 1.75$. This formula can be deduced as follows. In the eq.(5.20) defining the resonance integral, replacement of the operator \hat{h} by an assumed constant value of a leads to $\beta_{pq} = a S_{pq}$, and also in eq.(5.20) assumption of a simple average of the integrals for $p = q$ in place of the integral for $p \neq q$ yields $\beta_{pq} = (\alpha_p + \alpha_q)/2$. These characteristics are combined into the formula (5.27). This formula (5.27) leads to an important relationship that the resonance integral β_{pq} and the overlap integral S_{pq} have opposite signs, because $K > 0$ and $\alpha_p < 0$, $\alpha_q < 0$ based on the reasons given below. Also in the simple Hückel method, the resonance integral β_{pq} and the

overlap integral S_{pq} have opposite signs.

(3) Coulomb integral $H_{qq} = \alpha_q$ is nearly equal to the energy of the atomic orbital χ_q , and thus α_q is estimated by the following formula using the ionization energy I_q of the electron in χ_q .

$$\alpha_q = -I_q \quad (5.28)$$

Here, I_q is positive, and α_q is negative. An atom with strong negativity has a large ionization energy I_q , which leads to a large value of $|\alpha_q|$. Oppositely, $|\alpha_q|$ for an atom with weak negativity becomes small. Magnitudes of $|\alpha_q|$ for orbitals of valence electrons are usually in the range of 5 eV - 30 eV. On the other hand, magnitudes of $|\alpha_q|$ for atomic orbitals of inner shell electrons have much larger values in the range of several hundreds or thousands eV.

5.3 Overlap between orbitals and orbital interactions

Molecular orbitals (MO) are composed of atomic orbitals (AO), (1) mathematically linear combinations of functions, and (2) physically superposition of electron waves, and (3) chemically mixture of ingredients. Composition of molecular orbitals made of some atomic orbitals is in general governed by interactions between orbitals. Overlap of orbitals leads to interactions and mixing of orbitals, which results in formation of new orbitals. In this section, the mechanisms involved in the formation of new orbitals associated with overlap between orbitals are studied on the basis of Hückel molecular orbital method.

5.3.1 Overlap between orbitals

In the Hückel method, the magnitude of the resonance integral $|\beta|$ is most important for the formation mechanisms of molecular orbitals from atomic orbitals via interference of electron waves. The detail of the reason will be discussed below. Here, we will study characteristics of overlap integrals, since there is a relationship of eq.(5.27) that β is proportional to the overlap integral S .

Overlap integrals depend on types and combinations of atomic orbitals as well as on the distance between the nuclei at which the atomic orbitals are placed. Typical cases are illustrated in Fig.5.6.

In this figure, as an s orbital and a p orbital, 1s and 2p orbital functions are used, respectively. In order to represent the spatial distribution of each orbital, a circle is used for an s orbital, and a pair of ellipses are used for a p orbital. Signs of the functions are specified by + and - in the figures. Absolute values of atomic orbital functions are generally decreasing to vanish with the distance becoming very large. It should be noted that the same sign of electron distributions extending outside of the circles and the ellipses.

Fig.5.6(a) shows the R dependence of an overlap integral between two p orbitals having parallel directions, which decreases monotonically. Such an overlap between parallel p orbitals is called the π type orbital, and chemical bonds originating from this type of overlaps are called the π bonds. In π type overlaps, the axis connecting the atoms is included in a common nodal plane of the atomic orbitals. In a π orbital produced by the π type overlap, probabilities of finding an electron on the nodal plane containing the bond axis are vanishing. Fig.5.6(b),(c),(d) show the R dependence of overlap integrals between orbitals with no common nodal plane including the bond axis. These types of overlaps are called the σ type overlap, and chemical bonds originating from this type of overlaps are called the σ bonds. Although the overlap integral is not necessarily monotonous in the σ type, the overlaps become decreasing until vanishing on going to a large distance in R as in the case of the π type overlap. This is related to the general tendency that, associated with the increase of the overlap between orbitals approaching each other, the interference between electron waves becomes to be more significant.

In Fig.5.6(e)(f), overlap integrals are shown for combination of orbitals with and without a nodal plane including the bond axis, contrary to other cases. Although the absolute values of the orbital functions are the same at a pair of symmetrical points with respect to the plane including the bond axis, their signs are opposite for one orbital and the same for the other orbital. It follows that overlap integrals of these orbital functions are always vanishing irrespective of the distance R , because the lower and the upper contributions cancel out mutually. This type of overlaps is called the overlap without symmetry matching. When overlaps are vanishing, necessarily no interference occurs, and hence no bonds are formed.

As will be studied in detail below, the formation of a chemical bond is governed by the overlap between orbitals. This is called the principle of overlap, and interactions between orbitals are called orbital interactions. The magnitude of interorbital interactions depend on the magnitude of $|\beta|$ or $|S|$. According to the principle of overlap, the orbital interaction is forbidden for $\beta = 0 (S = 0)$ and allowed for $\beta \neq 0 (S \neq 0)$. The relationship of orbital interactions with overlaps between orbitals can be summarized as follows. **[Orbital interactions and overlap between orbitals]**

- (1) Orbitals without symmetry matching ($S = 0$) do not interact with each other.
- (2) Orbitals with overlaps ($S \neq 0$) interact with each other.
- (3) The magnitude of an orbital interaction increases with the increase of the overlap ($|S|$).
- (4) Orbital interactions become negligibly small for long distances (large R) and become large when the overlap increases for short distances.

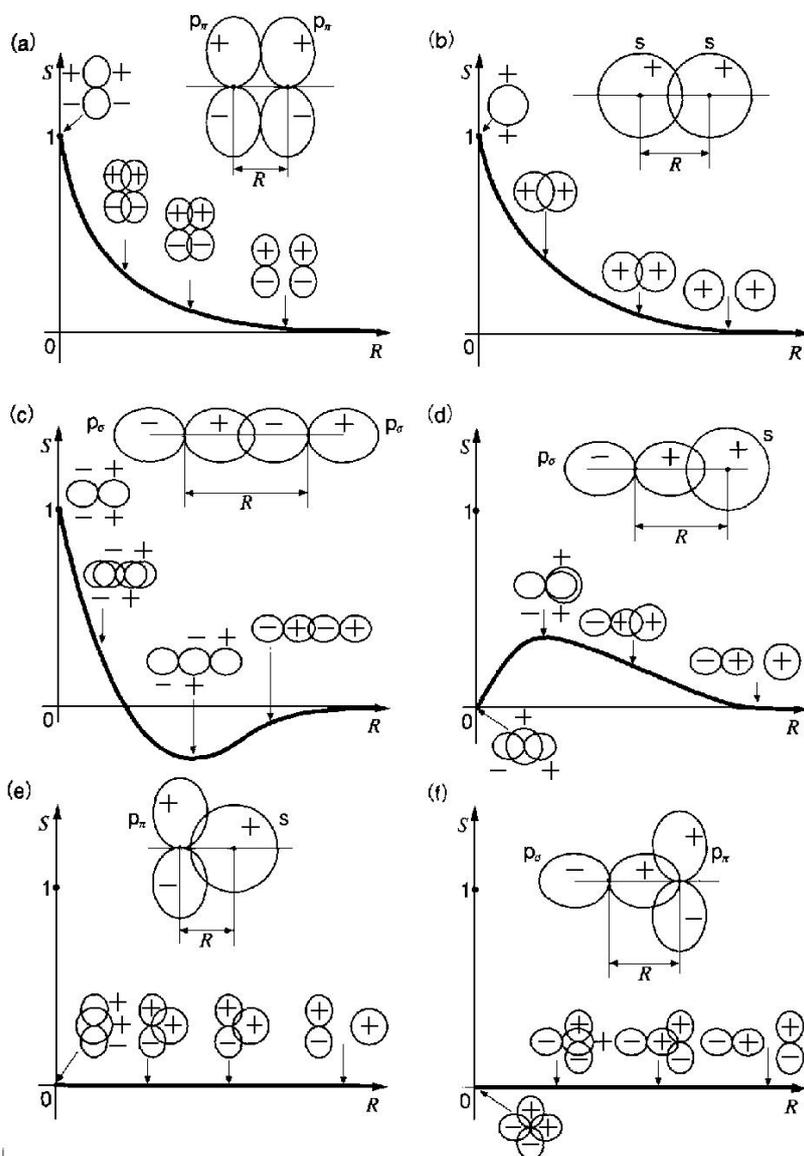


Figure 5.6: Overlap (overlap integrals S) between various atomic orbitals

5.3.2 The principles of orbital interactions

Let us study by the simple Hückel method the mechanism of orbital interactions between a pair of atomic orbitals χ_A and χ_B with orbital energies of α_A and α_B and their mutual resonance integral of β , yielding a molecular orbital of $\phi = C_A\chi_A + C_B\chi_B$ with an orbital energy of ε . First, we obtain ε by solving the secular equation (5.24). In this case, $H_{AA} = \alpha_A$, $H_{BB} = \alpha_B$, $H_{AB} = H_{BA} = \beta$, and thus the secular equation becomes

$$\begin{vmatrix} \alpha_A - \varepsilon & \beta \\ \beta & \alpha_B - \varepsilon \end{vmatrix} = 0 \quad (5.29)$$

Denoting the left-hand side as $f(\varepsilon)$ and expanding the determinant, we obtain a quadratic equation of ε .

$$f(\varepsilon) = \varepsilon^2 - (\alpha_A + \alpha_B)\varepsilon + \alpha_A\alpha_B - \beta^2 = 0 \quad (5.30)$$

Let us consider the following two cases depending on whether β is equal to zero or not.

For $\beta = 0$, factorization can easily be made to give $f(\varepsilon) = (\varepsilon - \alpha_A)(\varepsilon - \alpha_B) = 0$, and two solutions become α_A and α_B , which results in no changes from the original orbital energies and orbital functions. Such simple solutions of $(\varepsilon_A = \alpha_A, \phi_A = \chi_A)$ and $(\varepsilon_B = \alpha_B, \phi_B = \chi_B)$ satisfy the eq.(5.18), $\hat{h}\phi_A = \varepsilon_A\phi_A$ and $\hat{h}\phi_B = \varepsilon_B\phi_B$, to give no orbital mixing. It follows that for $\beta = 0$ there are no interactions between the orbitals to keep the orbital functions unchanged in their original forms.

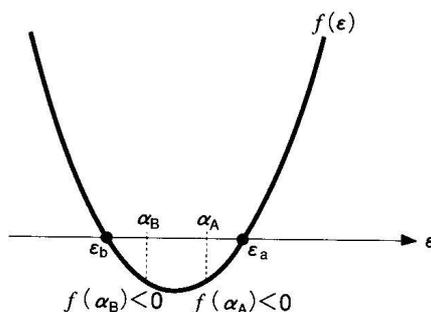
Next, let us consider variations of orbital energies for $\beta \neq 0$. We may use a convenience to set $\alpha_A \geq \alpha_B$ without losing the generality. Calculations of $f(\alpha_A)$ and $f(\alpha_B)$ lead to the following equation.

$$f(\alpha_A) = f(\alpha_B) = -\beta^2 < 0 \quad (5.31)$$

Since $f(\varepsilon)$ is a quadratic function with a concave in a parabolic form, there exist two solutions of $\varepsilon_a, \varepsilon_b$ ($\varepsilon_a \geq \varepsilon_b$), and we obtain the following inequality.

$$\varepsilon_a > \alpha_A \geq \alpha_B > \varepsilon_b \quad (5.32)$$

As verified later, the higher orbital energy ε_a corresponds to the energy level of the antibonding orbital, and the lower one ε_b corresponds to that of the bonding orbital.



These results can be summarized as the rules for orbital-energy changes.

Rules for orbital-energy changes

For a non-vanishing resonance integral ($\beta \neq 0$) orbital interactions give new orbital energies ($\varepsilon_a > \varepsilon_b$) which are different from the initial energies; the higher one (ε_a) is higher than the higher initial orbital energy of α_A , and the lower one (ε_b) is lower than the lower initial orbital energy of α_B .

Such changes of orbital energies are illustrated in Fig.5.7 for easy understanding; A and B at a long distance in the initial state are placed on both ends, while the new state for A and B in a short distance is shown in the middle of the figure.

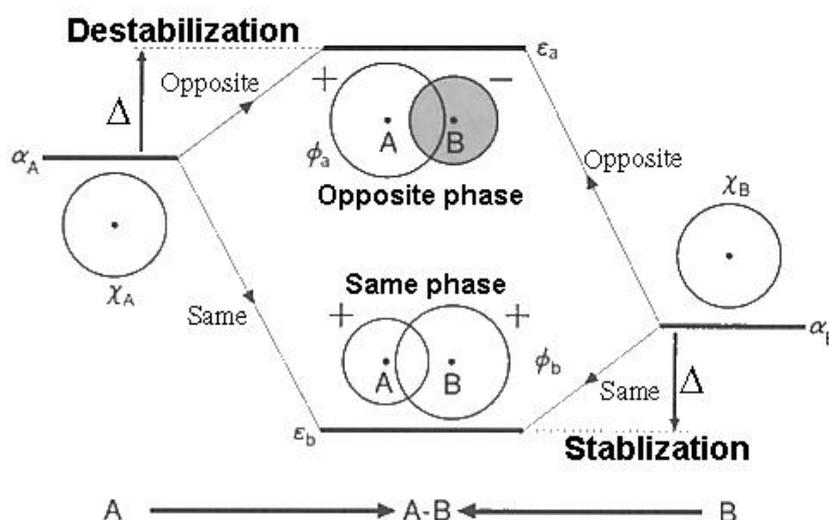


Figure 5.7: Orbital interactions

Amounts of the stabilization energy of $(\alpha_B - \varepsilon_b)$ and the destabilization energy of $(\varepsilon_a - \alpha_A)$ are found to be the same and are denoted as Δ .

$$\alpha_B - \varepsilon_b = \varepsilon_a - \alpha_A = \Delta = \frac{\sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2} - (\alpha_A - \alpha_B)}{2} \quad (5.33)$$

This quantity Δ is an index indicating how much extent the stabilization and the destabilization occur by interactions between orbitals.

In order to see what governs the extent of stabilization and destabilization Δ , let us study the possible range of Δ . Noting the convention of $\alpha_A \geq \alpha_B$, introducing a quantity t ($t \geq 0$) defined as $t = (\alpha_A - \alpha_B)/2|\beta|$, and further defining a function $F(t) = \sqrt{t^2 + 1} - t$, we obtain

$$\Delta = F(t)|\beta| \quad (5.34)$$

The function $F(t)$ decreases from $F(0) = 1$ monotonously with the increase of t for $t \geq 0$ and approaches 0 in the limit of $t \rightarrow \infty$, which results in $1 \geq F(t) > 0$. Thus we obtain the following inequalities.

$$|\beta| \geq \Delta > 0 \quad (5.35)$$

The equality in the left holds for $t = 0$, that is $\alpha_A = \alpha_B$, which gives the maximum of Δ . The magnitude of Δ is governed by the following two factors.

(1) **The principle of the energy difference**

One of the factors is the energy difference between α_A and α_B . The smaller it becomes, the smaller t becomes to yield the larger $F(t)$ resulting in the larger Δ . This indicates that the smaller energy difference between orbitals leads to the larger interactions between these orbitals. Conversely, a very large energy difference between orbitals such as one of valence orbitals and one of the inner shell orbitals leads to negligibly small interactions. Such an effect by the energy difference of $|\alpha_A - \alpha_B|$ on orbital interactions is called the principle of the energy difference.

(2) **The principle of the overlap**

Another factor is $|\beta|$. When it becomes large, t becomes small to lead to a large $F(t)$. In eq.(5.34), Δ is expressed as a product of $F(t)$ and $|\beta|$. Thus, the larger $|\beta|$, the larger Δ . Since $|\beta|$ can be considered to be proportional to $|S|$, the larger the overlap between orbitals becomes, the larger interactions between orbitals become. Conversely, the smaller the overlap as well as $|\beta|$, the smaller the orbital interactions. Such an effect of $|\beta|$ or $|S|$ on the extent of orbital interactions is called the principle of the overlap.

Next, let us consider forms of new orbitals produced by orbital interactions. From simultaneous equations of eq.(5.23), the following equation is obtained for C_A and C_B .

$$\frac{C_B}{C_A} = \frac{\varepsilon - \alpha_A}{\beta} \quad (5.36)$$

Substituting ε_a or ε_b into this equation and using $t = (\alpha_A - \alpha_B)/2|\beta|$ ($t \geq 0$) again, we obtain the following equation.

$$\frac{C_B}{C_A} = -\frac{|\beta|}{\beta}(t \pm \sqrt{t^2 + 1}) \quad (5.37)$$

The plus symbol of \pm in this formula gives (C_B^b/C_A^b) for the bonding orbital (ϕ_b, ε_b) , and the minus one gives (C_B^a/C_A^a) for the antibonding orbital (ϕ_a, ε_a) .

Since for the bonding orbital $t + \sqrt{t^2 + 1} \geq 1$ at any value of $t \geq 0$, we obtain the following inequalities.

$$|C_B^b| \geq |C_A^b| \quad (5.38)$$

$$C_A^b C_B^b \beta < 0 \quad (5.39)$$

Equation (5.38) shows that in the bonding orbital $\phi_b = C_A^b \chi_A + C_B^b \chi_B$, a contribution of $C_B^b \chi_B$ from the lower atomic orbital χ_B is dominant. Since the lower orbital is the more electronegative, electrons in the bonding orbital are displaced on the more electronegative atom. This explains the electric polarization associated with the formation of a chemical bond.

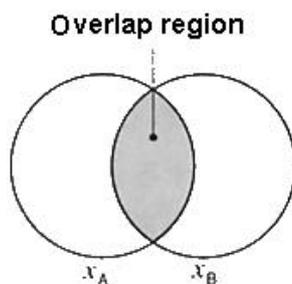
The equation (5.39) shows the constraint of the relative phases (signs) between the two orbital components. Using the relation of the opposite signs between the overlap integral S and the resonance integral β , we obtain

$$C_A^b C_B^b S_{AB} \iff -C_A^b C_B^b \beta > 0 \quad (\iff \text{indicates the opposite signs to each other})$$

Here, we should note that the sign of the overlap integral $S_{AB} = \int \chi_A \chi_B d\mathbf{r}$ is equal to the sign of $\chi_A \chi_B$ in the geometrical regions (the overlap regions) where absolute values for $\chi_A \chi_B$ become large. Thus, we obtain the following inequality.

$$(C_A^b \chi_A)(C_B^b \chi_B) = C_A^b C_B^b \chi_A \chi_B \iff C_A^b C_B^b S_{AB} > 0 \quad (5.40)$$

This result shows that in the bonding orbital $\phi_b = C_A^b \chi_A + C_B^b \chi_B$ the first component $C_A^b \chi_A$ and the second component $C_B^b \chi_B$ have the same sign (phase) in the overlap regions of χ_A and χ_B . Thus, electrons in the bonding orbital brings the positive interference strengthening the electron waves with the same sign, and hence electron densities in the overlap regions are increased. It follows that augmented electron densities between the nuclei result in binding forces acting on the two nuclei.



In the case of the antibonding orbital, always $1 \geq \sqrt{t^2 + 1} - t > 0$ for $t \geq 0$. Thus, we obtain.

$$|C_A^a| \geq |C_B^a| \quad (5.41)$$

$$C_A^a C_B^a \beta > 0 \quad (5.42)$$

Equation (5.41) shows that in the antibonding orbital $\phi_a = C_A^a \chi_A + C_B^a \chi_B$, the contribution from the higher atomic orbital χ_A is dominant. Using eq.(5.42), an analogous discussion with the case of the bonding orbital leads to the following inequality.

$$(C_A^a \chi_A)(C_B^a \chi_B) \iff C_A^a C_B^a S_{AB} \iff -C_A^a C_B^a \beta < 0 \quad (5.43)$$

This indicates that in the antibonding orbital $\phi_a = C_A^a \chi_A + C_B^a \chi_B$ the first component $C_A^a \chi_A$ and the second component $C_B^a \chi_B$ have the opposite signs (phases) in the overlap regions of χ_A and χ_B . Thus, electrons in the antibonding orbital brings the negative interference canceling out the electron waves with the opposite signs, and hence electron densities in the overlap regions are decreased. It follows that the decreased electron densities between the nuclei result in antibonding forces repelling two nuclei each other.

Next, let us consider the extent of orbital mixing. When one of the coefficients is zero, the extent of mixing is minimum. Thus, we introduce the following quantity μ representing the extent of mixing.

$$\mu = \left| \frac{C_A^b}{C_B^b} \right| = \left| \frac{C_B^a}{C_A^a} \right| = \sqrt{t^2 + 1} - t \quad (5.44)$$

The right side equals to $F(t)$ introduced before, which satisfies $1 \geq F(t) > 0$ for $t = (\alpha_A - \alpha_B)/2|\beta| \geq 0$. Thus, μ increases with the decrease of t . It follows that the extent of orbital mixing is governed by the principle of the energy difference and the principle of the overlap, as in the case of the extent of orbital energy changes.

The mechanisms producing new orbitals from mixing of two orbitals due to orbital interactions are summarized as rules of orbital mixing as follows.

Rules for orbital mixing When a pair of orbitals χ_A and χ_B ($\alpha_A \geq \alpha_B$) having mutual overlap (the resonance integral is not vanishing) interact with each other, a pair of new orbitals ϕ_a and ϕ_b ($\varepsilon_a > \alpha_A \geq \alpha_B > \varepsilon_b$) are produced (cf. Fig.5.7). Among them, the bonding orbital ϕ_b is made mainly of the lower orbital χ_B together with a small contribution of the higher orbital χ_A in the same phase. On the other hand, the antibonding orbital ϕ_a is made mainly of the higher orbital χ_A together with a small contribution of the lower orbital χ_B in the opposite phase. The extent of variation from the form of the main component, namely the extent of mixing, is governed by the principle of the energy difference and the principle of the overlap. Especially for $\alpha_A = \alpha_B$ (a case with no energy difference), mixing of the two components are equally weighted.

Summarizing the above mentioned rules for orbital-energy changes, rules for orbital mixing, the principle of the energy difference, and the principle of the overlap, we denote these rules and principles as the principles of orbital interactions.

[The principles of orbital interactions]

- (1) Without orbital interactions ($\beta = 0$), the orbital energy and form remain unchanged.
- (2) With nonvanishing orbital interactions ($\beta \neq 0$) (cf. Fig.5.7), both the orbital energy and the form are changed. A bonding orbital is formed, which is stabilized than the lower (relatively the more negative) initial orbital χ_B among a pair of orbitals χ_A and χ_B ($\alpha_A \geq \alpha_B$). On the other hand, an antibonding orbital is formed, which is destabilized than the higher (relatively the more positive) initial orbital. The extent of mixing is such that the lower orbital is the main component for the bonding orbital, whereas for the antibonding orbital the main component is the higher one. If the energy difference between orbitals is vanishing ($\alpha_A = \alpha_B$), two components are equally weighted.
- (3) The extent of orbital-energy changes and orbital mixing is governed by the energy difference and the overlap; they become larger for the smaller energy difference and the large overlap, and conversely they become smaller for the larger energy difference and the smaller overlap.

Example 5.1 (The two to one orbital interactions)

Two orbitals of χ_A and χ_B of one species having orbital energies of α_A and α_B ($\alpha_A > \alpha_B$) are mutually orthogonal and interact with another orbital χ_C of the other species (denoted as the partner) having an orbital energy of α_C . Respective resonance energies are β_{AC} and β_{BC} ($\beta_{AC} \neq 0, \beta_{BC} \neq 0$). Answer the following questions.

(1) Derive the following inequalities for three orbitals produced by interactions, which are denoted as $\varepsilon_a, \varepsilon_m, \varepsilon_b$ in the order of the higher energies.

$$\varepsilon_a > \alpha_A > \varepsilon_m > \alpha_B > \varepsilon_b$$

(2) Orbitals corresponding to the orbital energies of $\varepsilon_a, \varepsilon_m, \varepsilon_b$ are denoted as ϕ_a, ϕ_m, ϕ_b . Explain relative phases of the atomic orbital components χ_A, χ_B, χ_C in the new orbitals qualitatively, based on the principles of orbital interactions.

(Solution)

(1) Because of the mutual orthogonality between χ_A and χ_B , $S_{AB} = 0$ and thus the resonance integral is vanishing ($\beta_{AB} = 0$). Considering the given condition, we obtain the secular equation for the simple Hückel method.

$$\begin{vmatrix} \alpha_A - \varepsilon & 0 & \beta_{AC} \\ 0 & \alpha_B - \varepsilon & \beta_{BC} \\ \beta_{AC} & \beta_{BC} & \alpha_C - \varepsilon \end{vmatrix} = 0$$

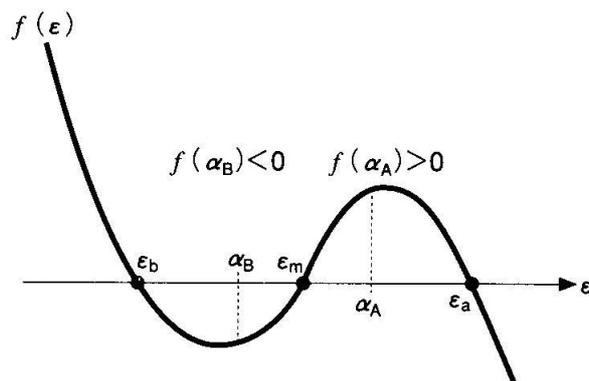
Expanding this equation and denoting it as $f(\varepsilon)$,

$$f(\varepsilon) = (\alpha_A - \varepsilon)(\alpha_B - \varepsilon)(\alpha_C - \varepsilon) - \beta_{AC}^2(\alpha_B - \varepsilon) - \beta_{BC}^2(\alpha_A - \varepsilon)$$

This is a cubic function of ε including $-\varepsilon^3$. In order to know the regions giving solutions, we look up signs of $f(\alpha_A)$ and $f(\alpha_B)$.

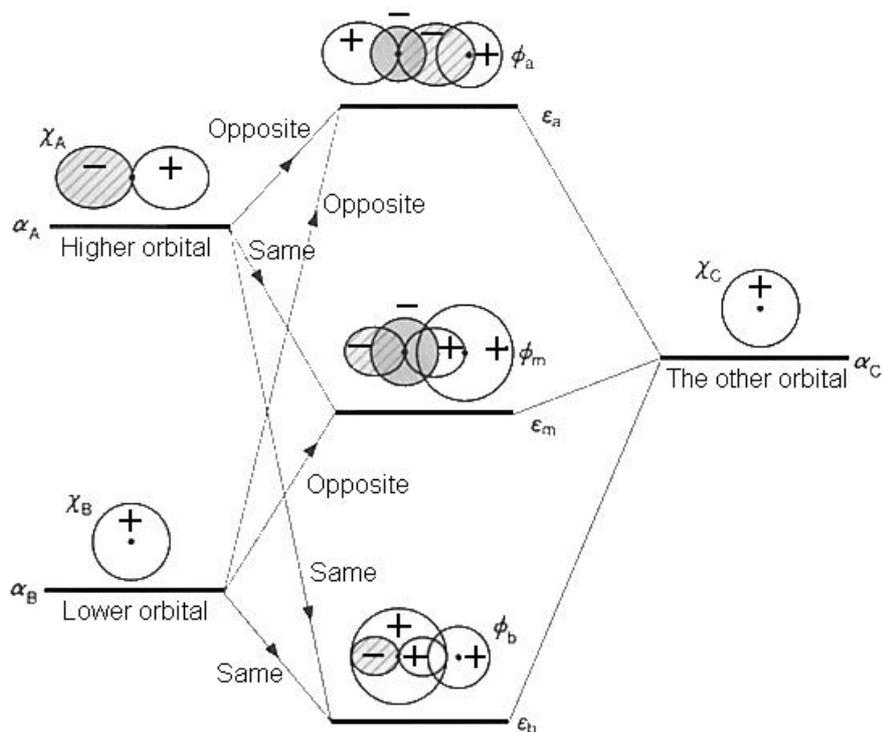
$$f(\alpha_A) = -\beta_{AC}^2(\alpha_B - \alpha_A) > 0, \quad f(\alpha_B) = -\beta_{BC}^2(\alpha_A - \alpha_B) < 0$$

Thus, the equation $f(\varepsilon) = 0$ has different three real solutions ($\varepsilon_a, \varepsilon_m, \varepsilon_b$), as can be seen from a figure below. Since $\alpha_A > \alpha_B$, ε_a is in the region of $\varepsilon > \alpha_A$, (ε_m) is in the region of $\alpha_A > \varepsilon > \alpha_B$, and (ε_b) is in the regions of $\alpha_B > \varepsilon$. It follows that $\varepsilon_a > \alpha_A > \varepsilon_m > \alpha_B > \varepsilon_b$.



(2) According to the principle of orbital interactions (cf. Fig.5.7), the contribution of an orbital lower than the new orbital is in the opposite phase with respect to the other orbital along an upward arrow, and the contribution of an orbital higher than the new orbital is in the same phase with respect to the other orbital along a downward arrow. These characteristics can be applied to relative phases of the components in new three orbitals (from the highest, ϕ_a, ϕ_m, ϕ_b), which are produced by interactions of the higher χ_A and the lower χ_B orbitals with the orbital χ_C of the partner as follows.

- ϕ_a : With respect to χ_C of the partner, both χ_A, χ_B interact upward in the opposite phase to yield a highly antibonding orbital.
- ϕ_m : With respect to χ_C of the partner, the higher χ_A interacts downward in the same phase, and the lower χ_B interacts upward in the opposite phase, to produce a weakly bonding or antibonding orbital depending on the magnitude of interactions with χ_C .
- ϕ_b : With respect to χ_C of the partner, both χ_A, χ_B interact downward in the same phase to give a highly bonding orbital.



5.4 AH type and AH₂ type molecules

The principle of orbital interactions studied in the previous section can be used to deducing form and energy levels of molecular orbitals qualitatively. Let us first summarize procedures using the principle of orbital interactions. Then we will apply it to simple hydride molecules and study mechanisms for production of the electric polarization in chemical bonds and mechanisms for determination of the bond angles.

5.4.1 Procedures using the principle of orbital interactions

Let us summarize procedures using the principle of orbital interactions for various problems. For readers who want to study from concrete examples, the next section for AH type molecules may be studied without reading this section, and if necessary, he may come back to refer this section.

[1] Consider electronic configurations for each system before interactions. Show energy levels to be considered in both sides separately. Usually energy levels from inner-shell electrons to valence electrons should be considered. Energy levels much higher than valence electron levels need not be considered from the beginning, since interactions with valence electrons can be neglected due to the principle of the energy difference. Treatments of inner-shell electrons are rather simple, and thus inner-shell electrons can be disregarded except for considering the total number of electrons.

[2] Using rules for orbital-energy changes in the principle of orbital interactions, deduce new energy levels, and show them in the intermediate space between the initial levels in both sides. Consider strengths of the interactions based on the principle of the energy difference and the principle of the overlap. Levels with no appreciable interactions should be shown at the same heights as before, since no level shifts are expected for them. Bonding orbitals should be stabilized to the lower energy, and antibonding orbitals should be unstabilized to the higher energy.

[3] When orbital forms are needed to be considered, deduce forms of new orbitals using the rules for orbital mixing in the principle of orbital interactions. For graphical illustrations, show an s orbital as a circle and a p orbital as a pair of ellipses in the figure of 8. Contributions of the components can be expressed by the size of circles and ellipses. Phases can be indicated by plus and minus symbols, or the signs can be specified by two ways of drawings, such as solid and dashed lines, thick and thin lines, or white and black paintings. The phase for the first component may be arbitrarily chosen, though the relative phases of other components should be represented in accordance with the first choice.

[4] Build up the new electronic configuration by placing electrons from both sides into new orbitals according to the Pauli principle. In the case of degenerate levels, Hund's rule should also be considered. Electrons should be shown as \uparrow or \downarrow in the energy levels in order to represent their spins. The choice of the spin for the first unpaired electron may be arbitrary. If spins can be disregarded, \circ or \bullet may be placed in the level diagram in place of the arrows.

5.4.2 AH type molecules

Chemical bonds between different atoms have an electric polarization. In order to discuss the electric polarization of bonds in connection with the bond formation, let us consider a H_2 molecule followed by LiH and HF molecules as typical examples of polar molecules.

H_2 molecule

Show energy levels of two H atoms in the right and the left sides separately. In this case, the electronic configuration of a H atom includes only one electron in 1s orbital, and thus only 1s energy level should be shown in the left and the right sides as in Fig.5.8. The higher energy levels such as 2s orbital need not be shown, since interactions of the 1s orbital with other orbitals in the higher levels can be neglected on account of the principle of the energy difference.

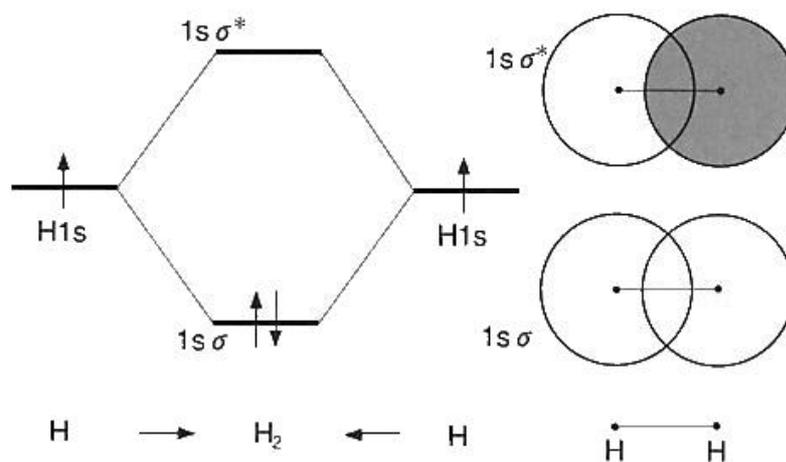


Figure 5.8: Molecular orbitals of H_2

Use rules for orbital-energy changes to deduce new energy levels. In this case, interactions between two 1s orbitals of H atoms due to a σ type overlap lead to a bonding orbital of $1s\sigma$ and an antibonding orbital of $1s\sigma^*$. The bonding orbital is stabilized to the lower energy with respect

to the $1s$ energy level of a H atom, and the antibonding orbital becomes more unstable to the higher energy.

Use rules for orbital mixing to deduce forms of new orbitals. Interactions between equivalent $1s$ orbitals lead to a couple of orbitals made of one to one mixing of two components. The bonding orbital has the same phase, while the antibonding orbital has the opposite phase.

In the final step, two electrons from the left and the right H atoms should be placed in the new energy levels from the lower one. In this case, the bonding $1s\sigma$ orbital accepts an electron pair, and they produce the stabilization of two bonding electrons. Since the $1s\sigma$ orbital is composed of even contributions of the left and the right H $1s$ orbitals, no electric polarization appear in the bond formed between the H atoms.

The bond in a H_2 molecule is formed by augmented electron densities between two nuclei due to a pair of electrons in a molecular orbital, and it follows that this bond can be considered as a prototype of a covalent bond or an electron-pair bond.

LiH molecule

Show energy levels for both atoms in the right and the left sides separately. Only $1s$ orbital may be considered for a H atom as in the case of a H_2 molecule. For a Li atom with the electronic configuration $(1s^2)(2p)^1$, only $1s$ and $2s$ electrons need to be considered. The Li $1s$ orbital is an inner-shell orbital, whose ionization energy is much larger than those for valence orbitals. On the other hand, the energy level for the Li $2s$ orbital is higher than that for the H $1s$ orbital. This situation can be understood from the fact that the ionization energy of a Li atom is much smaller than that of a H atom, because the electronegativity of a Li atom is much smaller than a H atom. Since the Li $2p$ levels are not so much higher than the $2s$ levels, the Li $2p$ levels had better be considered as well. However, we omit contributions from the Li $2p$ orbitals, because the same conclusion will be obtained for the chemical bond of a LiH molecule. The higher levels such as Li $3s$ and H $2s$ levels need not be considered, since they are considerably higher than the valence electron levels.

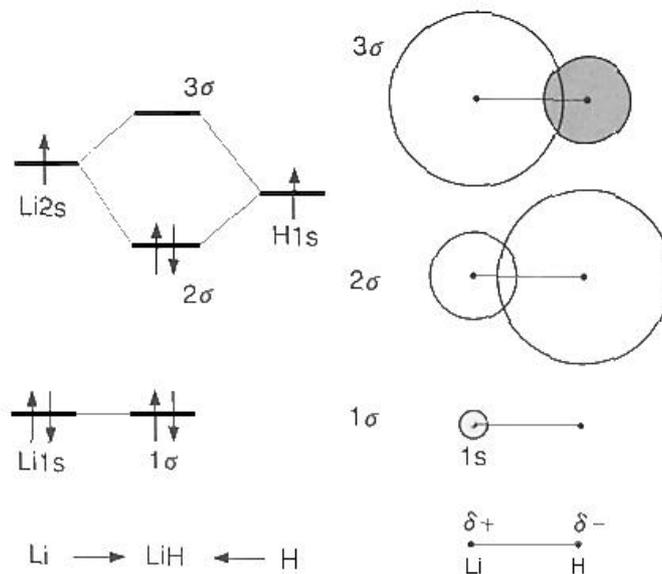


Figure 5.9: Molecular orbitals of LiH

Based on the principle of the energy difference, the Li $1s$ level, which is much lower than the H $1s$ level, becomes the most stable level with its orbital form unchanged from the shape of the Li $1s$ orbital. This new orbital is the most stable orbital classified as a σ orbital, and thus it is called 1σ orbital. Next, one to one interactions between Li $2s$ and H $1s$ orbitals lead to the 2σ orbital, which is more stable than the lower H $1s$ orbital, and the 3σ orbital, which is more unstable than the

higher Li2s orbital. The 2σ orbital is a bonding orbital, which is made mainly of the lower H1s orbital together with a small contribution of the higher Li2s orbital in the same phase. Valence electrons, one from Li and another from H, become an electron pair in the 2σ orbital for LiH. The dominant component of this electron pair is H1s, and it follows that the electron distribution is concentrated on the H atom to yield a strong polarization. Thus a LiH molecule is highly ionic with the negative charge on the H atom (cf. Table 5.1). This is consistent with the larger electronegativity of a H atom in comparison with a Li atom. The 3σ orbital is an antibonding orbital, which is made mainly of the higher Li2s orbital.

Table 5.1: Electric polarization for diatomic molecules

$A^{\delta+}B^{\delta-}$	Electric dipole moment $ \mu (10^{-30} \text{ C m})$	Dissociation energy $D_0(\text{eV})$	Equilibrium internuclear distance $R(\text{pm})$
H ₂	0.0	4.4781	74.144
HF	6.1	5.84	91.71
HCl	3.6	4.43	127.46
HBr	2.7	3.75	141.4
HI	1.4	3.06	160.9
LiH	19.4	2.5	159.6
LiF	21.0	6.6	156.4
NaF	27.2	5.3	192.6
NaCl	30.0	3.58	236.1

HF molecule

Electron configurations of the atoms are $H(1s)^1$ and $F(1s)^2(2s)^2(2p)^5$, and only orbitals contained in these configurations may be considered (Fig. 5.10).

F1s is an innershell level, and its energy is very low. Since a F atom is more electronegative and has larger ionization energy than a H atom, F2p level is lower than H1s level. F2s level is further lower than F2p level. The innershell F1s orbital may be treated to have no interaction with H1s due to the principle of the energy difference, and thus it becomes the most stable molecular orbital 1σ in a HF molecule, whose shape is nearly the same as the shape of a F1s atomic orbital. Interactions among valence orbitals are one to four interactions between H1s and F2s, F2p_x, F2p_y, F2p_z. On account of the symmetry for overlaps, these interactions are decomposed into the simpler ones.

H1s orbital is symmetric with respect to an arbitrary plane including the bonding axis (the axis connecting H and F atoms is taken as z axis), and thus H1s orbital does not interact with F2p_x and F2p_y orbitals having directions perpendicular to z axis and parallel with x and y axes. It follows that F2p_x and F2p_y levels become degenerate 1π levels for molecular orbitals of a HF molecule without modification from the atomic orbitals. These orbitals retain the shapes of the F2p atomic orbitals having perpendicular directions to the bonding axis. After all, the remaining F2s and F2p_z orbitals undergo two to one interactions with H1s to yield 2σ orbital, which is a bonding orbital having a dominant component of F2s orbital in the same phase with the H1s component and more stable than the lower F2s level. To this bonding orbital F2p_z orbital gives a small contribution in the same phase with the H1s component to strengthen the bonding character.

Since the contribution of H1s to 2σ is small, 2σ orbital has a strong electric polarization with the negative side on the F atom. 3σ level appears between the lower F2s and the higher F2p_z levels. 3σ orbital contains an out-of-phase contribution of the lower F2s orbital from the downward to the upward and an in-phase contribution of the higher F2p_z orbital from the upward to the downward with respect to H1s, and the main contribution is F2p_z with the nearer energy level to result in a weakly bonding orbital having a negative electric polarization on the F atom. 4σ level is higher than the higher F2p_z and in this case much higher than H1s. 4σ orbital is composed of out-of-phase contributions of both the higher F2p_z and the lower F2s with respect to H1s, which results in a strongly antibonding orbital having H1s orbitals as the main component.

Ten electrons, one from H and nine from F, are accommodated in the energy levels from the lower ones as electron pairs to give an electron configuration of $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4$, as can be seen from Fig.5.10. 1σ orbital is an inner shell orbital, and hence it does not contribute to the

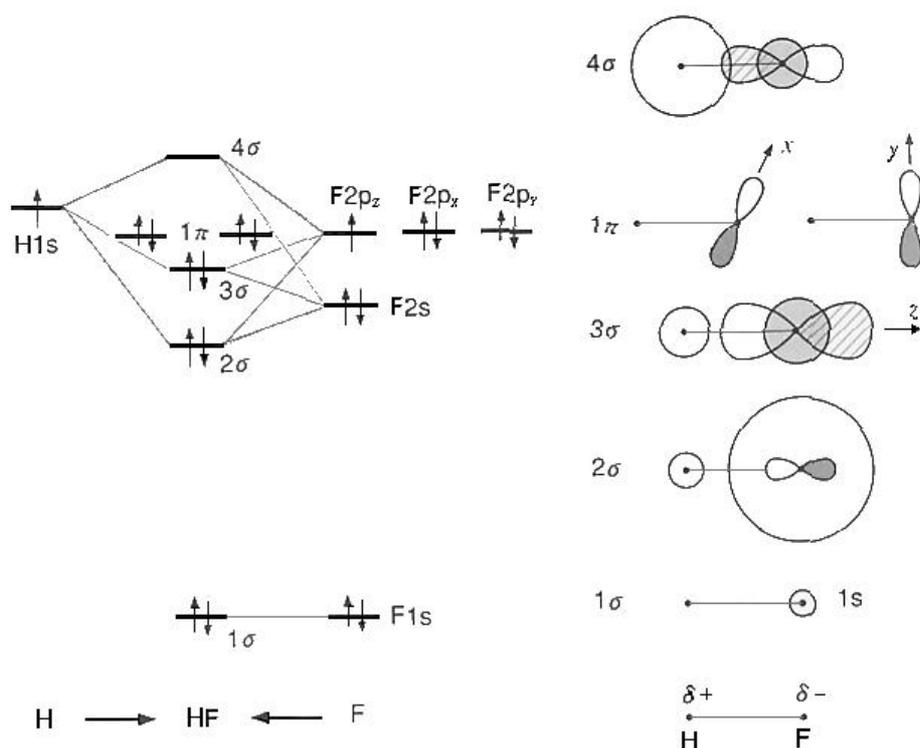


Figure 5.10: Molecular orbitals of HF

bonding force. The degenerate 1π orbitals almost purely composed of atomic F2p orbitals with a pair of electrons are nonbonding orbitals, and these may be considered as unshared electron pairs without bonding characters. 2σ and 3σ orbitals show bonding characters, and both orbitals have a negative electric polarization on the F atom. Thus, a HF molecule has an electric polarization with the negative side on the F atom (Fig.5.1).

Although both HF and LiH molecules have two electrons in a bonding orbital producing an enhancement of electron densities in the bonding regions between the two nuclei to result in a contribution of the electron-pair bond, the bond is highly polarized as an ionic bond in a NaCl molecule. In such a marginal case, the electron-pair bond and the ionic bond cannot clearly be distinguished from each other.

5.4.3 AH₂ type molecules

In an AH₂ type molecule such as H₂O, the bond angle is an important parameter for the molecular structure in addition to the bond length. Here, we will study composition of molecular orbitals for AH₂ type molecules from BeH₂ to H₂O and elucidate the mechanism for bond angles. Now, let us construct molecular orbitals of an AH₂ type molecule according to the following procedures.

[1] Step 1 in Fig.5.11

At first, advance a H atom toward another H atom up to a distance (ca.1.4 Å) approximately two times larger than the normal bond length of a H₂ molecule. This process produces formally a bonding 1σ level and an antibonding $1\sigma^*$ level, though the level shifts for stabilization and destabilization are small, because of a very small overlap due to the long distance. Forms of the produced orbitals are in-phase and out-of-phase combinations of H1s components, and these orbitals for a pseudo-hydrogen molecule are denoted as a bonding ϕ_b orbital and an antibonding ϕ_a orbital, respectively.

[2] Step 2 in Fig.5.11

Next, introduce the A atom (Be ~ O atoms) along a line bisecting the bond of the pseudo-hydrogen molecule (denoted as the z-axis) from the infinity toward the center of the bond up to a

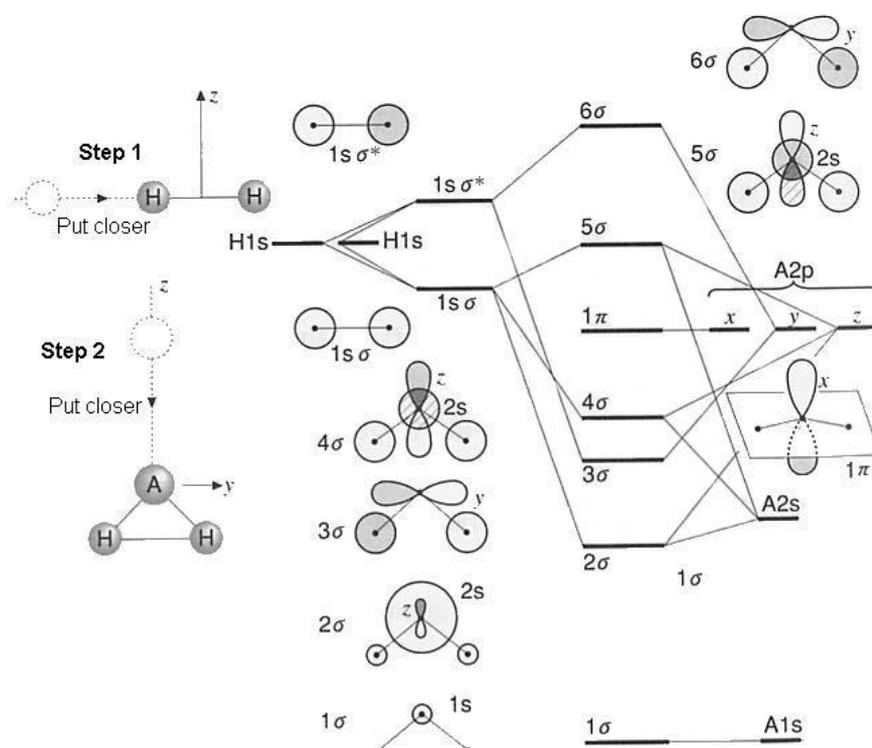


Figure 5.11: Molecular orbitals of an AH_2 type molecule (the right angle form)

distance just producing a right angle form. Via this procedure, we can easily construct molecular orbitals for the right angle form of an AH_2 molecule based on interactions between orbitals of a pseudo-hydrogen molecule and $1s$, $2s$, $2p$ orbitals of the A atom.

[3] Step 3 in Fig.5.12

Finally, vary the bond angle θ from the right angle form to the linear form with keeping the bond length constant, and study changes in the energy level diagram.

Composition of a right angle form AH_2 molecule

Composition of molecular orbitals of the right angle form begins with a set of $1s$, $2s$, and $2p_x$, $2p_y$, $2p_z$ orbitals for energy levels of the A atom (Be~O atoms). Among interactions of these orbitals with orbitals of the pseudo-hydrogen molecule, some interactions can be considered to be negligible. First of all, the $1s$ orbital of the A atom can be considered as a molecular orbital 1σ with the energy and orbital form almost unchanged, based on the principle of the energy difference, because the energy level of the inner shell $1s$ orbital of the A atom is very low.

Next, a direction bisecting the H-H with a right angle is taken as the z axis as shown in Fig.5.11, a direction parallel to H-H passing through the A atom is taken to be the y axis, and the normal direction to the $y-z$ plane is taken as the x axis. $A2p_x$ orbital is an antisymmetric orbital with its sign alternating depending on the position up or down with respect to the $y-z$ plane, whereas both of $1s\sigma$ and $1s\sigma^*$ orbitals are symmetric with respect to this plane. On account of the difference of the orbital symmetries, $A2p_x$ orbital does not interact with $1s\sigma$ and $1s\sigma^*$ orbitals, and then $A2p_x$ orbital becomes a molecular orbital 1π of the AH_2 molecule with nearly the same energy as the atomic energy level.

The remaining interactions are classified into two types, (1) interactions among symmetric orbitals with respect to the $x-z$ plane, and (2) interactions among antisymmetric orbitals with respect to the $x-z$ plane. For orbitals symmetric to the $x-z$ plane, $1s\sigma$, $A2s$, and $A2p_z$ orbitals interact with each other, according to the two to one orbital interactions. The most stable level arising from these interactions is located under the level of $A2s$ orbital. The corresponding molecular orbital 2σ includes $A2s$ orbital as a main component in addition to a component of $A2p_z$, which mix with the central part of $1s\sigma$ between two H atoms in the same phase. This molecular

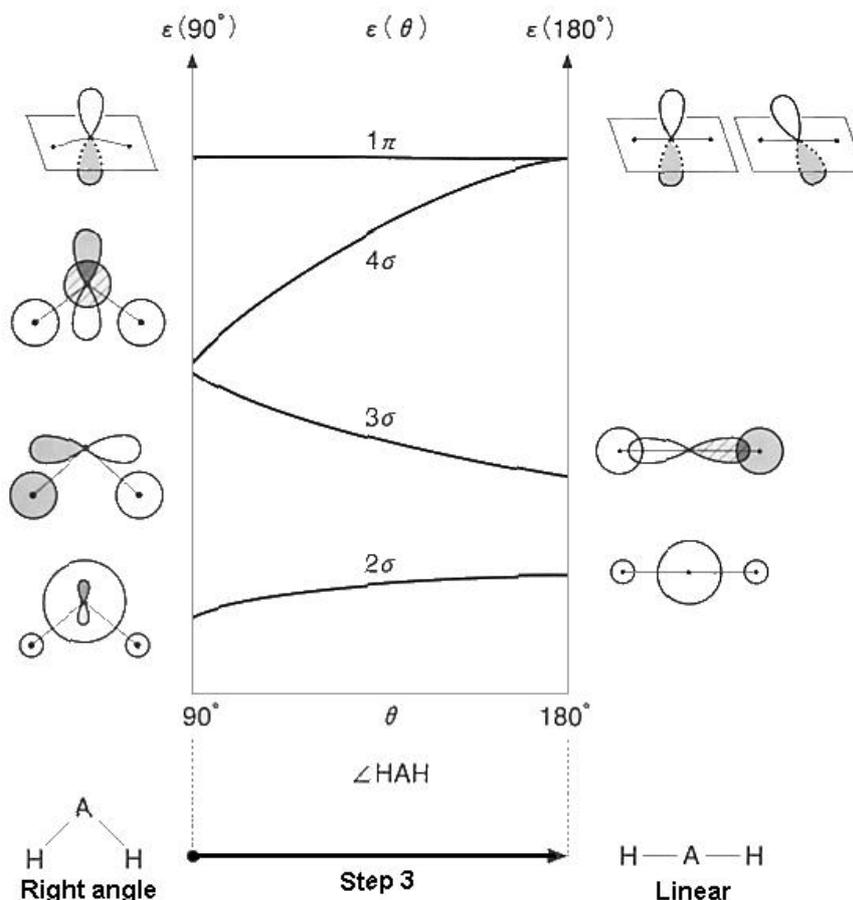


Figure 5.12: Molecular orbitals of an AH_2 type molecule as functions of the bond angle θ

orbital is a bonding orbital binding all three atoms mutually. The orbital energy level with an intermediate stability arising from the two to one orbital interactions appears between $A2s$ and $A2p_z$ levels. This intermediate level corresponds to 4σ orbital. This orbital is composed of an inphase component from upward to downward for the upper $A2p_z$ as well as an out-of-phase component from downward to upward for the lower $A2s$, and this orbital becomes antibonding between A and H and weakly bonding between H and H . As mentioned below, electrons in this orbital have an effect causing the angle $\angle HAH$ smaller.

The most unstable level arising from the two to one orbital interactions becomes higher than $1s\sigma$ and $A2p_z$ levels. The corresponding orbital is composed of the upper $A2p_z$ and the lower $A2s$, which mix with $1s\sigma$ in out-of-phase at the central part of H and H , and thus this orbital becomes 5σ molecular orbital, which is antibonding between A and H and almost nonbonding between H and H .

Antisymmetric orbitals with respect to the $x-z$ plane, $1s\sigma^*$ and $A2p_y$, interact with each other according to the one to one orbital interactions. The bonding orbital energy level arising from the interactions appears lower than both of $1s\sigma^*$ and $A2p_y$ orbital levels, and an in phase overlap of these two orbitals between A and H atoms gives a bonding type 3σ molecular orbital. The reason why this 3σ is lower than 4σ will be explained below.

The most important interactions are those between $A2p$ and $H1s$ orbitals. In the case of the right angle type, the direction of the p orbital component with respect to the AH bond is in the angle of 45° for both 3σ and 4σ orbitals. Therefore, overlaps between $A2p$ and $H1s$ orbitals are nearly the same for these cases. However, for 4σ orbital a contribution due to $A2s$, which overlaps with $H1s$ in an opposite phase contrary to the case of $A2p$, gives a weaker bonding character in the AH region than 3σ . This results in the higher energy level of 4σ than that of 3σ .

The most unstable energy level is due to 6σ orbital, which is a strongly antibonding orbital

composed of out-of-phase overlaps of $1s\sigma^*$ and $A2p_y$. This level is thus much higher than $1s\sigma^*$ and $A2p_y$ levels.

Changes from the right angle form to the linear form

Let us study changes of energy levels on going from the right angle form of the bond angle $\theta = 90^\circ$ to the linear form of $\theta = 180^\circ$. As for the lowest level, 1σ , which is almost entirely composed of $A1s$, is nearly independent of θ to give a horizontal line. Next, 2σ slightly goes up with the increase of θ , because the in-phase overlap between two H atoms decreases and also because the in-phase contribution of $A2p_z$ becomes vanishing at 180° by the symmetry. Since the overlap between $H1s$ and $A2p_z$ increases on going to the linear form, 3σ becomes a strongly decreasing curve toward larger angles. On the other hand, 4σ goes upwards on going to the linear form, because the in-phase overlap between two H atoms as well as the in-phase contribution of $A2p_z$ decrease, and finally it becomes a moiety of the degenerate π orbitals in the linear form. Since 1π orbital of the right angle form does not interact with other orbitals by the symmetry even if the θ increases up to 180° , its energy level remains to be horizontal. Although the antibonding character of 5σ has a little change, 6σ becomes more strongly antibonding and increases its energy on going to the linear form.

A graphic representation of orbital energies as functions of bond angles such as Fig.5.12 is called the Walsh diagram. As discussed below, we may anticipate bond angles qualitatively based on the Walsh diagram.

5.4.4 The Walsh diagram and the bond angle

When an electron is inserted in a level descending with the angle in Fig.5.12, it has a function opening the bond angle, since the system tends to decrease its energy. Conversely, an electron in a level ascending with the angle has an opposite function closing the bond angle. A horizontal level has no effect on the bond angle, since no energy change with angles is expected irrespective of the occupation number of electrons. Based on these principles, we can discuss a relationship between the bond angle and the number of valence electrons for the AH_2 molecule, as can be seen in Table 5.2.

Table 5.2: Molecular structures of AH_2 type molecules and electron configurations. The bond angle and the bond length for BeH_2 are theoretical values obtained from accurate calculations, since no experimental values are available. Other data are experimental values.

AH_2	Number of valence electrons	Bond angle θ°	Bond length R_{AH} (pm)	Electron configuration					Spin state
				1σ	2σ	3σ	4σ	1π	
BeH_2	4	180	133	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$			Singlet
BH_2	5	131	118	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow		Doublet
CH_2	6	136	108	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	Triplet
CH_2	6	102.4	111	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		Singlet
NH_2	7	103.4	102	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	Doublet
H_2O	8	104.5	96	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	Singlet

In BeH_2 there are four valence electrons, two from a Be atom and one from each H atom, and thus two levels up to 3σ are doubly occupied. Since 3σ level is steeply descending to the larger angles as can be seen from Fig.5.12, the linear form with a bond angle of 180° is most stable for BeH_2 .

There are five valence electrons in BH_2 , and one electron is added into 4σ level in comparison with BeH_2 . Careful studies on the angular dependence of overlaps between p and s orbitals lead to a conclusion that the energy change between 90° and 180° for 4σ is twice as large as that for 3σ . It is thus expected that one electron in 4σ nearly cancels out effects of two electrons in 3σ . This indicates that the bond angle of BH_2 may be in the middle of 90° and 180° , which is in good agreement with the observed angle of 131° .

Methylene CH_2 has one more electron. Based on the right angle form, doubly occupied levels from 1σ to 4σ results in a singlet state of methylene, which is expected to have a much smaller bond angle than 131° in BH_2 . The observed bond angle 102.4° for a singlet methylene is really

much smaller than the bond angle of BH_2 . On the other hand, in the linear structure, 4σ and 1π have the same energy to degenerate. Thus, Hund's rule suggests a triplet state in which one electron added as an unpaired electron into 1π has a parallel spin with that of an unpaired electron in 4σ . In a triplet methylene, levels from 1σ to 3σ are doubly occupied, whereas 4σ and 1π are singly occupied. An electron in the 1π level with a constant energy has no effect on the bond angle. It follows that the bond angle of a triplet methylene is expected to be nearly equal to the angle of BH_2 (131°), which agrees well with the really observed angle of 136° for a triplet methylene.

Further addition of an electron leads to an amino radical NH_2 with seven valence electrons. In this case, one electron addition to either methylene results in the same electron configuration, in which levels from 1σ to 4σ are doubly occupied, while an electron occupies 1π level. Since 1π electron is not related to bond angle changes, the bond angle of NH_2 is expected to be nearly the same as the bond angle for the singlet methylene (102.4°) with an electron configuration of fully occupied levels up to 4σ , which is in good agreement with the really observed bond angle of 103.4° for NH_2 .

In the last H_2O of the series, all levels up to 1π are doubly occupied. As 1π electrons are not related to the bond angle, the bond angle of H_2O is expected to be similar to those for the singlet methylene (102.4°) and NH_2 (103.4°). This expectation agrees well with the observed angle of 104.5° for H_2O .

5.5 A_2 type molecules

There are many types of bonds with various strengths. It is interesting to study how such varieties of chemical bonds are formed. In this section, let us qualitatively construct molecular orbitals and their energy levels of A_2 type molecules and study electron configurations and bond orders.

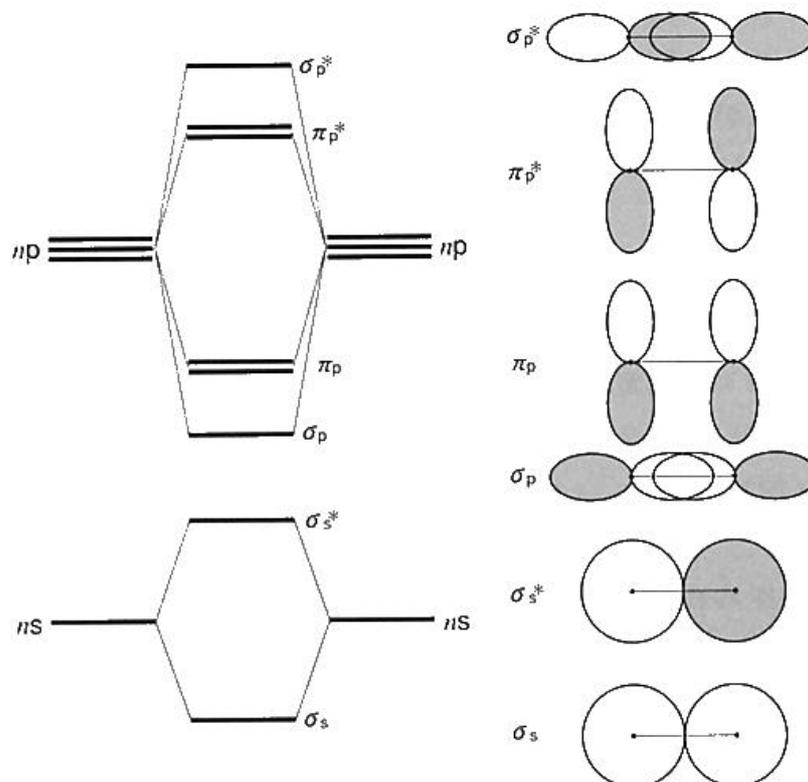


Figure 5.13: Orbital interactions in A_2 type molecules

A diatomic molecule A_2 composed of the same kind two A atoms is denoted as the homonuclear diatomic molecule. Since larger overlaps and smaller energy differences give stronger orbital interactions, construction of molecular orbitals of an A_2 molecule can be started with simple interactions between couples of the same type orbitals to obtain Fig.5.13. In-phase combinations yield bonding orbitals of σ_s , σ_p , π_p , and out-of-phase combinations give antibonding orbitals of σ_s^* , σ_p^* , π_p^* . π_p and π_p^* orbitals are composed of π type overlaps of p orbitals with directions vertical to the bonding axis z . Thus, two types of p orbitals with directions of x and y axes lead to the two-fold degeneracy for π_p and π_p^* orbitals.

In many electron atoms, orbital energy levels are in the order of $ns < np$, and overlaps between orbitals are in the order of $\pi_p < \sigma_p$. It follows that when the energy difference between ns and np levels ($ns - np$ energy gap) is very large, energy levels for an A_2 type molecule can be expressed by Fig.5.13 or Fig.5.14(a), σ_p becomes more stable and lower than π_p . On the other hand, σ_p^* becomes higher than π_p^* . Fig.5.13 or Fig.5.14(a) expresses the standard pattern of energy levels in A_2 type molecules with large $ns - np$ energy gaps. This pattern can be applied to right hand atoms in the periodic table.

In left hand atoms in the periodic table, interactions between s orbitals and p orbitals become significant, because $ns - np$ energy gaps are small as shown in Fig.5.14(b). It follows that the same symmetry orbitals, (σ_s, σ_p) and (σ_s^*, σ_p^*) , mix with each other to yield modified energy levels. Rules for mixing in orbitals can be summarized as follows.

- (1) The lower orbital increases its bonding character (or decrease its antibonding character) to decreases its energy.
- (2) The higher orbital increases its antibonding character (or decrease its bonding character) to increases its energy.

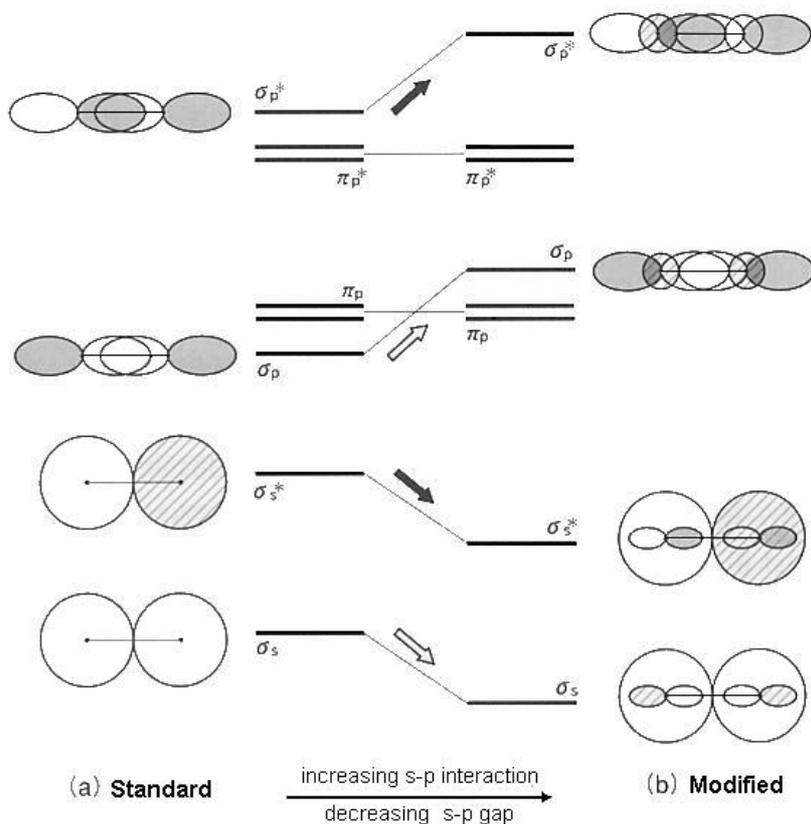


Figure 5.14: Energy levels for homonuclear diatomic molecules

For example, the more stable σ_s is formed by a little mixing of σ_p into σ_s in order to increase in-phase overlap in the middle regions between two nuclei. The more stable σ_{s^*} is produced by a little mixing of σ_{p^*} into σ_{s^*} so that out-of-phase overlap may be decreased to strengthen the bonding character relatively. Modified energy levels for A_2 type molecules make the σ_p level higher than the π_{p^*} level in comparison with the standard form.

Whether a chemical bond is formed or not depends on the electron configuration in the energy levels of Fig.5.14(a) or (b). As a qualitative index that indicates the strength of the bond in an A_2 type molecule, the bond order can be defined by the following equation.

$$P = \frac{(\text{number of electrons in bonding orbitals} - (\text{number of electrons in antibonding orbitals}))}{2} \quad (5.45)$$

According to this equation, a pair of bonding electrons give a bond order of unity. In this equation, a pair of electrons in an antibonding orbital decrease the bond order by one. This definition of the bond order is a useful index to understand the multiplicity of electron-pair bonds (covalent bonds).

Let us compose electron configurations based on Fig.5.14 and obtain bond orders by using Eq.(5.45). H_2 has an electron configuration of $(\sigma_{1s})^2$, and its bond order is given as $P = (2-0)/2 = 1$. Thus the hydrogen molecule has a single bond with a pair of bonding electrons. He_2 has an electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ leading to a bond order of $P = (2-2)/2 = 0$. $P = 0$ does not give a stable chemical bond. In the case of Li_2 , σ_{2s} orbitals contain electrons (see Fig.5.15), the electron configuration becomes $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2$. In this expression, inner core $1s$ electrons of $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ corresponds to the electron configuration for He_2 . This part gives no contribution to the bond order. Thus, only valence electrons are significant in the bond order. The configuration of valence electrons in this case is $(\sigma_{2s})^2$, and thus the bond order for Li_2 becomes $P = 1$ as in the case of $(\sigma_{1s})^2$ in H_2 . In general, a homonuclear diatomic molecule of the first Group element (H, Li, Na, K, etc.) in the periodic table has an electron configuration of $(\sigma_{ns})^2$ ($n = 1, 2, 3, \dots$), and atoms are connected by a single bond of $P = 1$.

In Be_2 σ_{2s}^* also contains a pair of electrons, and the valence electron configuration becomes $(\sigma_{2s})^2(\sigma_{2s}^*)^2$ to give $P = 0$, which means no chemical bond as in the case of He_2 . Similarly, a homonuclear diatomic molecule of the second Group element of the periodic table is expected not to form a stable molecule. However, diatomic molecules of Mg_2 and Ca_2 do exist though their bonds are thermally unstable to decompose very easily. The dissociation energy D_0 of Ca_2 is only 0.13 eV, which is 3% of $D_0(4.478 \text{ eV})$ of H_2 .

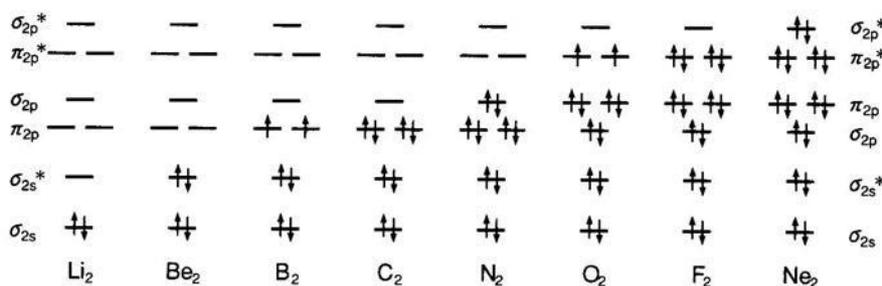


Figure 5.15: Valence electron configurations for $Li_2 - Ne_2$

B_2 has six valence electrons, and the last two electrons are contained in either π_{2p} or σ_{2p} . In the case of a B atom, the s-p gap is so small that the modified type of energy levels in Fig.5.14 should be used, and degenerate π_{2p} levels accept two electrons. It follows that the valence electron configuration of B_2 becomes to be a triplet with a pair of unpaired electrons with a parallel spin owing to Hund's rule as can be seen in Fig.5.15. Thus, a group of B_2 molecules show paramagnetic properties that an application of a magnetic field yields a magnetization along the direction of the field. In B_2 , contributions to the bond order from $(\sigma_{2s})^2$ and $(\sigma_{2s}^*)^2$ cancel out each other,

and then only a contribution from $(\pi_{2p})^2$ remains to give $P = 1$. Therefore, a B_2 molecule has a π bond, which is considered as a single bond with a bond order of 1.

In C_2 π_{2p} accepts electrons prior to σ_{2p} as in the case of B_2 , and the π_{2p} orbital becomes the HOMO. The chemical bond in C_2 is a double bond $P = 2$ composed of two π bonds. It is interesting to compare B_2 and C_2 molecules. The dissociation energy of a doubly bonded C_2 molecule (6.21 eV) is nearly twice as large as that of a B_2 molecule (3.02 eV). The equilibrium bond length of C_2 is much shorter than B_2 .

N_2 is just at the border of the standard and the modified types in Fig.5.14. Either type gives the bond order of $P = 3$ for the bond of a N_2 molecule, which is a triple bond made up of two π bonds and one σ bond. Experiments such as photoelectron spectroscopy give a confirmation that the HOMO is σ_{2p} rather than π_{2p} , which indicates that the modified levels are more consistent with the observation. The dissociation energy of a N_2 molecule (9.759 eV), which is slightly larger than triple times of the dissociation energy of B_2 (3.02 eV), is the largest among homonuclear diatomic molecules.

In O_2 the standard type should be used because of the large 2s-2p gap, and hence the degenerate antibonding π_{2p}^* orbitals become to be the HOMOs to yield a triplet type electron configuration. The bond order of O_2 should be decreased by one from that of N_2 , because two additional electrons are accommodated in the antibonding orbitals, and thus an O_2 molecule has a double bond made up of one π bond and one σ bond. The electron configuration of O_2 is a triplet of two unpaired electrons with a parallel spin as in the case of B_2 , and it follows that oxygen has paramagnetic properties. In F_2 further addition of two electrons in π_{2p}^* orbitals decreases the bond order by one from that of O_2 , which makes a single bond of a σ bond.

In the electron configuration of Ne_2 , electrons fully occupy up to σ_{2p}^* , and bonding characters gained by bonding orbitals are completely canceled by antibonding electrons to result in a bond order of $P = 0$. It follows that a stable Ne_2 molecule is expected not to exist as in the case of He_2 . However, Ne_2 really exists under a special condition in which thermal effects are not effective to decompose molecules. The dissociation energy of Ne_2 is very small as 0.0036 eV, which is about one tenth of the kinetic energy of a molecule in gaseous state at room temperature.

Table 5.3 lists valence electron configurations, bond orders, dissociation energies, equilibrium nuclear distances for homonuclear diatomic molecules and some of their ions. When properties are compared among A_2 type molecules of the same row elements, the larger the bond order becomes, the larger the dissociation energy becomes, and then the shorter the bond length (equilibrium internuclear distance) becomes. When a comparison is made among A_2 type molecules of the same Group elements, the bond strength for $P > 0$ is larger for the higher elements. This indicates that upper row atoms have compact electron orbitals to result in shorter distances between augmented electron densities in the bonding region (the covalent electron pair) and two nuclei, which causes strong binding forces between the nuclei. Very weak bonds of $P = 0$ such as Mg_2 , Ca_2 , Ne_2 , and Ar_2 are quite different from the usual electron-pair bonds (covalent bonds), and their dissociation energies become larger on going to the lower rows in the periodic table.

Example 5.2 Obtain the bond order P of O_2^+ . Compare the dissociation energy D_0 and the bond length R of O_2^+ with those of O_2 and N_2 .

(Solution) The electron configuration of O_2^+ is given by $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$, in which the number of electrons in π_{2p}^* is decreased to one from two in the case of O_2 . Noting 8 electrons in bonding orbitals and 3 electrons in antibonding orbitals, we obtain the bond order of O_2^+ as $P(O_2^+) = (8 - 3)/2 = 2.5$.

Since O_2 has one more antibonding electron than O_2^+ , the bond order of O_2 can easily be obtained as $P(O_2) = 2$. In N_2 an antibonding electron is removed from the electron configuration of O_2^+ , and thus $P(N_2) = 3$. In general, the larger P becomes, D_0 becomes larger and R becomes smaller. It follows that we obtain the following conclusions (see Table 5.3).

Dissociation energy	$D_0(N_2) > D_0(O_2^+) > D_0(O_2)$
Bond length	$R(N_2) < R(O_2^+) < R(O_2)$

Table 5.3: Electron configurations and structures for homonuclear diatomic molecules and ions

Molecule	Valence electron configuration						Bond order	Dissociation energy $D_0(\text{eV})$	Bond length $R(\text{pm})$
	σ_{2s}	σ_{2s}^*	σ_{2p}	π_{2p}	π_{2p}^*	σ_{2p}^*			
H ₂	2						1	4.4781	74.144
He ₂	2	2					0		
Li ₂	2						1	1.046	267.29
Be ₂	2	2					0		
B ₂	2	2		2			1	3.02	159.0
C ₂	2	2		4			2	6.21	124.25
N ₂	2	2	2	4			3	9.759	109.77
O ₂	2	2	2	4	2		2	5.116	120.75
F ₂	2	2	2	4	4		1	1.602	141.19
Ne ₂	2	2	2	4	4	2	0	0.0036	309
Na ₂	2						1	0.73	307.9
Mg ₂	2	2					0	0.0501	389.1
Si ₂	2	2	2	2			2	3.21	224.6
P ₂	2	2	2	4			3	5.033	189.34
S ₂	2	2	2	4	2		2	4.3693	188.92
Cl ₂	2	2	2	4	4		1	2.4794	198.8
Ar ₂	2	2	2	4	4	2	0	0.0104	376
K ₂	2						1	0.514	390.51
Ca ₂	2	2					0	0.13	427.73
Br ₂	2	2	2	4	4		1	1.9707	228.11
Kr ₂	2	2	2	4	4	2	0	0.0160	400.7
I ₂	2	2	2	4	4		1	1.5424	266.6
Xe ₂	2	2	2	4	4	2	0	0.0230	436.2
H ₂ ⁺	1						0.5	2.648	106.0
He ₂ ⁺	2	1					0.5	2.365	108.1
N ₂ ⁺	2	2	1	4			2.5	8.71	111.64
O ₂ ⁺	2	2	2	4	1		2.5	6.663	111.64
Ar ₂ ⁺	2	2	2	4	4	1	0.5	1.33	248
Kr ₂ ⁺	2	2	2	4	4	1	0.5	1.15	279
Xe ₂ ⁺	2	2	2	4	4	1	0.5	1.03	317

5.6 Hybridization of orbitals

In the preceding sections, we studied some examples how orbitals are mixed to form new orbitals via orbital interactions. In some cases, both of two orbitals in one atom interact with an orbital in the other atom. In such cases, new orbitals can be considered to be produced from interactions of hybrid orbitals composed of two orbitals in one atom with orbitals of the other atom. In this section, we will study hybridization of orbitals and some applications of hybrid orbitals.

5.6.1 Mixtures of orbitals in the same atom

Let us study effects of mixtures of orbitals in the same atom. As shown in Fig.5.16(a), a mixture of p_x and p_y orbitals becomes equivalent with a p orbital with a direction rotated in the $x - y$ plane. The direction depends on coefficients of the linear combination, and any direction within the plane including the axes of the two p orbitals is possible. a mixture of three p orbitals, p_x , p_y , and p_z , may produce a p orbital with arbitrary direction in the full three dimensional space. It is thus possible to reorganize p orbitals to produce the most suitable linear combination to overlap efficiently with the orbital of the incoming atom or molecule, even if the other species comes from any direction. Basically, selection of directions of p orbitals or choice of coordinates can be made arbitrarily for computational convenience. However, essential characteristics of orbital interactions do not depend on the choice of the coordinate system, and this nature of orbital interactions can be denoted as the invariance in the coordinate system. Reorganization of p orbitals is an important property that guarantee the invariance in the coordinate system.

Next, we will study mixtures of an s orbital and p orbitals of the same atom. Since a mixture of p orbitals is equivalent to one p orbital with a suitable direction, we only need to consider a mixture of one s orbital and one p orbital. The result can be seen in Fig.5.16(b); a constructive effect occurs in the direction where phases coincide for s and p orbitals, whereas the mixing effect is destructive in the opposite direction. These effects result in a production of a big lobe at the in-phase direction together with a small lobe at the opposite direction. Such an augmentation of directional properties associated with mixture of the same atom orbitals to produce a highly directional orbital is denoted as hybridization, and produced orbitals are called hybridized orbitals or hybrid orbitals.

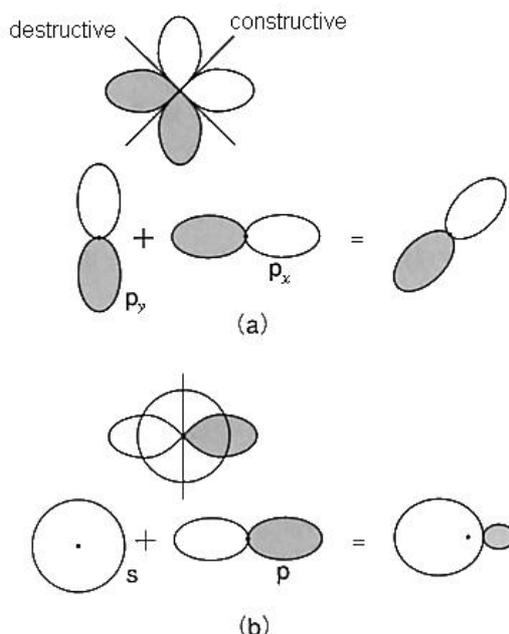


Figure 5.16: Mixing effects of the same atom orbitals. (a) Directional change on mixture of p orbitals with different directions. (b) Augmentation of direction on mixture of s orbital and p orbital (the hybridization effect).

Hybrid orbitals have the following important characteristics related to formation of chemical bonds.

[Characteristic features of hybrid orbitals]

- (1) Directionality becomes higher, and the overlap with a coming species from the direction increases.
- (2) The electron distribution of itself becomes asymmetric, and electron densities at the augmented direction become higher to produce a strong attractive force between its nucleus and the incoming nucleus.

Although many textbooks comment only on the feature (1), the feature (2) is also very important, as easily be understood from Feynman's electro static theorem in Section 4.2. In addition, a mixture of 2p orbitals into 1s orbital as well as a mixture of 3d orbitals into 2s and 2p orbitals also have some effects mentioned above.

Such mixing effects of higher orbitals other than valence orbitals on deformation of electron distributions around an atom are denoted as polarization effects. Additional functions with higher azimuthal quantum numbers other than valence orbitals to improve basis functions are called polarization functions. In comparison with hybridization effects of orbital mixing among orbitals of the same principal quantum number, polarization effects are rather moderate by the principle of the energy difference, since polarization effects involve orbitals with higher principal quantum numbers. Calculations with minimal basis sets which only contain valence orbitals include hybridization effects but neglect polarization effects.

5.6.2 sp hybridization

One to one hybridization of valence s and p orbitals gives sp hybrid orbitals, which are composed of mutually orthonormal two orbitals expressed as follows.

$$\begin{aligned}\phi_a &= \frac{s+z}{\sqrt{2}} \\ \phi_b &= \frac{s-z}{\sqrt{2}}\end{aligned}\tag{5.46}$$

Here, we used (p_z) orbital as the p orbital. p_z and s orbital functions are expressed simply as \mathbf{z} and \mathbf{s} . Two hybrid orbitals in eq.(5.46) are equivalent for their energies and shapes, though the directions are different with a mutual angle of 180° as can be seen in Fig.5.17. The energy of sp hybrid orbitals ε_{sp} is just an average value of orbital energies of s and p orbitals, which are expressed as α_s and α_p , respectively.

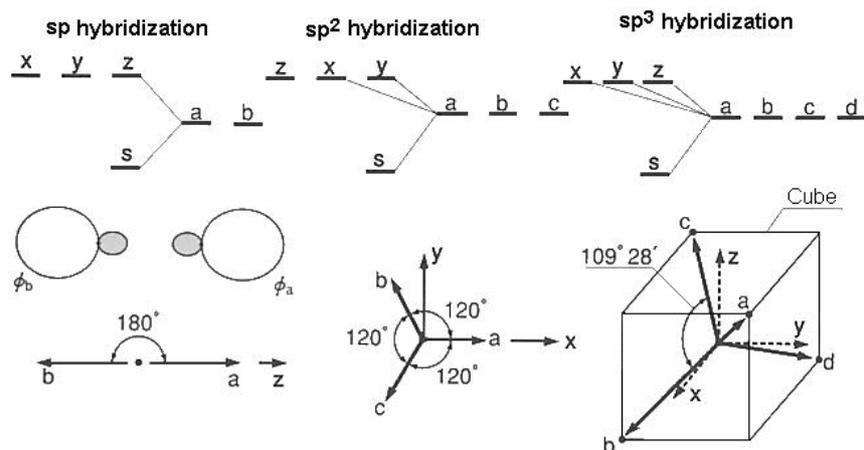
$$\varepsilon_{sp} = \frac{\alpha_s + \alpha_p}{2}\tag{5.47}$$

sp hybrid orbitals lead to linear molecules of A–B–C or A–B–C–D (such as BeCl_2 , HgBr_2 , HCN , C_2H_2) linearly connected by σ bonds with bond angles of 180° . In HCN and C_2H_2 , in addition to $\text{CN}\sigma$ and $\text{CC}\sigma$ bonds formed by sp hybridization two sets of π bonds due to π type overlaps by p orbitals with directions parallel to the σ bond, and it follows that triple bonds of $\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{C}$ are formed.

5.6.3 sp² hybridization

From one s orbital and two p orbitals (p_x and p_y orbitals, whose functions are expressed simply by \mathbf{x} and \mathbf{y}), we can construct a set of three hybrid orbitals, ϕ_a, ϕ_b, ϕ_c , which are equivalent in energies and shapes with directions mutually 120° displaced within a plane (Fig.5.17) and denoted as sp² hybrid orbitals.

$$\begin{aligned}\phi_a &= \frac{1}{\sqrt{3}}\mathbf{s} + \sqrt{\frac{2}{3}}\mathbf{x} \\ \phi_b &= \frac{1}{\sqrt{3}}\mathbf{s} - \frac{1}{\sqrt{6}}\mathbf{x} + \frac{1}{\sqrt{2}}\mathbf{y} \\ \phi_c &= \frac{1}{\sqrt{3}}\mathbf{s} - \frac{1}{\sqrt{6}}\mathbf{x} - \frac{1}{\sqrt{2}}\mathbf{y}\end{aligned}\tag{5.48}$$

Figure 5.17: sp^n hybrid orbitals ($n = 1, 2, 3$)

These orbitals satisfy the orthonormality. Since electron density is proportional to $|\phi|^2$, squares of atomic orbital coefficients give relative magnitude of s and p components; the s orbital component is estimated as $(1/\sqrt{3})^2 = 1/3$, and the p orbital component is $(\sqrt{2}/3)^2 = (1/\sqrt{6})^2 + (1/\sqrt{2})^2 = 2/3$. It follows that $s : p = 1 : 2$. The energy of sp^2 hybrid orbitals ε_{sp^2} is an average value of orbital energies of s and p orbitals with weights of $s : p = 1 : 2$.

When sp^2 hybrid orbitals make three σ bonds with other species in the directions of $0^\circ, 120^\circ, 240^\circ$, they produce triangle form molecules such as $\text{NH}_3^+, \text{BH}_3, \text{BF}_3$ with all bond angles of 120° and ethylene C_2H_4 in which angles are slightly deformed from 120° , $\angle\text{HCH} = 117.5^\circ$. Benzene C_6H_6 can also be produced by sp^2 hybridization. In ethylene and benzene, π type overlaps between out-of-plane p orbitals which are not involved in sp^2 hybridization yield π bonds. Thus, an ethylene molecule has a CC double bond. Six CC π bonds in benzene are equivalent, and they have an intermediate character between a single bond and a double bond, which can be confirmed from bond-orders by molecular orbital methods.

5.6.4 sp^3 hybridization

From one s orbital and three p orbitals (orbital functions are expressed simply by x, y , and z), we can construct a set of four hybrid orbitals, $\phi_a, \phi_b, \phi_c, \phi_d$, as shown in Fig.5.17. Energies and shapes of these orbitals are equivalent, and they are directed to four corners from the center of a tetrahedron.

$$\begin{aligned}\phi_a &= \frac{s+x+y+z}{2} \\ \phi_b &= \frac{s+x-y-z}{2} \\ \phi_c &= \frac{s-x-y+z}{2} \\ \phi_d &= \frac{s-x+y-z}{2}\end{aligned}\quad (5.49)$$

These orbitals satisfy the orthonormality. The electron density is proportional to $|\phi|^2$. Thus, squares of atomic orbital coefficients give relative magnitude of s and p components. The s orbital component is estimated as $(1/2)^2 = 1/4$, and the p orbital component is $(1/2)^2 \times 3 = 3/4$. It follows that $s : p = 1 : 3$. The energy of sp^3 hybrid orbitals ε_{sp^3} is an average value of orbital energies of s and p orbitals with weights of $s : p = 1 : 3$.

$$\varepsilon_{sp^3} = \frac{\alpha_s + 3\alpha_p}{4} \quad (5.50)$$

When sp^3 hybrid orbitals make four σ bonds with other species, they produce tetrahedral molecules such as $\text{CH}_4, \text{SiH}_4, \text{NH}_4^+$ with the tetrahedral bond angles of 109.47° .

5.6.5 other types of hybridization

In addition to the above hybrid orbitals, some other types of hybrid orbitals involving d orbitals are important. As shown in Table 5.4, they are related to formation of various molecular structures.

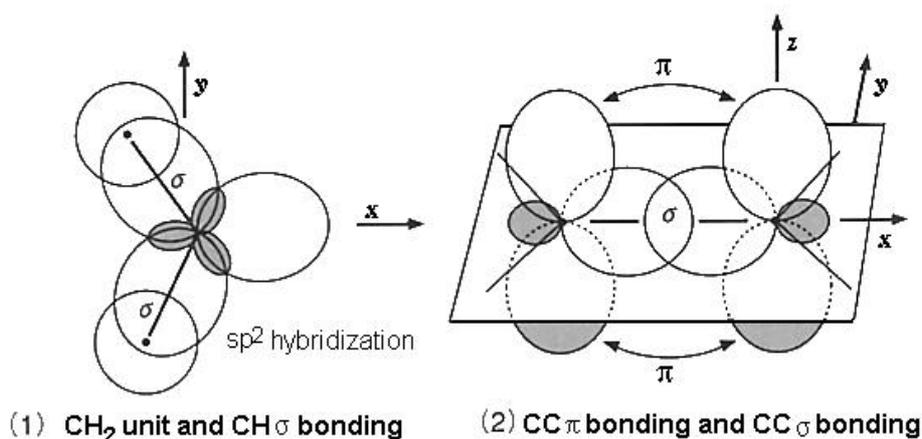
Table 5.4: Hybridization and molecular structures

Hybrid orbital	Structure	Bond angle	Example
sp	Linear form	180°	C ₂ H ₂ , HCN, BeH ₂ , HgCl ₂
sp ²	Equilateral triangle	120°	BF ₃ , NH ₃ ⁺ , C ₆ H ₆
sp ³	Tetrahedron	109.47°	CH ₄ , NH ₄ ⁺ , SiH ₄ , SO ₄ ²⁻
dsp ²	Square plane	90°	Ni(CN) ₄ ²⁻ , AuCl ₄ ⁻
sp ³ d	Trigonal-bipyramid	90° 120° 180°	PCl ₅ , AsF ₅ , SbCl ₅ (Note)
d ² sp ³	Octahedron	90°	Co(NH ₃) ₆ ³⁺ , PtCl ₆ ²⁻
sp ³ d ²	Octahedron	90°	SF ₆

(Note) The trigonal-bipyramid structure of PCl₅ can be explained by three-center-two electron bonds as discussed below.

Example 5.3 Explain the molecular structure of ethylene C₂H₄ using hybrid orbitals.

(Solution) In each C atom, three sp² hybrid orbitals together with a perpendicular p orbital can be considered for valence orbitals, and four valence electrons are inserted in either one of the four orbitals. A combination of sp² hybrid orbitals of two C atoms yields a CC bond due to σ type overlaps. Remaining two sp² hybrid orbitals with angles of 120° with respect to the CC bond axis can be used to form a pair of CHσ bonds of σ type overlaps, which results in a production of a CH₂ unit. In this step, two CH₂ units can rotate with each other along the CC bond axis, since the CC bond is a single bond, which can rotate freely to have an arbitrary angle of the rotation.



However, an overlap between a pair of p orbitals remaining at each C atom produces a CC bond due to the π type overlap, which is most effectively formed, when the p orbitals have parallel directions, namely two CH₂ become coplanar. Thus, between two C atoms, one CCσ bond between two sp² hybrid orbitals and additionally one CCπ bond from a pair of parallel p orbitals are formed to give a CC double bond. On account of the restriction of the rotation around the CC

axis by the π bond, all six atoms are located in a plane, and it follows that an ethylene molecule has a planar structure.

Effects of electrostatic attractive forces due to bonding electrons on the carbon nuclei are much stronger in the CC double bond than in CH single bonds. Thus the pulling forces by the bonding electron densities are stronger along the double bond, and hence the HCH bond angle (the bond angle between two CH bonds) should become a little smaller than 120° so that resultant forces from electron densities in two CH bonds may be balanced with the opposite force caused by the electron densities in the CC double bond; really the observed HCH angle is 117.5° .

5.7 The three-center-two-electron-bond and the hydrogen bond

As studied in the earlier parts of this chapter, a pairing of electrons is not necessary to bind two nuclei by attractive forces caused by electron densities located at middle regions between the nuclei. It is important for formation of bonds how electron densities distribute in the bonding regions between the nuclei. In this section, we will study bonds of three atoms formed by an action of two electrons.

5.7.1 Three center orbital interactions

Let us study orbital interactions involved in a system of three atoms, A, B, and C, in which C is the middle, using the simple Hückel molecular orbital method. An orbital of C χ_C can interact with orbitals χ_A , χ_B of both ends of A and B, where resonance integrals are $\beta_{AC} \neq 0$, $\beta_{BC} \neq 0$. Since the resonance integral for the long distance can be neglected, $\beta_{AB} = 0$. Coulomb integrals for these atoms are denoted as α_A , α_B , α_C . The secular equation to obtain molecular orbitals is given as follows.

$$\begin{vmatrix} \alpha_A - \varepsilon & 0 & \beta_{AC} \\ 0 & \alpha_B - \varepsilon & \beta_{BC} \\ \beta_{AC} & \beta_{BC} & \alpha_C - \varepsilon \end{vmatrix} = 0 \quad (5.51)$$

This is just the same as the secular equation in Example 5.1 (the two to one orbital interactions) in section 5.3. Thus, among the new orbitals produced by the interactions of three orbitals, the most stable orbital ϕ_b becomes lower than the lower one of χ_A , χ_B , and the most unstable orbital ϕ_a becomes higher than the higher one of χ_A , χ_B , as can be seen from Fig.5.18.

ϕ_b is a highly bonding orbital, which is composed of the same phase combinations of the central atomic orbital with those of both ends in order to increase electron densities in the middle regions between nuclei. ϕ_a is a highly antibonding orbital, which is made of the opposite phase combinations of the central atomic orbital with those of both ends in order to exclude electron densities out of the middle regions between the nuclei. On the other hand, the new orbital with intermediate stability ϕ_m is formed in an intermediate level between the levels of orbitals for both ends. If orbitals of both ends degenerate, the level of the intermediate orbital is equal to the degenerate levels. In the shape of ϕ_m , the higher one mixes with the central orbital in the same phase, and the lower one mixes with the opposite phase. This leads to a weakly bonding character in ϕ_m , as shown in Fig.5.18(a). It should be noted that, if orbitals of both ends are degenerate, one of them might be in the same phase, but the other necessarily becomes in the opposite phase. By symmetry in the degenerate case, the contribution from the central atom is completely vanishing in ϕ_m as shown in Fig.5.18(b), thus ϕ_m becomes almost nonbonding, because direct interactions between both ends are negligible from the distance.

When an electron is included in the bonding orbital ϕ_b of the three-center interactions, three atoms can be connected with their neighbors. A pair of electrons in ϕ_b gives the more strong bonding. Such types of bonds produced by a pair of electrons in the bonding orbital of the three center are called the three-center-two-electron-bond. Now, let us study some examples.

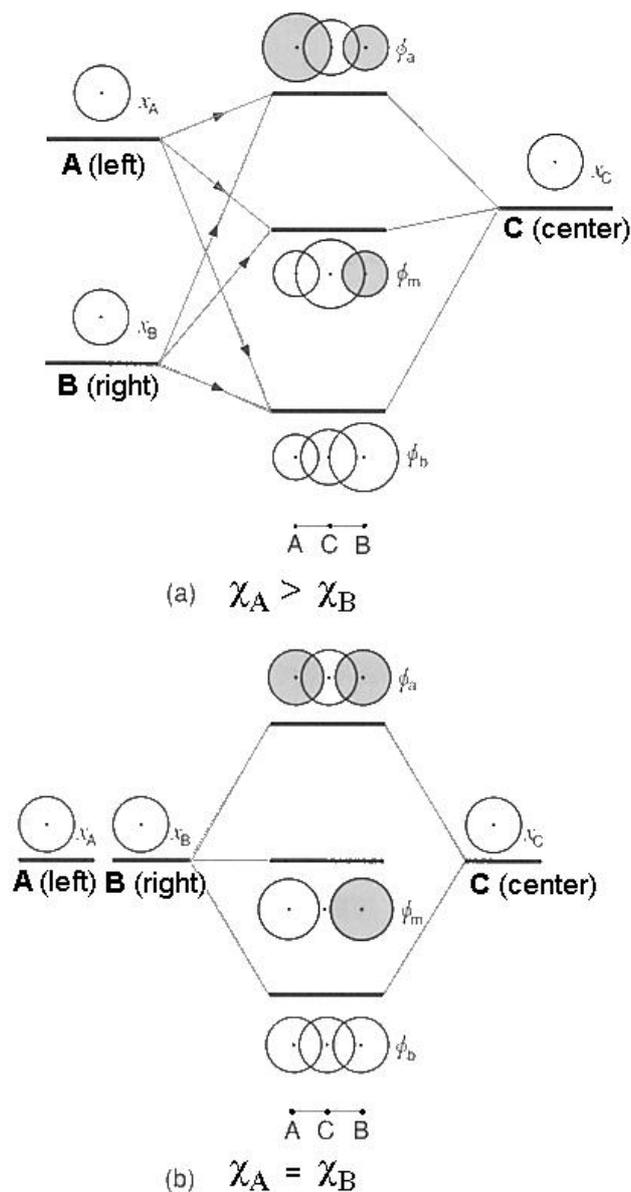
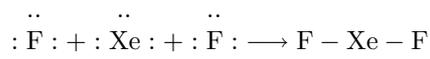


Figure 5.18: Three center orbital interactions

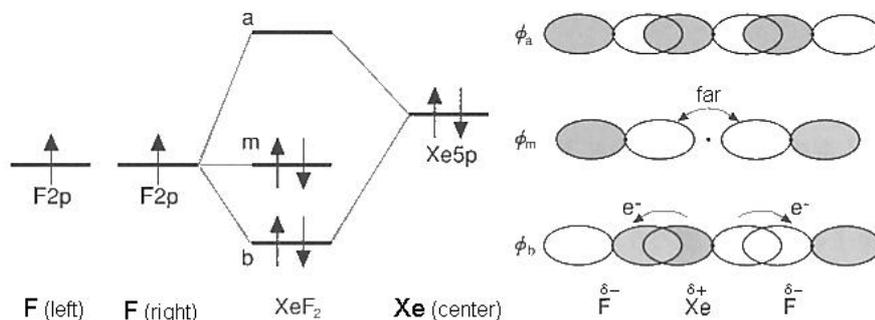
5.7.2 Linear three-center-two-electron-bonds

Putting fluorine F atoms on both sides of a xene Xe atom, we can obtain a XeF_2 molecule, in which a pair of electrons in a 5p orbital of a Xe atom interact with unpaired electrons in 2p orbitals of two F atoms aligned linearly with the central Xe atom.



Relevant energy levels can be summarized in Fig.19.

Ionization energies of a Xe atom and a F atom are 12.1 eV and 17.4 eV, respectively. Thus, Xe5p orbitals have higher energy levels than F2p orbitals. F2p orbitals do not interact each other because of the long distance and shown in the left-hand side of Fig.5.19. An electron-pair in the bonding molecular orbital ϕ_b is displaced nearer to the lower energy F2p, and a Xe atom and a F atom are bonded by electron densities of an electron. The molecular orbital of the intermediate

Figure 5.19: Three center two electron bonds in XeF_2

stability ϕ_m can be considered as a nonbonding orbital, and a pair of electrons in this orbital have no effects on the bonding and they are distributed on both F atoms, one by one in average. It follows that XeF_2 has linear three-center-two-electron-bonds with a bond-order of 1/2 for each XF bond. Although these bonds are also denoted as the three-center-four-electron-bonds, they are essentially the three-center-two-electron bonds.

Replacing a Xe atom by an iodide ion I^- with the same electron configuration and also replacing F atoms by other halogen atoms I or Cl, we can obtain linear molecular ions of I_3^- and ICl_2^- shown in Fig.5.20. In XeF_2 , one electron-pair of a 5p orbital is used for a set of three-center-two-electron-bonds. Here, another electron-pair of other 5p orbitals can also be used to produce another set of three-center-two-electron-bonds with a different direction. These two sets of three-center-bonds yield a square planar form of XeF_4 (Fig.5.20). One more set of the electron-pair in $\text{Xe}5p$ can also be used to obtain XeF_6 . The observed form of XeF_6 is slightly distorted from the expected octahedral shape.

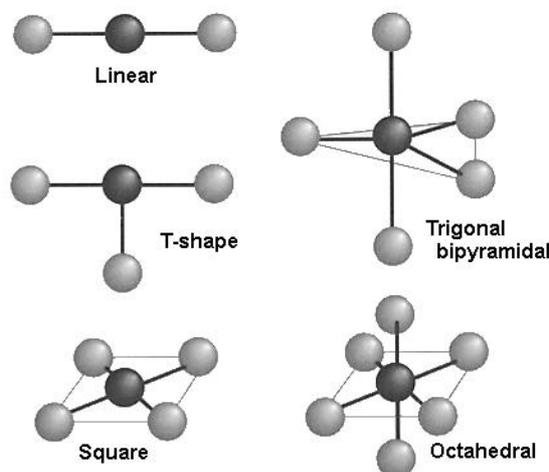


Figure 5.20: Various shapes of molecular structures

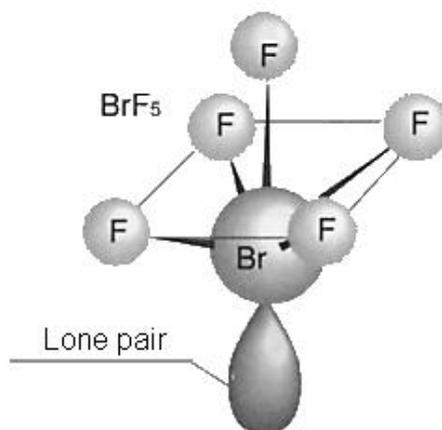
There are many other examples for the three-center-two-electron-bonds composed of an electron-pair in a p orbital and a couple of unpaired electrons in halogen atoms. In a PCl_5 molecule, each of three sp^2 hybrid orbitals around the P atom has an unpaired electron and makes an electron-pair bond with an unpaired electron in a Cl atom. It follows that an equilateral triangular form is produced. Remaining two electrons among five valence electrons of the P atom are in a vertically directed 3p orbitals as an electron-pair, which may be used to form a set of three-center-two-electron-bonds with unpaired electrons in two Cl atoms. Thus a trigonal bipyramidal molecule can be produced (Fig.5.20). Three covalent PCl bonds with a bond-order of unity in the triangle

plane are denoted as equatorial bonds (experimental bond-length is 201.7 pm), which are stronger and much shorter than two vertical PCl bonds denoted as axial bonds (experimental bond-length is 212.4 pm), since these bonds are weak bonds with a bond-order of 1/2. Although the trigonal bipyramidal structure of PCl_5 can be explained by hybrid orbitals in Table 5.4, it becomes difficult to explain differences in the bond lengths.

As similar examples including sp^2 hybrid orbitals together with a vertical p orbital leading to a set of three-center-two-electron-bonds, AB_3 type molecules, such as ClF_3 and BrF_3 can be produced. In these cases, the hybrid orbitals of the central halogen atom are composed of one unpaired electrons and two electron-pairs, and the unpaired electron is able to form a covalent bond with an unpaired electron in a F atom. Two electron-pairs in the hybrid orbitals become unshared electron-pairs. A p orbital vertical to the plane of hybridization contains an electron-pair, which can be used to produce a set of three-center-two-electron-bonds with two F atoms. Thus a T shaped molecule shown in Fig.5.20 can be formed. The horizontal line of the T shape is made of three-center bonds, and therefore the distances from the central atom in the horizontal bonds are longer than the vertical bonds (covalent bonds). Unshared electron-pairs made of hybrid orbitals are more tightly attracted with the central atom than the electron-pair in the covalent bond, and it follows that the central atom is pulled upward to give a slightly deformed form like an upward arrow \uparrow .

Example 5.4 The molecular structure of BF_5 is a form of the following figure. Using a combination of covalent bonds and three-center-two-electron-bonds, explain the molecular structure of this molecule.

(Solution) The outer-most shell electron configuration of a Br atom is $(4s)^2(4p)^5$. In a Br atom,



$4p_x$ and $4p_y$ orbitals contain an electron-pair, and a pair of sp hybrid orbitals composed of $4s$ and $4p_z$ orbitals are formed. One of the sp hybrid orbitals (towards lower) contains an electron-pair, and another one (towards upper) contains an unpaired electron. On the other hand, each F atom has an unpaired electron in a p orbital. An unpaired electron of the sp hybrid orbital in the z direction can form a covalent bond coupled with a F atom. $4p_x$ and $4p_y$ orbitals of the Br atom can be used to produce three-center-two-electron-bonds with F atoms in both x and y directions, and a square structure where four F atoms are placed on the corners is formed. The BrF bond directed upward is a strong covalent bond with a shorter bond length (the observed bond length is 171.8 pm), and BrF bonds in the horizontal plane are weak bonds due to three-center-two-electron-bonds with a longer bond length (the observed bond length is 178.8 pm). The Br atom is slightly displaced to the downward from the plane of the square, since the downward directed electron-pair pulls the Br atom more strongly than the upward directed electron-pair in the covalent bond does (the observed angle is $\angle \text{F}(\text{horizontal})\text{BrF}(\text{vertical}) = 85.1^\circ$). Alternatively an octahedral structure by sp^3d^2 hybridization can be assumed, but the short axial bond of the square pyramid will become difficult to be explained.

5.7.3 Bent three-center-two-electron-bonds

An interesting example includes bent three-center bonds with a H atom in the middle. Such a bond can be seen in hydrated compounds of boron (generally called borane). Diborane B_2H_6 is a typical example. There are two BHB bonds in a diborane molecule, and the geometrical shape has a bridge structure as shown in Fig.5.12.

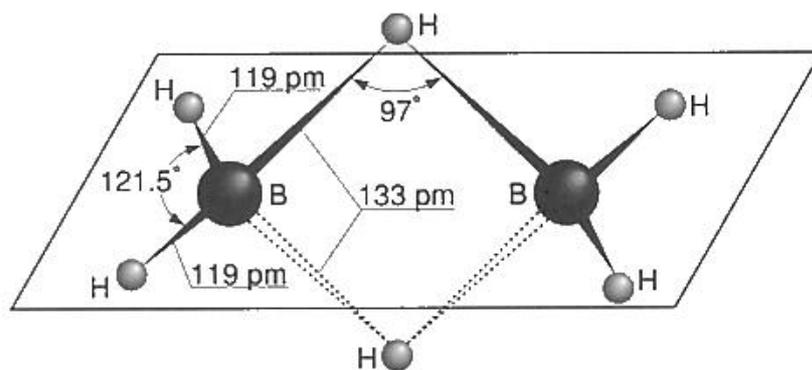


Figure 5.21: The bridge structure in diborane B_2H_6

For the B atoms sp^3 hybridization can be assumed. Two of the four sp^3 hybrid orbitals have unpaired electrons, one has an electron-pair, and the remaining one is a vacant orbital with no electron. Each of two unpaired electrons makes a covalent BH bond with a H atom, whose bond-order is unity. In the bridge structure, an unpaired electron in a H atom in the middle interact with an electron-pair in a B atom and also with a vacant orbital of another B atom to give energy levels shown in Fig.5.22, since the ionization energy of a H atom is much larger than a B atom. Orbital interactions yield bent orbitals as shown in the figure. Only the bonding orbital ϕ_b contains an electron-pair. The B atoms and a middle H atom are bonded by three-center-two-electron-bonds with a bond-order of $1/2$. Depending on the difference in the bond-orders, bridge BH bonds have longer bond lengths than the terminal BH bonds.

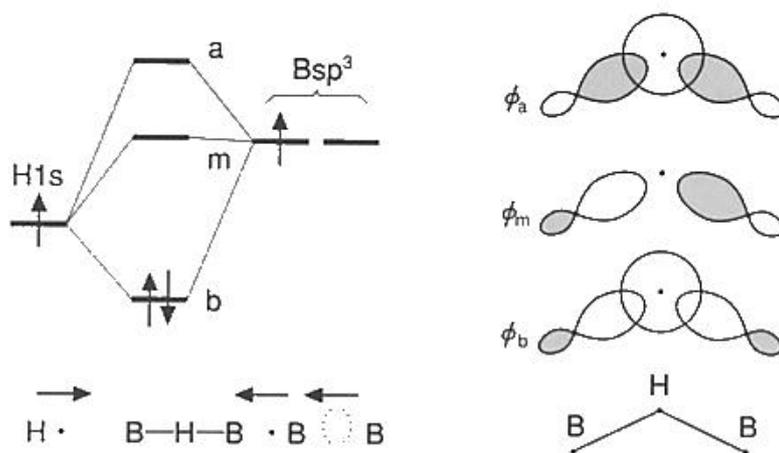


Figure 5.22: Molecular orbitals of diborane

5.7.4 The hydrogen bond

When a H atom bonded to a strongly electronegative atom X makes a new bond with another electronegative atom Y, such a bond is called the hydrogen bond. The hydrogen bond can also be considered as a sort of the three-center-two-electron-bonds. In this case, the unpaired electron energy level is rather high in comparison with valence orbitals of the electronegative atoms, and energy levels in Fig.5.23 are obtained. In this figure negative atoms X and Y are shown in the same side for convenience, though they are separated in a long distance and may be different in their energies. The electron-pair in the bonding orbital ϕ_b connect three atoms via the H atom. The XH bond becomes rather weaker than the case without the hydrogen bonding. When the negativity of the Y atom is not strong enough, the electron-pair of the bonding ϕ_b orbital concentrates its electron densities on the XH bond. The electron-pair of the ϕ_m orbital is almost nonbonding, and it has no effect on formation or dissociation of the hydrogen bond.

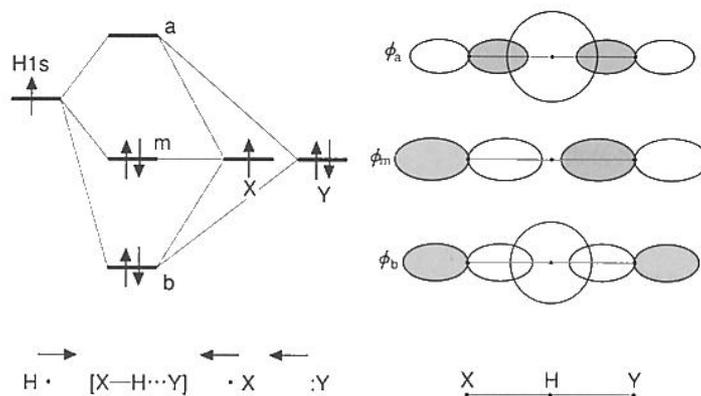


Figure 5.23: The hydrogen bond

5.8 Electron energy levels and photoelectron spectra

As studied in section 4.3, the orbital energy ε_i can be related with the observed ionization energy I_i via Koopmans formula.

$$I_i = -\varepsilon_i \quad (5.52)$$

This relationship is approximate, and the exact numerical agreement cannot be expected. As far as molecules with the singlet ground electronic states are concerned, observed ionization energies have been found to give a satisfactory one-to-one correspondence with energy levels of molecular orbitals. In this section, we will study relationships among photoelectron spectra, ionization energies, and energy levels of molecular orbitals. A photoelectron spectrum of the hydrogen molecule will also be studied in connection with the dissociation energies.

5.8.1 Photoelectron spectra and electron energy levels of molecular orbitals

The kinetic energy $\frac{1}{2}mv^2$ of a photoelectron ejected from a substance irradiated by a photon of $h\nu$ with a frequency ν in the photoelectric effect can be given by the following formula.

$$\frac{1}{2}mv^2 = h\nu - I_i \quad (5.53)$$

Here, I_i is the ionization energy of the substance. Using Koopmans' formula we obtain

$$\frac{1}{2}mv^2 = h\nu + \varepsilon_i \quad (5.54)$$

Thus, the kinetic energy of the photoelectron depends on the energy level of the molecular

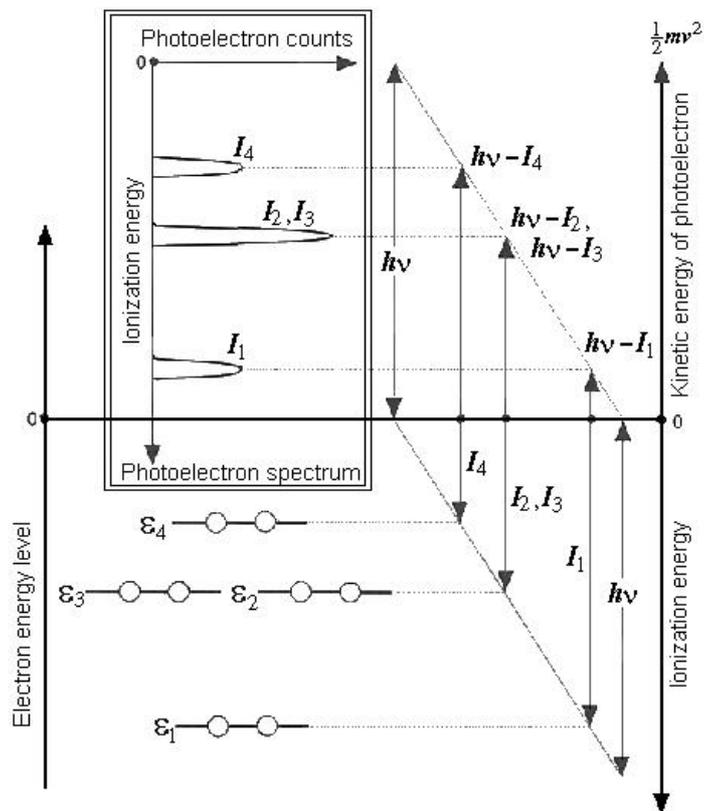


Figure 5.24: Relationships between photoelectron spectra and electron energy levels of molecular orbitals

orbital from which the photoelectron is ejected. It follows that measurements of kinetic energy distributions of photoelectrons caused by a given energy photons $h\nu$ give a photoelectron spectrum, which correspond to energy levels of molecular orbitals, as illustrated in Fig.5.24.

In general, a method measuring counts of electrons as functions of electron kinetic energies is called the electron spectroscopy. An application of the electron spectroscopy to photoelectrons ejected from sample substances by photoelectric effects is the photoelectron spectroscopy.

Fig.5.25 shows an example of an X-ray photoelectron spectrum (XPS) for a H_2O molecule measured with a photon source of the characteristic X-ray of Mg ($K\alpha$ line: 1253.6 eV). In this spectrum, there are clearly resolved five peaks corresponding to molecular orbitals. One of them is a group of the slowest photoelectrons, which can be assigned to a molecular orbital mainly composed of oxygen 1s orbital. The formula of eq.(5.54) gives a transformation of the kinetic energy to the ionization energy, and thus we obtain $I(\text{O}1s) = 539.9$ eV. Other photoelectrons have much larger energies with higher velocities, and they are slightly smaller than the photon energy 1253.6 eV of the X-ray source, since the ionization energies of the corresponding valence orbitals are much smaller than the ionization energy of the inner shell O1s level. Among the valence photoelectrons, the slowest ones give a peak of a molecular orbital mainly composed of O2s orbital, and the corresponding ionization energy is determined as $I(\text{O}2s) = 32.2$ eV. Further, peaks with ionization energies of 18.5 eV, 14.7 eV, 12.6 eV can be assigned as the following molecular orbitals of the H_2O molecule.

- 18.5 eV OH bonding molecular orbital containing $\text{O}2p_y$ atomic orbital.
- 14.7 eV HH bonding molecular orbital containing $\text{O}2p_z$ atomic orbital.
- 12.6 eV Nonbonding molecular orbital containing $\text{O}2p_x$ atomic orbital.

Based on the above correspondence, we can confirm that ten electrons in a water molecule are

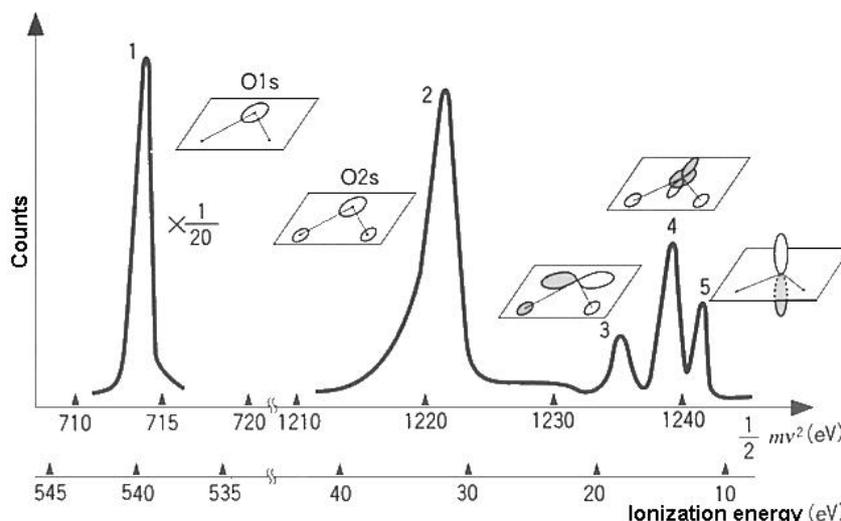


Figure 5.25: X-ray photoelectron spectrum (XPS) of the H_2O molecule measured with the Mg $K\alpha$ line

accommodated in the five molecular orbitals; in each orbital two electrons are contained as an electron-pair.

Table 5.5 lists a comparison of ionization energies I from an X-ray photoelectron spectrum with calculated orbital energies ε by an *ab initio* molecular orbital method. Although exact agreement could not be obtained, absolute values of the orbital energies agree well with the observed ionization energies within the error of 10%.

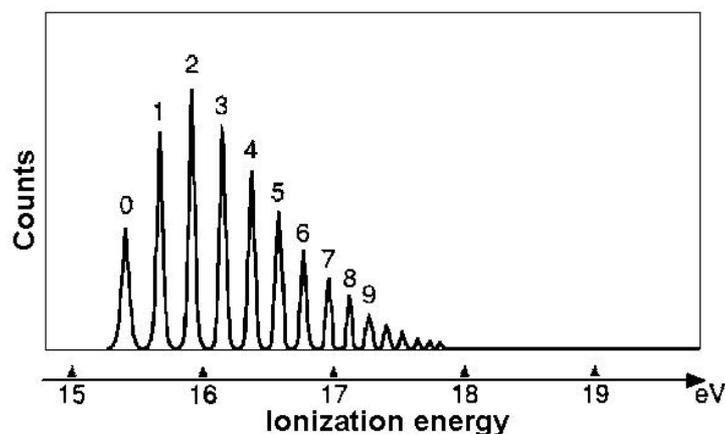
Table 5.5: Ionization energies I by XPS and orbital energies ε by an *ab initio* molecular orbital method for H_2O

Peak number	I (eV)	ε (eV)	Molecular orbital character	Main atomic orbital component
1	539.9	-558.3	Inner shell	O1s
2	32.2	-36.8	Bonding	O2s
3	18.5	-19.3	OH Bonding	O2p _y
4	14.7	-15.2	HH bonding	O2p _z
5	12.6	-13.6	Nonbonding	O2p _x

5.8.2 Photoelectron spectrum of the hydrogen molecule and the binding energies

A photoelectron spectrum measured with the ultraviolet photons is called ultraviolet photoelectron spectrum (UPS). For measurements of UPS, photons of 21.22 eV irradiated from a helium discharge, which are due to $2^1\text{P} \rightarrow 1^1\text{S}$ transitions (from 2p orbital to 1s orbital), are used in many cases. Since ultraviolet (UV) photons have much smaller energies in comparison with X-ray photons, UV photons are not enough to ionize inner-shell electrons. However, electron kinetic energies are so small that more fine structures can be resolved in UPS. When a molecular vibration is excited upon ionization, the kinetic energy of the photoelectron becomes smaller by an amount of the energy required for the vibrational excitation, since this energy is further consumed from the photon energy. In highly resolved photoelectron spectra, vibrational fine structures often appear as many peaks. In Fig.5.26 a photoelectron spectrum of the hydrogen molecule is shown as an example.

Peaks labeled by 0, 1, 2, ... in the figure indicate the vibrational quantum v of the vibrational states of produced ion H_2^+ . $v = 0$ corresponds to the vibrational ground state of H_2^+ , which is the state of zero-point vibration of the hydrogen molecule-ion. Fig.5.26 shows the most strong

Figure 5.26: Ultraviolet photoelectron spectrum of the H_2 molecule

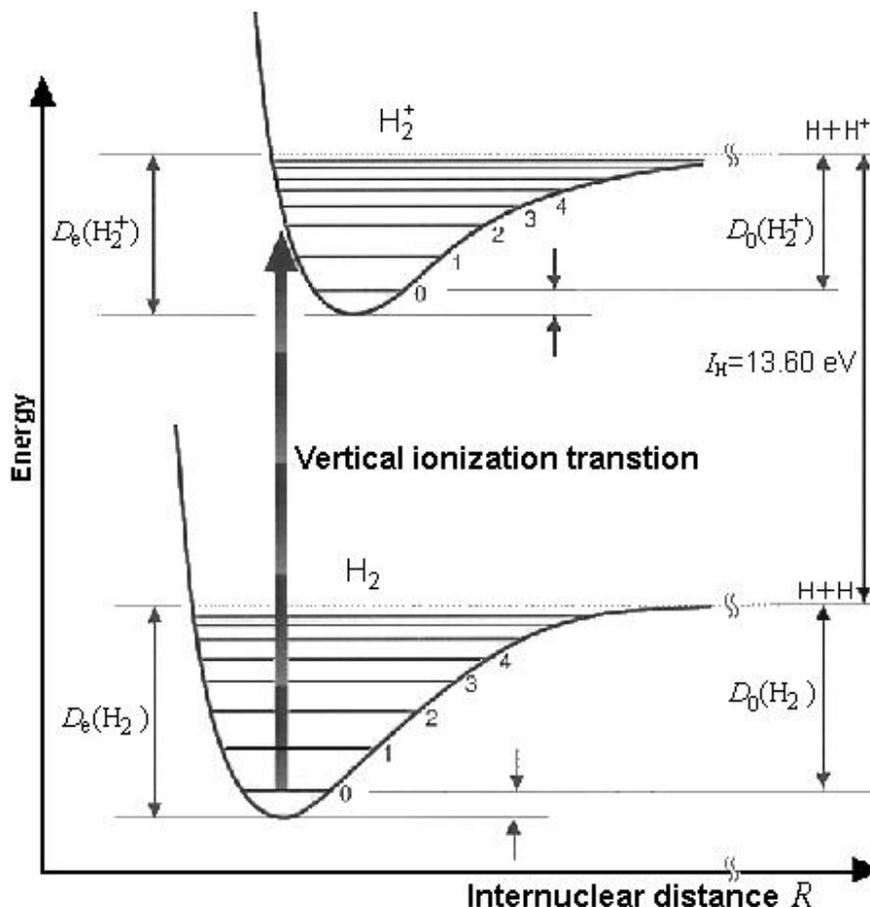
peak for $v = 2$. This is related to Franck-Condon principle, which is a well known rule for electronic transitions in molecules. According to Franck-Condon principle, electronic transitions can be considered to occur without nuclear motion. It follows that for potential energy curves as in Fig.5.27 only vertical transitions are acceptable. In real cases, vertical transitions are most likely to occur, and slightly displaced transitions can also appear though the probabilities are small. Transitions requiring large nuclear displacements hardly occur.

Since the bonding force becomes weaker in the hydrogen molecule-ion, the equilibrium nuclear distance is expected to become longer in the ion than the hydrogen molecule. The most outstanding peak of $v = 2$ in the photoelectron spectrum in Fig.5.26 indicates that just on the vertical line from the equilibrium position of H_2 the potential curve of the ion crosses with the vibrational level of $v = 2$. The ionization energy corresponding to the vertical transition is called the vertical ionization energy in general. In the case of ionization of the hydrogen molecule, the vertical ionization energy can be determined as 15.96 eV from Fig.5.26. The minimum ionization energy of the hydrogen molecule on the other hand correspond to an ionization transition to the level of $v = 0$ in the ion. Such a minimum ionization energy without vibrational excitation is called the adiabatic ionization energy, which is estimated to be 15.43 eV in the case of H_2 .

What does the limit of $v \rightarrow \infty$ in the vibrational excitation means? This corresponds to a dissociated state where the bond is completely broken. In the photoelectron spectrum in Fig.5.26 this limit of $v \rightarrow \infty$ corresponds to a dissociation of H_2^+ into a H atom and a H^+ ion. Thus, if the position of $v \rightarrow \infty$ in the spectrum can be deduced, the dissociation energy of H_2^+ , $D_0(\text{H}_2^+)$ can be obtained from $I(\infty) - I(0)$. Noting that intervals between the peaks in the spectrum decrease with the increase of v , a graphical plot of the intervals as functions of v gives a position where the interval becomes vanishing. From this procedure we can obtain the right position of the dissociation limit. The result becomes $I(\infty) = 18.08 \text{ eV}$. From this value, we obtain $D_0(\text{H}_2^+) = I(\infty) - I(0) = 18.08 - 15.43 = 2.65 \text{ eV}$ (see Table 5.3). Further, a correction of the zero point energy leads to determination of the binding energy D_e (in the case of H_2 , it is the bond energy). A careful study of peak intervals shows that the intervals almost linearly decrease. From this line we can obtain the vibrational interval at $v = 0$, and one half of this can be a good estimate of the zero-point energy. Thus we obtain

$$D_e(\text{H}_2^+) = D_0(\text{H}_2^+) + 0.14 = 2.79 \text{ eV}$$

From the spectrum in the figure, the vibrational energy quantum of H_2^+ can be estimated as about 0.28 eV. This corresponds to a wave number of ca. 2260 cm^{-1} , which is considerably smaller than the wavenumber of 4401 cm^{-1} for the molecular vibration in H_2 . This is because in the ion a loss of a bonding electron decreases the bonding force. In general, a loss of bonding electrons causing a reduction of the bonding force, which results in a reduction of the vibrational wavenumber. When a loss of antibonding electrons oppositely causes a relative increase of the bonding force to result in an increase of the vibrational wavenumber.

Figure 5.27: Potential energy curves for H_2 and H_2^+

Example 5.5 From the photoelectrons spectrum of Fig.5.26 and the ionization energy of the hydrogen atom (13.60 eV), obtain the dissociation energy of the hydrogen molecule.

(Solution) Let us denote the dissociation energy of the hydrogen molecule as $D_0(\text{H}_2)$, the ionization energy of the hydrogen atom as I_{H} , an energy required for ionization of the hydrogen molecule and dissociation of H_2^+ ion at the same time as $I(\infty)$. Then, we obtain the following relation.

$$D_0(\text{H}_2) + I_{\text{H}} = I(\infty)$$

Both sides of this equation correspond to the energy required to produce a dissociated state of the hydrogen molecule ion (a state dissociated into H and H^+) starting from the vibrational ground state (the zero-point vibrational state) of the hydrogen molecule. The left side is a path of dissociation of a hydrogen molecule in the first step followed by ionization of one of two hydrogen atoms in the second. The right side is another path of a direct transition into the dissociated ionic state. The latter can be estimated from Fig.5.26 as

$$I(\infty) = 18.08 \text{ eV}$$

Then, using $I_{\text{H}} = 13.60 \text{ eV}$, we obtain

$$D_0(\text{H}_2) = I(\infty) - I_{\text{H}} = 18.08 - 13.60 = 4.48 \text{ eV} \quad (\text{see Table 5.3})$$

Exercises

5.1 The secular equation of π orbitals for allyl CH_2CHCH_2 in the simple Hückel method is given by

$$\begin{vmatrix} \alpha - \varepsilon & \beta & 0 \\ \beta & \alpha - \varepsilon & \beta \\ 0 & \beta & \alpha - \varepsilon \end{vmatrix} = 0$$

Solve this equation, and obtain π orbital functions and their energy levels for allyl.

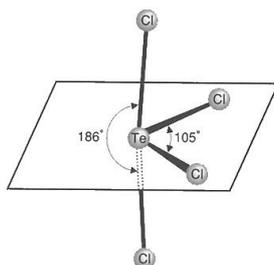
5.2 Obtain the bond-order P of N_2^+ , and compare the dissociation energy D_0 and the bond-length R of N_2^+ with those of O_2 and N_2 .

5.3 Explain qualitatively molecular orbitals and their energy levels of the HCl molecule using the principle of orbital interactions.

5.4 Explain qualitatively molecular orbitals and their energy levels of the N_2 molecule based on the principle of orbital interactions and the Example 5.1 for the two to one orbital interactions.

5.5 Explain the molecular structure of propene $\text{CH}_3\text{CH}=\text{CH}_2$ using hybrid orbitals.

5.6 Explain the molecular structure of the TeCl_4 molecule as shown in the following figure.



5.7 Using atomic orbitals (χ_j), $1s$ for the H atom, $1s, 2s, 2p_x, 2p_y, 2p_z$ for a F atom, molecular orbitals ($\phi_i = \sum_j C_{ji}\chi_j$) of the HF molecule were calculated and listed in Table 5.6. The uppermost row shows orbitals energies (ε_i eV) for molecular orbitals ϕ_i ($i = 1, \dots, 6$). In the lower rows, coefficients C_{ji} for atomic orbitals χ_j are listed. Phases (signs) for χ_j were chosen as follows; phases of s orbitals were chosen to be positive at longer distances, and phases for p orbitals were chosen to be positive at the positive direction on the respective coordinate axis commonly defined for all atoms. Carefully study this table, and answer the following questions.

- (1) Classify $\phi_1 - \phi_6$ into σ orbitals and π orbitals.
- (2) Which one among $\chi_1 - \chi_6$ is F1s orbital?
- (3) Which one among $\chi_1 - \chi_6$ is H1s orbital?
- (4) Which is(are) vacant orbital(s) among $\phi_1 - \phi_6$?
- (5) Which orbital(s) among $\phi_1 - \phi_6$ is(are) most responsible for the bonding force between the H and F atoms.

Table 5.6:

ϕ_i		ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ε_i (eV)		-704.8	-40.03	-15.92	-12.63	-12.63	-17.12
χ_1	C_{1i}	0.995	-0.249	0.083	0	0	0.085
χ_2	C_{2i}	0.023	0.936	-0.435	0	0	-0.560
χ_3	C_{3i}	0	0	0	1	0	0
χ_4	C_{4i}	0	0	0	0	1	0
χ_5	C_{5i}	-0.003	-0.090	-0.702	0	0	0.825
χ_6	C_{6i}	-0.006	0.158	0.521	0	0	1.090

5.8 Molecular orbitals (MO) of C_2H_4 were calculated as linear combinations of atomic orbitals (AO), 1s for the H atom and 1s, 2s, $2p_x$, $2p_y$, $2p_z$ for the C atom, and Table 5.7 lists the results for nine MO from the lowest in energy. The uppermost row includes orbital energies of molecular orbitals in the unit of eV. The lower rows list coefficients for AO (1 ~ 14). As AO, Slater type orbitals (STO) called STO3G were used in the calculations. Phases for s orbitals were chosen to be positive in the longer distances, and phases for p orbitals were chosen to be positive at the positive direction on the respective coordinate axis. Table 5.8 lists employed Cartesian coordinates for six atoms in the unit of Å. Carefully study these results, answer the following questions. Note that only one answer is not assumed, and find all possible answers.

- (1) Which are hydrogen atomic orbitals among 1 ~ 14 in Table 5.7 ?
- (2) Which is carbon 2s atomic orbital among 1 ~ 14 in Table 5.7 ?
- (3) Which is the lowest unoccupied molecular orbitals (LUMO) among MO (1) ~ (9) in Table 5.7 ?
- (4) Which MO contribute to formation of the $CC\pi$ bond among MO (1) ~ (9) in Table 5.7 ?
- (5) Which MO contribute to formation of the $CH\sigma$ bond among MO (1) ~ (9) in Table 5.7 ?
- (6) Which AO is $2p_x$ orbital for (1) atom in Table 5.8 ?
- (6) Which AO is 1s orbital for (5) atom in Table 5.8 ?

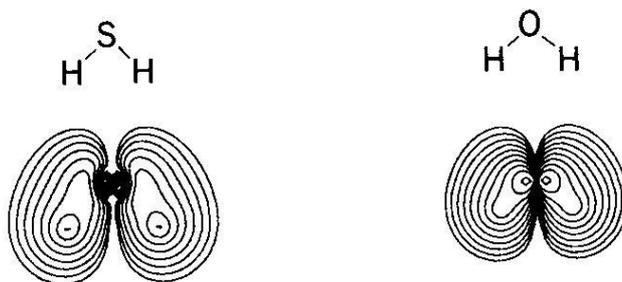
Table 5.7:

エネルギー (eV)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	-299.9	-299.8	-26.6	-20.2	-16.4	-14.4	-12.6	-8.8	8.6
1	0.702	0.701	-0.178	-0.137	0.000	0.015	0.000	0.000	0.000
2	0.702	-0.701	-0.178	0.137	0.000	0.015	0.000	0.000	0.000
3	0.020	0.031	0.471	0.416	0.000	-0.026	0.000	0.000	0.000
4	0.020	-0.031	0.471	-0.416	0.000	-0.026	0.000	0.000	0.000
5	0.002	-0.004	-0.112	0.198	0.000	0.502	0.000	0.000	0.000
6	-0.002	-0.004	0.112	0.198	0.000	-0.502	0.000	0.000	0.000
7	0.000	0.000	0.000	0.000	-0.394	0.000	0.392	0.000	0.000
8	0.000	0.000	0.000	0.000	-0.394	0.000	-0.392	0.000	0.000
9	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.636	0.810
10	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.636	-0.810
11	-0.005	0.005	0.115	-0.224	-0.260	0.217	-0.348	0.000	0.000
12	-0.005	0.005	0.115	-0.224	0.260	0.217	0.348	0.000	0.000
13	-0.005	-0.005	0.115	0.224	-0.260	0.217	0.348	0.000	0.000
14	-0.005	-0.005	0.115	0.224	0.260	0.217	-0.348	0.000	0.000

Table 5.8:

	X	Y	Z
(1)	1.338	0.0	0.0
(2)	0.0	0.0	0.0
(3)	-0.564	0.929	0.0
(4)	-0.564	-0.929	0.0
(5)	1.902	0.929	0.0
(6)	1.902	-0.929	0.0

5.9 Next figures show electron density contour maps for molecular orbitals in H₂O and H₂S molecules, which are most responsible for production of OH and SH bonds, respectively. Deduce relative magnitude of ionization energies of three atoms, S, O, and H based on these figures.



5.10 A figure below shows an observed photoelectron spectrum of the nitrogen molecule N₂ using ultraviolet photons of $h\nu = 21.218$ eV emitted from a helium discharge. Peaks of (1)-(3) are associated with vibrational structures due to excitation of molecular vibrations of N₂⁺ ion. A comparison of observed vibrational frequencies (wavenumbers) for ionic states with those for N₂ (2345 cm⁻¹) leads to the following conclusions; (1) is a weakly bonding orbital, (2) is a strongly bonding orbital, and (3) is a weakly antibonding orbital. Assign the observed bands of (1)-(3) to molecular orbitals 1 π_u , 3 σ_g , 2 σ_u , whose electron density maps are shown in Fig.4.5. Deduce the order of bondlengths of N₂⁺ in the ionic states corresponding to (1)-(3) by comparing with the bondlength for N₂.

