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By
Dr. Uttam Kumar Das, Assistant Professor
Department of Chemistry
School of Physical Sciences
Mahatma Gandhi Central University, Bihar

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 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 H_2^+ , in Fig. 1, 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 σ or σ^* denote σ -bonding or antibonding (nonzero overlap integral centered at bonding region).

The single electron of H_2^+ simply occupies the lowest σ bonding orbital as $(1\sigma_g)^1$, where g denotes the even parity of the orbital.

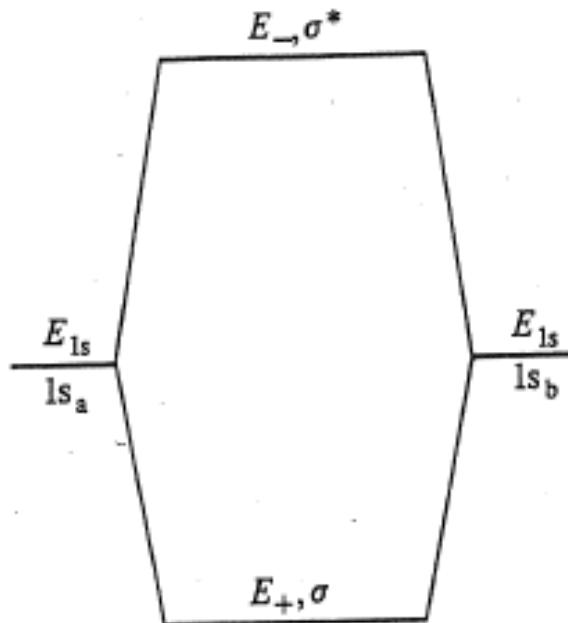


Fig. 1. Molecular orbital energy level diagram for H₂

For molecule H₂, there are two electrons. They can both occupy the bonding state σ with opposite spins. The corresponding electron configuration is $(1\sigma_g)^2$.

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 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 σ bond state

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

as discussed in the earlier, with ϕ_a and ϕ_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 electrons and $r_{ab} = R$ is the separation between the two protons. The energy expectation $E = \langle \psi | \mathbf{H} | \psi \rangle$ can be done analytically, though it is much more tedious than that of H_2^+ . The numerical results give energy minimum at $R = r_{ab} = 74$ pm and dissociation energy (the energy difference between 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.

The He_2 molecule is 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 σ_g and the other two are in the antibonding orbital σ_u^* .

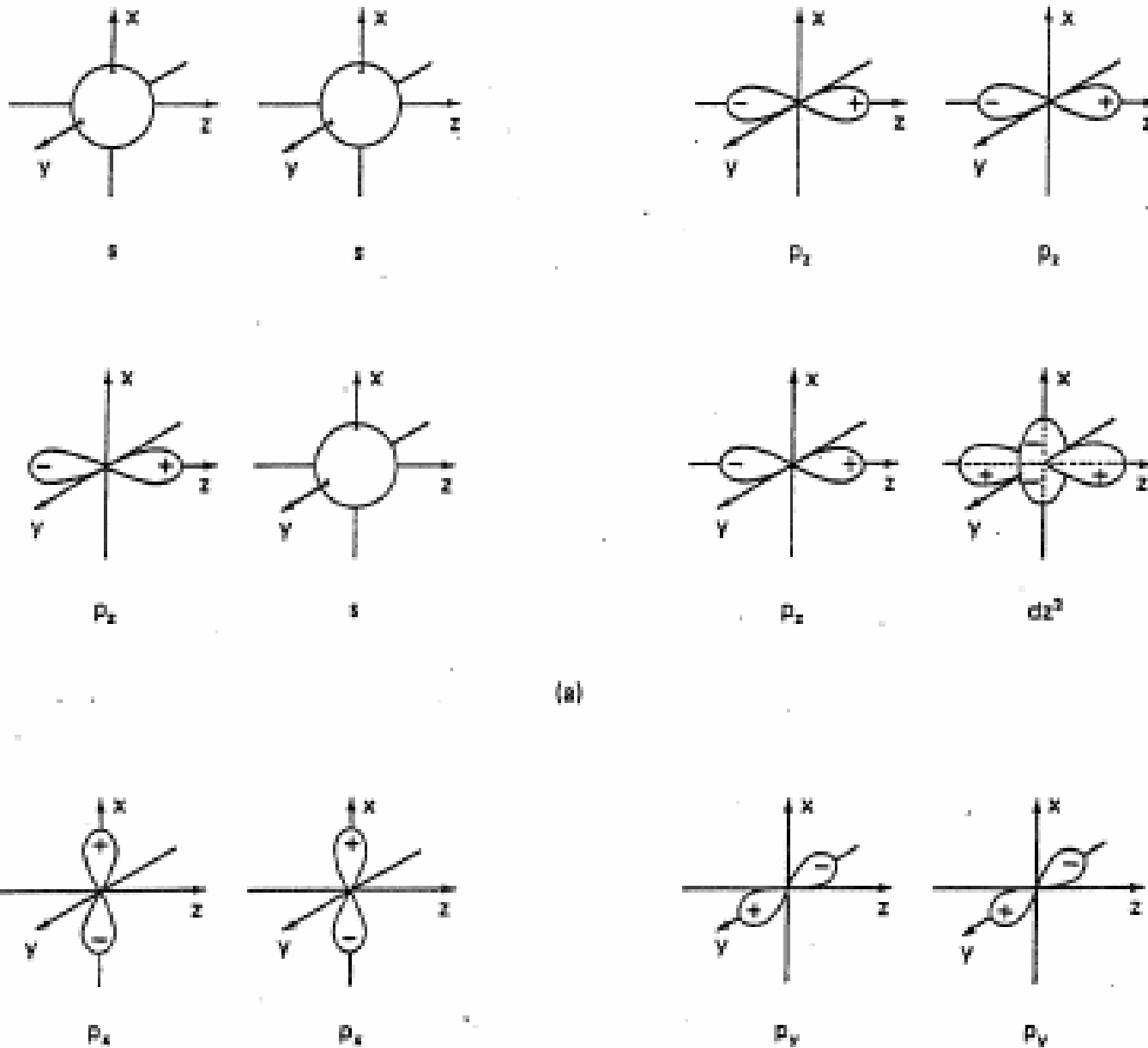
We can show that the negative bonding energy between the first two electrons will mostly be canceled by the positive antibonding energy of the other two electrons and that is why that He_2 molecule is unstable.

- We can extend this qualitative argument to the 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 He_2 is zero and He_2 is unstable. In order to discuss other higher order homonuclear diatomic molecules, we need to construct more molecule orbitals.

- From discussion of σ bonding of 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. 2**.
- 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 σ -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 π -orbitals. Notice that overall overlap integrals between $p_{x,y}$ -orbitals and p_z -, s-orbitals are zero due to their atomic orbital symmetry.



(a)

Figure 2: 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 (σ) and antibonding (σ^*). The next two from (2s) orbitals of similar levels. For the p-orbitals, p_z -orbitals contribute two σ orbitals and $p_{x,y}$ contribute four π orbitals. This 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 lower 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



where each of π -orbital (with x, y components) can take up to 4 electrons, and Each of σ can take up to 2 electrons.

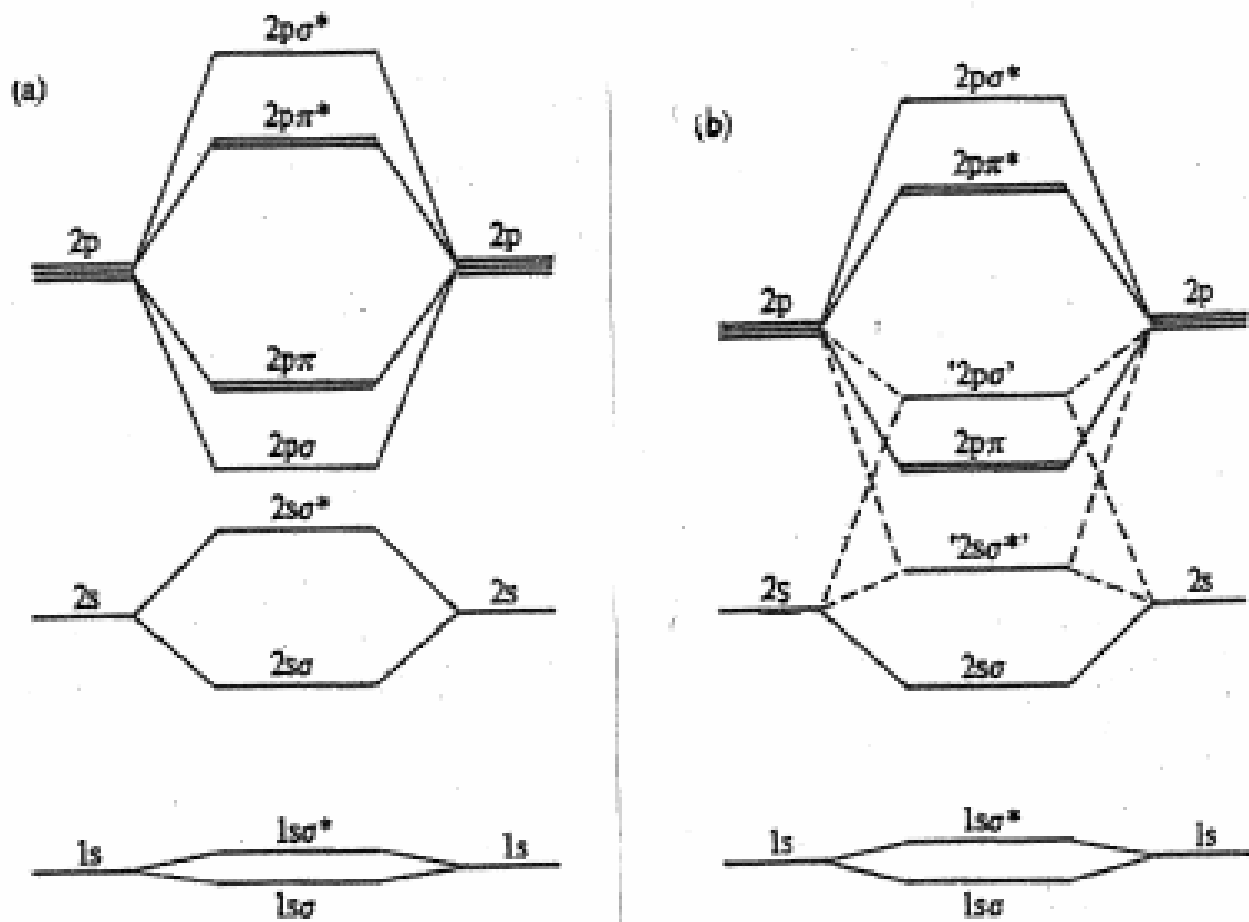


Fig. 6. (a) Simple and (b) more accurate MO energy level diagram.

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



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

For O_2 , the 16 electron will be in the configuration



where the last two electrons in the π^* -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 enters π^* 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-bonded species (the bond order is 2).

The molecule F_2 has configuration ... $(2p\pi_u)^4(2p\sigma_g)^2(2p\pi_g^*)^4$.
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 $(2p\pi_u)^3(2p\sigma_g)$, 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 manybody theory will provide better descriptions of molecular ground and excited states.

Reference:

- 1) Molecular Quantum mechanics, Atkins and Friedman,
4th edition**
- 2) Physical Chemistry by K. L. Kapoor**
- 3) Physical Chemistry by Levine**