

# Chapter 4

## Introduction to Molecular QM

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### Basic Questions

- A. What is Born-Oppenheimer approximation?
- B. What are molecular orbitals?
- C. Is  $He_2$  a stable molecule?

## 4.1 Born-Oppenheimer approximation and electron terms

Consider a general many-body Hamiltonian of a molecule

$$\hat{H} = \hat{H}_e + \hat{H}_n + \hat{H}_{en},$$

where  $\hat{H}_e$  is the Hamiltonian of many-electrons in the molecule,  $\hat{H}_n$  is that of nuclei, and  $\hat{H}_{en}$  describes the interaction potential between the two subsystems. As nuclear mass is much larger (about 2000 times larger) than electron mass, it is a good approximation to ignore nuclear's motion and focus on the dynamics of electrons for given nuclear configuration.

We use general coordinate  $x = (x_1, x_2, \dots)$  for all electrons (spatial and spin coordinates) and  $X = (X_1, X_2, \dots)$  for all nuclei's. The total wavefunction of a molecule is separable as

$$\Psi(x, X) = \Psi_e(x, X)\Psi_n(X).$$

If we approximate  $\hat{H}_n\Psi_e(x, X) \approx \Psi_e(x, X)\hat{H}_n$  (the noncommuting kinetic part is proportional to  $1/M$ , where  $M$  is nuclear mass), we have separable Schrödinger equations, namely

$$(\hat{H}_e + \hat{H}_{en})\Psi_e(x, X) = E\Psi_e(x, X), \quad E = E(X)$$

for electrons motion with nuclei's coordinates  $X$  as parameters, and

$$[\hat{H}_n + E(X)]\Psi_n(X) = E_n\Psi_n(X)$$

for the nuclei motion. This is called **Born-Oppenheimer approximation**. Notice that  $E = E(X)$  plays a role of potential in the nuclei Schrödinger equation. Unlike QM of atoms, where energy levels are certain numbers, energy levels  $E(X)$  here are not numbers but functions of parameters  $X$ , or the distances between the nuclei in the molecule. We also refer these energy levels  $E(X)$  as **electron terms** for the molecule, as they reflect the symmetries of the molecular structures. Electron terms of diatomic molecules are functions of only one parameter, the distance  $R$  between two nuclei.

The atomic states are represented by spectral terms  $^{(2S+1)}L_J$ . The classification of atomic terms is according to the values of the total orbital angular momentum  $L$  as discussed in Chapter 2. In molecules, there is no law of conservation for total angular momentum because electric field of several nuclei is not centrally symmetric. However, for diatomic molecules, the field has axial symmetry about an axis passing through two nuclei, hence its angular momentum component is conserved. We can

therefore classify molecular energy levels according to values of this component. The quantum number for this orbital angular momentum component is usually denoted as  $\Lambda$ . For  $\Lambda = 0, 1, 2, \dots$ , the notation of electron terms are  $\Sigma, \Pi, \Delta, \dots$  etc. The total spin is denoted as upper-left index as

$$^{(2S+1)}\Lambda .$$

For example,  $^3\Pi$  denote an energy state of the molecule with  $\Lambda = 1$  and  $S = 1$ .

There is also reflection symmetry about the axis  $\pm$ , and notation  $^{(2S+1)}\Lambda^\pm$ . For diatomic molecule of two similar atoms, there is another symmetry at the center point bisecting the line joining the two nuclei, the parity symmetry (Hamiltonian remains unchanged if all electrons coordinates change sign). Even wavefunction denotes by  $g$  and odd denoted by  $u$ . The electron terms for such diatomic molecules are denoted as  $^{(2S+1)}\Lambda_{u,g}^\pm$ . We will mainly study diatomic molecules in this chapter.

## 4.2 Molecular orbitals

As stated in Born-Oppenheimer approximation, we will try to solve Schrödinger equation for electrons in a molecule for a given nuclei configuration, i.e., ignoring nuclear kinetic energy. A practical approach will be to use atomic wavefunctions of each atom in the molecule. For the ground state and low-lying excitation states, a linear combination of atomic ground states associated with each nucleus will be a good starting point. Such states are often referred to as **molecular orbitals**. We will use the variational method discussed in Chapter 3 to obtain approximations for the ground state and ground-state energy of a molecule.

Consider a trial wavefunction  $\Psi$  as given by a linear combination of atomic orbitals  $\psi_i$  ( $i = 1, 2, \dots$ ) with index  $i$  denoting different nuclei,

$$\Psi = \sum_i c_i \phi_i ,$$

where  $c_i$  are parameters (assumed real) to be determined by variational method for a given molecular Hamiltonian  $\hat{H}$ . Introducing two special integrals,

$$H_{ij} \equiv \langle \phi_i | \hat{H} | \phi_j \rangle , \quad S_{ij} \equiv \langle \phi_i | \phi_j \rangle ,$$

where  $H_{ij}$  is referred to as Hamiltonian matrix and  $S_{ij}$  the overlap integrals. The energy expectation is given by

$$E = \langle \hat{H} \rangle = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_{i,j} c_i c_j H_{ij}}{\sum_{i,j} c_i c_j S_{ij}} .$$

Variational equations  $\partial E/\partial c_k = 0$  is derived as

$$\begin{aligned} \frac{\partial E}{\partial c_k} &= \frac{\sum_j c_j H_{kj} + \sum_i c_i H_{ik}}{\sum_{i,j} c_i c_j S_{ij}} - \frac{(\sum_j c_j S_{kj} + \sum_i c_i S_{ik}) \sum_{i,j} c_i c_j H_{ij}}{(\sum_{i,j} c_i c_j S_{ij})^2} \\ &= \frac{\sum_j c_j [H_{kj} - ES_{kj}] + \sum_i c_i [H_{ik} - ES_{ik}]}{\sum_{i,j} c_i c_j S_{ij}} = 0, \end{aligned}$$

where in the last equation, we have used the expression for  $E$ . This is satisfied if each term in the numerator vanishes,

$$\sum_i c_i [H_{ik} - ES_{ik}] = 0.$$

The condition for existence of solutions is that the secular determinant should be zero

$$\det |H_{ik} - ES_{ik}| = 0.$$

Therefore, the basic procedure in molecular calculations is to first calculate the Hamiltonian matrix  $H_{ik}$  and overlap integrals  $S_{ik}$ , and then to diagonalize the above secular determinant to obtain eigenvalues  $E$  and the coefficients  $c_i$ . We will discuss the simplest case  $\text{H}_2^+$  first in the next section and then use its solutions to discuss the structures of other diatomic molecules. The basic strategy is similar to that employed in atomic physics discussed in Chapter 2.

### 4.3 Hydrogen molecular ion

In order to study a diatomic molecule, we first consider hydrogen molecular ion  $\text{H}_2^+$ , namely, one electron moving in the field of two protons. This strategy is similar to atomic QM, where we first study hydrogen atom and use its wavefunctions as basis for other atoms. Using Born-Oppenheimer approximation, let two protons fixed at positions  $\pm \mathbf{R}/2$ , the single electron eigenequation becomes

$$\left( -\frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{R}/2|} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} + \mathbf{R}/2|} + \frac{e^2}{4\pi\epsilon_0 R} \right) \psi(\mathbf{r}, \mathbf{R}) = E(R)\psi(\mathbf{r}, \mathbf{R}),$$

where the 2nd and 3rd terms are attractive interaction between the electron and the two protons and the last term (constant) is the repulsive interaction between two protons. These two contributions combine to give total energy with a minimum at an equilibrium position  $R_0$  (the size of the molecule), as shown in Fig. 1. Qualitatively, we can understand the energy curve as in the following argument. At large

separation  $R \rightarrow \infty$ , the electron will be bound to one of nucleus, the energy is about  $-13.6$  eV. When  $R \rightarrow 0$ , the electron will be bound to  $Z = 2$  nucleus with energy  $-13.6Z^2 = -54.4$  eV plus nuclear repulsion energy which goes to infinity as  $R \rightarrow 0$ . The equilibrium minimum energy  $E(R_0)$  is between these two positions.

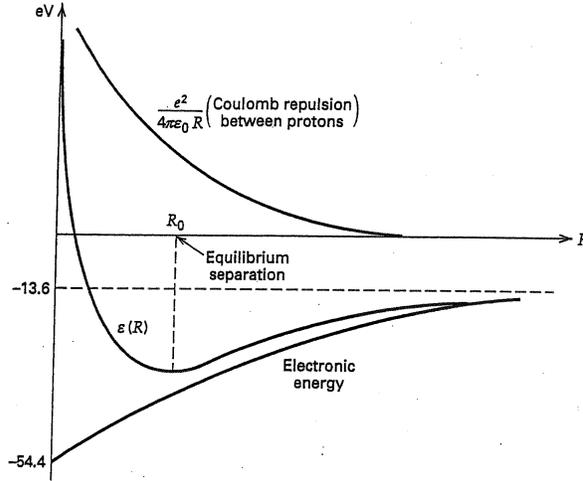


Fig. 1 Hydrogen ion energy as a function of separation of the two protons.

We follow the procedure as discussed in Sec. 2 to calculate the ground-state energy, using molecular orbital method. We consider a trial wavefunction based on single hydrogen ground-state wavefunctions  $\phi = \phi_{1s}$  centered at  $\mathbf{R}/2$  denoted as  $\phi_1$  and at  $-\mathbf{R}/2$  denoted as  $\phi_2$ . Our trial wavefunction is a linear combination of these two hydrogen ( $1s$ ) orbitals,

$$\psi(\mathbf{r}, \mathbf{R}) = c_1\phi_1 + c_2\phi_2 ,$$

where

$$\phi_1 = \frac{1}{\sqrt{\pi a_0^3}} e^{-|\mathbf{r}-\mathbf{R}/2|/a_0}, \quad \phi_2 = \frac{1}{\sqrt{\pi a_0^3}} e^{-|\mathbf{r}+\mathbf{R}/2|/a_0} .$$

The overlap integral  $S$  is

$$S = S_{12} = S_{21} = \langle \phi_1 | \phi_2 \rangle .$$

Note that  $S_{11} = S_{22} = 1$  due to normalization of  $1s$  orbitals. The Hamiltonian matrix

$$\alpha = H_{11} = H_{22} = \langle \phi_1 | \hat{H} | \phi_1 \rangle , \quad \beta = H_{12} = H_{21} = \langle \phi_1 | \hat{H} | \phi_2 \rangle .$$

The secular equation from Sec. 2 is

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0 , \quad \text{or } \alpha - E = \pm(\beta - ES) .$$

This equation has solutions

$$E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S}.$$

The corresponding values for the coefficients (see Exercise 4),

$$c_1 = c_2 = c_+ = \frac{1}{\sqrt{2(1+S)}} \quad \text{for } E_+$$

and

$$c_1 = -c_2 = c_- = \frac{1}{\sqrt{2(1-S)}} \quad \text{for } E_-.$$

The actual values for  $S$ ,  $\alpha$  and  $\beta$  can be calculated exactly by using the so-called ellipsoidal coordinates (see Handout 4). Here we just quote the results. The overlap integral is given by

$$S = \left[ 1 + \frac{R}{a_0} + \frac{1}{3} \left( \frac{R}{a_0} \right)^2 \right] e^{-R/a_0}.$$

The diagonal Hamiltonian matrix element is

$$\alpha = E_{1s} - J + \frac{e^2}{4\pi\epsilon R}, \quad J \equiv \frac{e^2}{4\pi\epsilon} \langle \phi_1 | \frac{1}{r_2} | \phi_1 \rangle = \frac{e^2}{4\pi\epsilon R} \left[ 1 - \left( 1 + \frac{R}{a_0} \right) e^{-2R/a_0} \right],$$

where the first term is the hydrogen ground-state energy, second term  $J > 0$  corresponds to the electrostatic energy between electron with charge distribution  $\phi_1^2$  and the nucleus 2. The off-diagonal element is

$$\beta = \left( E_{1s} + \frac{e^2}{4\pi\epsilon R} \right) S - K, \quad K \equiv \frac{e^2}{4\pi\epsilon} \langle \phi_1 | \frac{1}{r_1} | \phi_2 \rangle = \frac{e^2}{4\pi\epsilon a_0} \left( 1 + \frac{R}{a_0} \right) e^{-R/a_0},$$

where  $K > 0$  has no direct classical analogue. It represents the interaction between the overlap charge  $-e\phi_1\phi_2$  and the nucleus 1. Notice that all three special integrals  $S, J, K \rightarrow 0$  as  $R \rightarrow \infty$ .

In summary, the two energies of hydrogen ion using MO are

$$\begin{aligned} E_+ &= E_{1s} + \frac{e^2}{4\pi\epsilon R} - \frac{J+K}{1+S}, \\ E_- &= E_{1s} + \frac{e^2}{4\pi\epsilon R} - \frac{J-K}{1-S}, \end{aligned}$$

and the corresponding two states are

$$\psi_+ = c_+(\phi_1 + \phi_2), \quad \psi_- = c_-(\phi_1 - \phi_2).$$

As both  $J$  and  $K$  are positive,  $E_+$  is lower than  $E_-$ . Their behaviors as functions of separation  $R$  are shown in Fig. 2. There is a clear minimum  $R_0$  for  $E_+$ . We refer state  $\psi_+$  as bonding orbital with lower energy and  $\psi_-$  as antibonding state with higher energy. Numerically, the bonding energy has a minimum at  $R_0 = 130$  pm and the dissociation energy ( $E_{1s} - E_+$ ) is about 170 kJ/mol. The experimental values are 106 pm and 251 kJ/mol. More accurate calculations reveal major bonding energy comes from further shrinkage of the orbitals on to the nuclei which is beyond the simple approximation employed here.

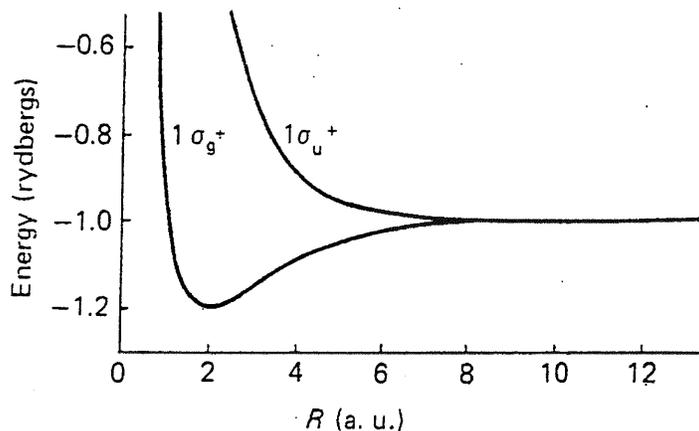


Fig. 2. Energy of bonding state  $\psi_+$  (denoted as  $\sigma_g$ ) and of antibonding state  $\psi_-$  (denoted  $\sigma_u$ ) as function of separation  $R$ .

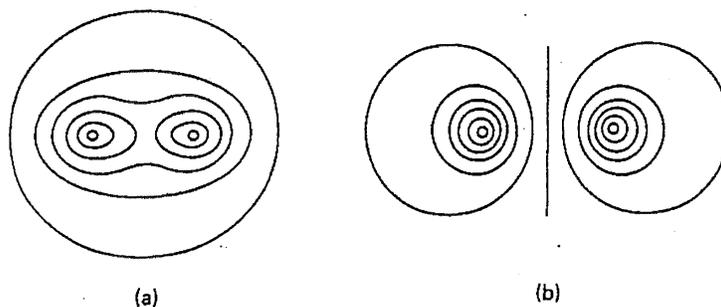


Fig. 3. Charge distribution  $|\psi|^2$  of  $\text{H}^+_2$ . (a) Bonding state. (b) Antibonding state.

## Special integrals using ellipsoidal coordinates

For hydrogen molecule ion, we introduce ellipsoidal coordinates

$$\mu = \frac{r_1 + r_2}{R}, \quad \nu = \frac{r_1 - r_2}{R}$$

with volume element in integral

$$d^3r = \frac{1}{8}R^3(\mu^2 - \nu^2)d\mu d\nu d\phi, \quad 1 \leq \mu < \infty, \quad -1 \leq \nu \leq 1, \quad 0 \leq \phi \leq 2\pi.$$

Using the transformation

$$r_1 = \frac{1}{2}(\mu + \nu), \quad r_2 = \frac{1}{2}(\mu - \nu),$$

the integrals become elementary. For example, the overlap integral

$$\begin{aligned} S &= \langle \psi_1 | \psi_2 \rangle = \frac{1}{\pi a_0^3} \int d^3r e^{-(r_1+r_2)/a_0} = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\infty d\mu \int_{-1}^1 d\nu \frac{1}{8} R^3 (\mu^2 - \nu^2) e^{-\mu R/a_0} \\ &= \left[ 1 + \frac{R}{a_0} + \frac{1}{3} \left( \frac{R}{a_0} \right)^2 \right] e^{-R/a_0}. \end{aligned}$$

Please note  $S \rightarrow 0$  as  $R \rightarrow \infty$ .

## 4.4 Structures of homonuclear diatomic molecules

We now extend our discussion to other molecules. We will use the molecular version of the building-up principle. We first determine molecular orbitals (by linear combination of atomic orbitals as shown for  $\text{H}_2^+$ ) and the order of their energies and then feed in the appropriate number of electrons into the lowest available orbitals consistent with Pauli exclusion principle.

As discussed in previous section for  $\text{H}_2^+$ , in Fig. 4, we sketch the molecular energy diagram, indicating two hydrogen atomic energies at each side, and the lower bonding energy and higher antibonding energy levels in the middle. The notation  $\sigma$  or  $\sigma^*$  denote  $\sigma$  bonding or antibonding (nonzero overlap integral centered at bonding region). The single electron of  $\text{H}_2^+$  simply occupies the lowest  $\sigma$  bonding orbital as  $(1s\sigma_g)^1$ , where  $g$  denotes the even parity of the orbital.

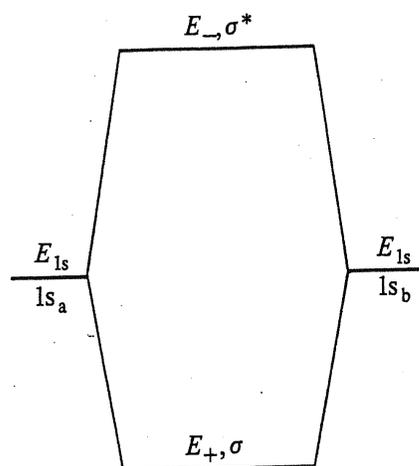


Fig. 4. Molecular orbital energy level diagram for  $\text{H}_2$ .

For molecule  $\text{H}_2$ , there are two electrons. They can both occupy the bonding state  $\sigma$  with opposite spins. The corresponding electron configuration is  $(1s\sigma_g)^2$ . The molecular electron term symbol is then  $^1\Sigma_g$  because both spin and orbital angular momentum (the component in the nuclear axis) are zero. The full form of  $\text{H}_2$  wavefunction is

$$\Psi(1, 2) = \psi_+(\mathbf{r}_1)\psi_+(\mathbf{r}_2)\chi_{12}, \quad \chi_{12} = \frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2),$$

where  $\psi_+(\mathbf{r})$  is the  $\sigma$  bond state

$$\psi_+(\mathbf{r}) = c_+[\phi_a(\mathbf{r}) + \phi_b(\mathbf{r})]$$

as discussed in the previous section, with  $\phi_a$  and  $\phi_b$  as the two hydrogen ground-state (1s) orbitals centered at the two protons respectively. The hydrogen molecule Hamiltonian  $\hat{H}$  will contain additional terms for the second electron, similar to the first electron of hydrogen molecule ion,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{1a}} - \frac{e^2}{4\pi\epsilon_0 r_{1b}} - \frac{e^2}{4\pi\epsilon_0 r_{2a}} - \frac{e^2}{4\pi\epsilon_0 r_{2b}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{ab}},$$

where the term containing  $r_{12}$  represents the Coulomb repulsion potential between the two electron and  $r_{ab} = R$  is the separation between the two protons. The energy expectation  $E = \langle \Psi | \hat{H} | \Psi \rangle$  can be done analytically, though it is much more tedious than that of  $\text{H}_2^+$ . The numerical results give energy minimum at  $R = r_{ab} = 74$  pm and dissociation energy (the energy difference between  $\text{H}_2$  and two well separated H atoms) is 350 kJ/mol, comparing with experimental results of 74.2 pm and 432 kJ/mol. Although these results are reasonable, there is room for improvement.

We next consider a possible molecule  $\text{He}_2$  formed by two He atoms. There are 4 electrons. The electron configuration is  $(1s\sigma)^2(1s\sigma^*)^2$ , i.e., two electrons are in the bonding orbital  $\sigma_g$  and the other two are in the antibonding orbital  $\sigma_u^*$ . Qualitatively, we can argue that the negative bonding energy between the first two electrons will mostly be canceled by the positive antibonding energy of the other two electrons. We conclude that  $\text{He}_2$  is unstable. We can extend this qualitative argument to other molecules. We define **bonding order** as the difference between number of bonds and that of antibonds (two electrons forming a single bond). The bonding order of  $\text{He}_2$  is zero and  $\text{He}_2$  is unstable.

In order to discuss other higher order homonuclear diatomic molecules, we need to construct more molecule orbitals. From discussion of  $\sigma$  bonding of  $\text{H}_2^+$ , we recognize that the overlap between atomic orbitals centered at different nuclear positions is crucial in establishing bonding. We need to discuss overlap between higher order atomic orbitals. The symmetries of atomic wavefunction are therefore important. For atomic orbitals, we review their wavefunction symmetries by sketching their structures in Fig. 5. Using symmetry argument, we conclude that s- and  $p_z$ -orbitals have nonzero overlap and may participate in bonding and give rise to cylindrically symmetric orbitals. We refer these orbitals as  **$\sigma$ -orbitals**. On the other hand, the perpendicular  $p_x$ - and  $p_y$ -orbitals may overlap in broadside sense and give rise to the so-called  **$\pi$ -orbitals**. Notice that overall overlap integrals between  $p_{x,y}$ -orbitals and  $p_z$ -, s-orbitals are zero due to their atomic orbital symmetry.

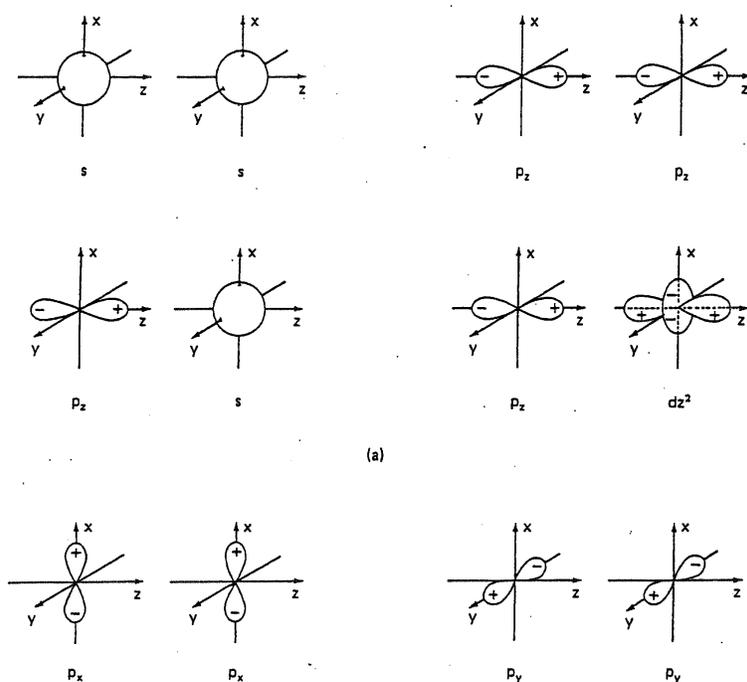


Fig. 5. Structures of atomic orbitals.

We can now set up molecular-orbital (MO) energy level diagram as shown in Fig. 6. The two lowest levels are from (1s) bonding ( $\sigma$ ) and antibonding ( $\sigma^*$ ). The next two from (2s) orbitals of similar levels. For the p-orbitals,  $p_z$ -orbitals contribute two  $\sigma$  orbitals and  $p_{x,y}$  contribute four  $\pi$  orbitals. These energy structure is shown in Fig. 6(a). The more detailed calculations show that due to the overlap between 2s orbital with  $p_z$  orbitals, forming **hybrid orbitals**. The  $2s\sigma^*$  level is pushed lowered slightly and  $2p\sigma$  level is pushed up and becomes higher than the energy of  $2p\pi$  orbital. Therefore we have new, more accurate energy level diagram as shown in Fig. 6(b). The corresponding electron configuration is then given by

$$(1s\sigma_g)(1s\sigma_u^*)(2s\sigma_g)(2s\sigma_u^*)(2p\pi_u)(2p\sigma_g)(2p\pi_g^*)(2p\sigma_u^*) \cdots ,$$

where each of  $\pi$ -orbital (with  $x, y$  components) can take up to 4 electrons, and each of  $\sigma$  can take up to 2 electrons.

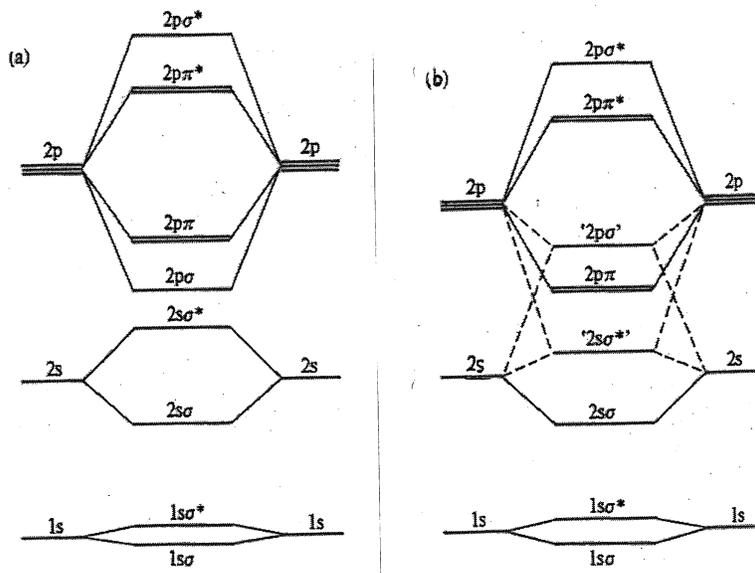


Fig. 6. (a) Simple and (b) more accurate MO energy level diagram.

Using this MO energy diagram, we can now consider other higher-order diatomic molecules. Nitrogen molecule  $N_2$  has 14 electrons. Its electron configuration is

$$(1s\sigma_g)^2(1s\sigma_u^*)^2(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\pi_u)^4(2p\sigma_g)^2,$$

and the molecular term is  $^1\Sigma_g$ . The bonding order is 3. So  $N_2$  molecule has a triple bond consisting two  $\pi$ -bonds and one  $\sigma$ -bond.

For  $O_2$ , the 16 electron will be in the configuration

$$(1s\sigma_g)^2(1s\sigma_u^*)^2(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\pi_u)^4(2p\sigma_g)^2(2p\pi_g^*)^2,$$

where the last two electrons in the  $\pi^*$ -orbitals can be accommodated in different ways. If they both enter the same orbital (hence total angular momentum about the axis is  $\pm 2\hbar$ ), we have term symbol  $^1\Delta$  as total spin must be zero. If one electron enter  $\pi^*$  orbital with  $l = 1$  and the other with  $l = -1$ , we have term symbol  $^1\Sigma$  or  $^3\Sigma$ , depending on their total spin. Here we can use Hund's rule of atomic physics and argue that energy level with the largest total spin has lower energy due to reducing the Coulomb repulsion. Therefore  $^3\Sigma_g$  is the ground state of  $O_2$  and  $O_2$  is a doubly-bounded species (the bond order to 2).

The molecule  $F_2$  has configuration  $\cdots(2p\pi_u)^4(2p\sigma_g)^2(2p\pi_g^*)^4$ . The ground state is  $^1\Sigma_g$  with a single bond.

The case of  $C_2$  is instructive. Using the building-up principle as before, we have configuration

$$(1s\sigma_g)^2(1s\sigma_u^*)^2(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\pi_u)^4 ,$$

hence  $^1\Sigma_g$ . But in fact the ground state of  $C_2$  molecule is found to be  $^3\Pi_u$ . The reason is the last two electrons enter the orbitals in different way as  $\cdots(2p\pi_u)^3(2p\sigma_g)$ , i.e., one in  $2p\pi_u$ -orbital and the other in  $2p\sigma_g$ -orbital. Although  $2p\sigma_g$  has higher energy than  $2p\pi_u$  is, this is more than compensated by the reducing electron-electron repulsion due to the fact that electrons are in different space. This example shows the limitation of our molecular orbitals approach. The electron configuration of  $C_2$  is therefore

$$(1s\sigma_g)^2(1s\sigma_u^*)^2(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\pi_u)^3(2p\sigma_g)^1 .$$

The bond order is two. In general, more accurate calculations by a quantum many-body theory will provide better descriptions of molecular ground and excited states.

Most discussion of molecule QM in this chapter can be found in *Molecular Quantum Mechanics*, P.W. Atkins, Oxford University Press, 1983.