

### CHEM 352: Examples for chapter 3.

1. a) Show that  $sp^2$  hybrid orbital  $h = \frac{1}{\sqrt{3}}(s + \sqrt{2}p_x)$  is normalized. The functions  $s$  and  $p_x$  denote normalized hydrogenlike atomic orbitals.

b) Normalize the following molecular orbital  $\psi = \psi_{s,A} + \lambda\psi_{s,B}$  where  $\psi_{s,A}$  and  $\psi_{s,B}$  are normalized and  $\lambda$  is a parameter. Use the notation  $S$  for overlap integral to simplify the result.

Solution:

$$\begin{aligned} \text{a) } \int |h|^2 d\tau &= \frac{1}{3} \int (s + \sqrt{2}p_x)^2 d\tau = \frac{1}{3} \left[ \underbrace{\int s^2 d\tau}_{=1} + 2\sqrt{2} \underbrace{\int sp_x d\tau}_{=0} + 2 \underbrace{\int p_x^2 d\tau}_{=1} \right] \\ &= \frac{1}{3} \times 3 = 1. \end{aligned}$$

$$\begin{aligned} \text{b) } N^2 \int |\psi|^2 d\tau &= N^2 \int |\psi_{s,A} + \lambda\psi_{s,B}|^2 d\tau \\ &= N^2 \left[ \underbrace{\int |\psi_{s,A}|^2 d\tau}_{=1} + 2\lambda \underbrace{\int \psi_{s,A}^* \psi_{s,B} d\tau}_{=S} + \lambda^2 \underbrace{\int |\psi_{s,B}|^2 d\tau}_{=1} \right] \\ &= N^2(1 + 2\lambda S + \lambda^2) = 1 \Rightarrow N = \pm \frac{1}{\sqrt{1+2\lambda S+\lambda^2}} \end{aligned}$$

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2. Consider hydrogen molecule (H(A)–H(B)) with the LCAO-MO orbitals formed from the atomic orbitals  $1s_A$  and  $1s_B$ :

$$1\sigma_g = N_1(1s_A + 1s_B) \text{ and } 1\sigma_u^* = N_2(1s_A - 1s_B)$$

a) Show that the Slater determinant corresponding to the ground state solution is antisymmetric.

b) One of the excited states of  $H_2$  corresponds to the following Slater determinant:

$$\psi_{MO} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1\sigma_g(1)\alpha(1) & 1\sigma_u^*(1)\alpha(1) \\ 1\sigma_g(2)\alpha(2) & 1\sigma_u^*(2)\alpha(2) \end{vmatrix}$$

What electron configuration does this correspond to?

Solution:

a) The Slater determinant is:

$$\begin{aligned}\psi_{MO} &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1\sigma_g(1)\alpha(1) & 1\sigma_g(1)\beta(1) \\ 1\sigma_g(2)\alpha(2) & 1\sigma_g(2)\beta(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} [1\sigma_g(1)1\sigma_g(2)\alpha(1)\beta(2) - 1\sigma_g(1)1\sigma_g(2)\beta(1)\alpha(2)] \\ &= \frac{1}{\sqrt{2}} \underbrace{1\sigma_g(1)1\sigma_g(2)}_{\text{symmetric}} \times \underbrace{[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}_{\text{antisymmetric}}\end{aligned}$$

A product of symmetric and antisymmetric functions given overall an antisymmetric function.

b) This corresponds to an electron configuration  $(1\sigma_g^1)^1(1\sigma_u^*)^1$  with parallel spins. The term symbol is therefore  $^3\Sigma$ .

3. Determine the valence electron configurations and bond orders in the following molecules:  $\text{C}_2^+$ ,  $\text{C}_2$ ,  $\text{C}_2^-$ ,  $\text{N}_2^+$ ,  $\text{N}_2$ ,  $\text{N}_2^-$ ,  $\text{O}_2^+$ ,  $\text{O}_2$ ,  $\text{O}_2^-$ . Which of these molecules are paramagnetic and what are their term symbols?

Solution:

Use the correlation diagram to determine the order of orbitals for  $\text{C}_2$ :

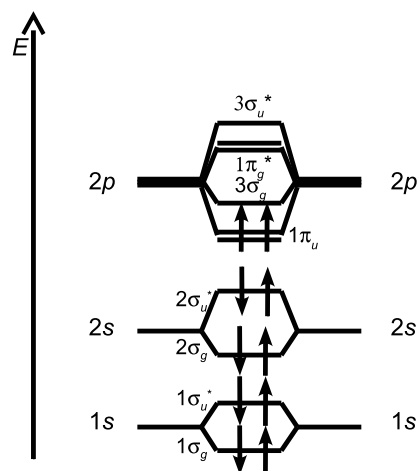
$\text{C}_2^+$	$\dots 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^3$	Bond order = 1.5 (weakest bonding); $^2\Pi_u$ .
$\text{C}_2$	$\dots 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4$	Bond order = 2; $^1\Sigma_g^+$ .
$\text{C}_2^-$	$\dots 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4 3\sigma_g^1$	Bond order = 2.5 (strongest bonding); $^2\Sigma_g^+$ .
$\text{N}_2^+$	$\dots 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4 3\sigma_g^1$	Bond order = 2.5; $^2\Sigma_g^+$ .
$\text{N}_2$	$\dots 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4 3\sigma_g^2$	Bond order = 3.0 (strongest bonding); $^1\Sigma_g^+$ .
$\text{N}_2^-$	$\dots 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4 3\sigma_g^2 1\pi_g^{*1}$	Bond order = 2.5; $^2\Pi_g$ .
$\text{O}_2^+$	$\dots 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*1}$	Bond order = 2.5 (strongest bonding); $^2\Pi_g$ .
$\text{O}_2$	$\dots 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*2}$	Bond order = 2; $^3\Sigma_g^-$ .
$\text{O}_2^-$	$\dots 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*3}$	Bond order = 1.5 (weakest bonding); $^2\Pi_g$ .

Molecules with multiplicity other than one are paramagnetic.

4. Sketch the molecular orbital diagram for  $\text{B}_2$  molecule by using  $1s$ ,  $2s$  and  $2p$  atomic orbitals and all 10 electrons. What is the term symbol?

Solution:

The MO diagram is:



The term symbol is  $^3\Sigma_g$ .

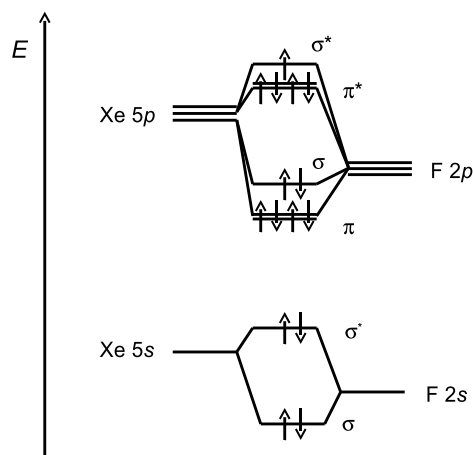
5. a) Sketch a molecular orbital diagram for XeF molecule and determine the electronic configuration. Would XeF<sup>+</sup> have shorter bond length than XeF?

b) Construct a molecular orbital diagram for the double bond (4 electrons) in ethene by using the carbon  $sp^2$  hybrid orbitals as basis set. Choose the energy order of the  $\sigma$  and  $\pi$  orbitals in such a way that a stable molecule is formed.

c) Explain why Ne<sub>2</sub> molecule is not stable. Why are atoms with the outmost  $s$  and  $p$  orbitals full (e.g. the octet electronic configuration) chemically inert?

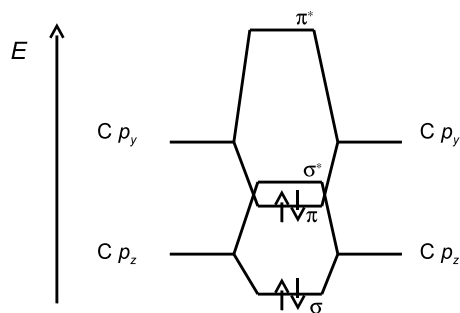
Solution:

a) XeF is not a homonuclear diatomic molecule. Thus the atomic orbitals that form MOs originate from different principal quantum number levels. The MO diagram is:



The bond order for XeF is  $(8 - 7)/2 = 0.5$  and for  $\text{XeF}^+$   $(8 - 6)/2 = 1$ . Thus the equilibrium bond length for  $\text{XeF}^+$  is expected to be shorter than for XeF.

b) Consider the MOs of the C=C fragment:



Note that the order of the  $\pi$  and  $\sigma^*$  orbitals must be as shown above. If this was not the case, the C=C fragment would not be bound!

c) All the resulting bonding and antibonding orbitals become fully occupied. As antibonding orbitals cause more repulsion than bonding orbitals binding, the result is no chemical binding. In general, the octet electronic structure in atoms (e.g. rare gases) tends to lead to efficient population of the anti-bonding molecular orbitals and hence they are chemically inert.

6. Use the variational principle to obtain the lowest energy solution to the hydrogen atom Schrödinger equation in spherical coordinates by using the following trial wavefunctions:

a)  $\psi_{trial} = e^{-kr}$  with  $k$  as a variational parameter.

b)  $\psi_{trial} = e^{-kr^2}$  with  $k$  as a variational parameter.

Note that both trial functions depend only on  $r$  and the angular terms disappear from the Laplacian. You may find the following integrals useful:

$$\begin{aligned}\int_0^\infty x^n e^{-ax} dx &= \frac{n!}{a^{n+1}} \\ \int_0^\infty x^m e^{-ax^2} dx &= \frac{\Gamma[(m+1)/2]}{2a^{(m+1)/2}} \\ \Gamma[n+1] &= n!, \text{ with } 0! = 1 \text{ (} n \text{ is integer)} \\ \Gamma[n+1] &= n\Gamma[n] \\ \Gamma\left[\frac{1}{2}\right] &= \sqrt{\pi}\end{aligned}$$

Solution:

Use the variational principle and employ spherical coordinates in integrations:

$$\begin{aligned}E &= \frac{\int \psi_{trial}^* H \psi_{trial} d\tau}{\int \psi_{trial}^* \psi_{trial} d\tau} \\ \text{a)} \quad \int \psi_{trial}^* \psi_{trial} d\tau &= \int_0^\infty e^{-2kr} \underbrace{4\pi r^2 dr}_{d\tau} = 4\pi \int_0^\infty r^2 e^{-2kr} dr = \frac{\pi}{k^3} \\ \int \psi_{trial}^* H \psi_{trial} d\tau &= \int (e^{-kr}) \left( -\frac{\hbar^2}{2m_e} \Delta - \frac{e^2}{4\pi\epsilon_0 r} \right) (e^{-kr}) d\tau \\ &= \int_0^\infty (e^{-kr}) \left( -\frac{\hbar^2}{2m_e} \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] - \frac{e^2}{4\pi\epsilon_0 r} \right) (e^{-kr}) (4\pi r^2 dr) \\ &= -\frac{4\pi\hbar^2}{2m_e} \int_0^\infty (e^{-kr}) \left( k^2 e^{-kr} - \frac{2k}{r} e^{-kr} \right) r^2 dr - \frac{e^2}{\epsilon_0} \int_0^\infty \frac{e^{-2kr}}{r} r^2 dr \\ &= -\frac{4\pi\hbar^2}{2m_e} \int_0^\infty e^{-2kr} (r^2 k^2 - 2kr) dr - \frac{e^2}{\epsilon_0} \int_0^\infty r e^{-2kr} dr\end{aligned}$$

$$\begin{aligned}
&= -\frac{2\pi\hbar^2 k^2}{m_e} \underbrace{\int_0^\infty r^2 e^{-2kr} dr}_{=\frac{2}{(2k)^3}} + \frac{4\pi\hbar^2 k}{m_e} \underbrace{\int_0^\infty r e^{-2kr} dr}_{=\frac{1}{(2k)^2}} - \frac{e^2}{\epsilon_0} \underbrace{\int_0^\infty r e^{-2kr} dr}_{=\frac{1}{(2k)^2}} \\
&= -\frac{\pi\hbar^2}{2m_e k} + \frac{\pi\hbar^2}{m_e k} - \frac{e^2}{4k^2\epsilon_0}
\end{aligned}$$

These results give:

$$\begin{aligned}
\frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} &= \left( -\frac{\pi\hbar^2}{2m_e k} + \frac{\pi\hbar^2}{m_e k} - \frac{e^2}{4k^2\epsilon_0} \right) / (\pi/k^3) \\
&= -\frac{\hbar^2 k^2}{2m_e} + \frac{\hbar^2 k^2}{m_e} - \frac{e^2 k}{4\pi\epsilon_0} = \frac{\hbar^2 k^2}{2m_e} - \frac{e^2 k}{4\pi\epsilon_0}
\end{aligned}$$

This expression must be minimized with respect to variational parameter  $k$ :

$$\begin{aligned}
\frac{dE}{dk} &= d \left( \frac{\hbar^2 k^2}{2m_e} - \frac{e^2 k}{4\pi\epsilon_0} \right) / dk = \frac{\hbar^2 k}{m_e} - \frac{e^2}{4\pi\epsilon_0} = 0 \\
\Rightarrow k &= \frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} \Rightarrow E = -\frac{1}{2} \frac{m_e e^4}{(4\epsilon_0)^2 \hbar^2} = -hcR
\end{aligned}$$

where  $R$  is the Rydberg constant.

b) The logic is exactly the same as in part a).

$$\int \psi_{trial}^* \psi_{trial} d\tau = \int_0^\infty e^{-2kr^2} \underbrace{4\pi r^2 dr}_{d\tau} = \frac{4\pi\Gamma[3/2]}{2(2k)^{3/2}} = \frac{\pi^{3/2}}{(2k)^{3/2}}$$

The Laplacian of this function is given by:

$$\Delta\psi_{trial} = \frac{\partial}{\partial r} \left( -2kre^{-kr^2} \right) + \frac{2}{r} (-2kr) e^{-kr^2} = (4k^2 r^2 - 6k) e^{-kr^2}$$

Thus the energy expectation value is (without normalization):

$$\begin{aligned}
& \int_0^\infty \left( -\frac{2\hbar^2 k^2 r^2}{m_e} + \frac{3k\hbar^2}{m_e} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \right) e^{-2kr^2} \times 4\pi r^2 dr \\
&= 4\pi \int_0^\infty \left( -\frac{2\hbar^2 k^2 r^4}{m_e} + \frac{3k\hbar^2 r^2}{m_e} - \frac{e^2 r}{4\pi\epsilon_0} \right) e^{-2kr^2} dr \\
&= -\frac{8\pi\hbar^2 k^2}{m_e} \underbrace{\int_0^\infty r^4 e^{-2kr^2} dr}_{\frac{\Gamma[5/2]}{2(2k)^{5/2}} = \frac{3\sqrt{\pi}}{8(2k)^{5/2}}} + \frac{12\pi k\hbar^2}{m_e} \underbrace{\int_0^\infty r^2 e^{-2kr^2} dr}_{\frac{\Gamma[3/2]}{2(2k)^{3/2}} = \frac{\sqrt{\pi}}{4(2k)^{3/2}}} - \frac{e^2}{\epsilon_0} \underbrace{\int_0^\infty r e^{-2kr^2} dr}_{\frac{\Gamma[1]}{2(2k)} = 1/(4k)} \\
&= -\frac{3\pi^{3/2}\hbar^2}{4m_e\sqrt{2k}} + \frac{3\pi^{3/2}\hbar^2}{2m_e\sqrt{2k}} - \frac{e^2}{4\epsilon_0 k} \\
&\Rightarrow \frac{\int \psi_{trial}^* \psi_{trial} d\tau}{\int \psi_{trial}^* \psi_{trial} d\tau} = \frac{-\frac{3\pi^{3/2}\hbar^2}{4m_e\sqrt{2k}} + \frac{3\pi^{3/2}\hbar^2}{2m_e\sqrt{2k}} - \frac{e^2}{4\epsilon_0 k}}{\frac{\pi^{3/2}}{(2k)^{3/2}}} = -\frac{3\hbar^2 k}{2m_e} + \frac{6\hbar^2 k}{2m_e} - \frac{e^2\sqrt{2k}}{2\pi^{3/2}\epsilon_0} \\
&= \frac{3\hbar^2 k}{2m_e} - \frac{e^2\sqrt{k}}{\sqrt{2}\pi^{3/2}\epsilon_0}
\end{aligned}$$

To find the minimum value for energy (with respect to  $k$ ), we calculate the first derivative and set it to zero:

$$\begin{aligned}
E &= \frac{3\hbar^2 k}{2m_e} - \frac{e^2\sqrt{k}}{\sqrt{2}\pi^{3/2}\epsilon_0} \\
\Rightarrow \frac{\partial E}{\partial k} &= \frac{3\hbar^2}{2m_e} - \frac{e^2}{2\sqrt{2}\pi^{3/2}\epsilon_0\sqrt{k}} = 0 \\
\Rightarrow k &= \left( \frac{m_e e^2}{3\sqrt{2}\pi^{3/2}\epsilon_0\hbar^2} \right)^2 = \frac{m_e^2 e^4}{18\pi^3 \epsilon_0^2 \hbar^4}
\end{aligned}$$

The total energy at this point is:

$$\begin{aligned}
E &= \frac{3\hbar^2}{2m_e} \times \frac{m_e^2 e^4}{18\pi^3 \epsilon_0^2 \hbar^4} - \frac{e^2}{\sqrt{2}\pi^{3/2}\epsilon_0} \times \frac{m_e e^2}{3\sqrt{2}\pi^{3/2}\epsilon_0 \hbar^2} = \frac{m_e e^4}{12\pi^3 \epsilon_0^2 \hbar^2} - \frac{2m_e e^4}{12\pi^3 \epsilon_0^2 \hbar^2} \\
&= -\frac{m_e e^4}{12\pi^3 \epsilon_0^2 \hbar^2} = -\frac{8}{3\pi} hcR \approx -0.85 hcR
\end{aligned}$$

c) The function in a) gives lower energy and therefore that trial function is better.

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7. Calculate the  $\pi$  orbitals of allyl radical (corresponding to localized structure  $\text{CH}_2\text{-C=CH}_2$ , however, assume delocalization in your calculation) by using the Hückel theory.

a) What is the wavelength of the LUMO  $\leftarrow$  HOMO electronic transition when  $\beta = -22,000 \text{ cm}^{-1}$ ?

b) Calculate the charge densities and bond orders from the Hückel wavefunction. Definitions for these observables are given below:

Electron density on atom  $i$ :

$$\rho(i) = \sum_{j=1}^{N_{MO}} |c_i^j|^2 n_j$$

where  $n_j$  is the number of electrons on orbital  $j$  and  $c_i^j$  is the Hückel MO coefficient of the basis function centered on atom  $i$  for orbital  $j$ . The summation runs over the occupied orbitals.

Bond order between atoms  $i$  and  $j$ :

$$\text{bond order} = \sum_{k=1}^{N_{MO}} c_i^k c_j^k n_k$$



where the symbols are defined as above.

Solution:

First we construct the secular equation (matrix form) corresponding to the Hückel approximation:

$$\begin{pmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0$$

Denote  $x = (\alpha - E)/\beta$  and recall this set of equations has a non-trivial solution only if the corresponding determinant is zero:

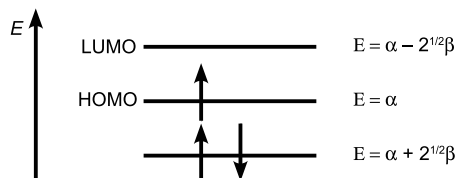
$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

By expanding this determinant, we get:

$$x(x^2 - 1) - x = x^3 - 2x = x(x^2 - 2) = 0 \Rightarrow x = \begin{cases} 0 \\ +\sqrt{2} \\ -\sqrt{2} \end{cases}$$

$$\Rightarrow E = \begin{cases} \alpha \\ \alpha - \sqrt{2}\beta \\ \alpha + \sqrt{2}\beta \end{cases}$$

Thus we have the following energetics for the orbitals:



a) The energy difference between HOMO and LUMO orbitals is:

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} = \alpha - \sqrt{2}\beta - \alpha = -\sqrt{2}\beta = -\sqrt{2} \times (-22,000\text{cm}^{-1})$$

$$\rightarrow \Delta E = 3.86\text{eV (320 nm)}$$

b) Next we calculate the coefficients  $c_1, c_2$  and  $c_3$  for the lowest energy orbital: Here  $E = (\alpha \pm \sqrt{2}\beta)$ , which with  $(\alpha - E)c_1 + \beta c_2 = 0$  gives  $c_2 = \pm\sqrt{2}c_1$ . Exactly the same way, equation  $\beta c_2 + (\alpha - E)c_3 = 0$  gives  $c_2 = \pm\sqrt{2}c_3$ . Finally, normalization gives:  $c_1^2 + c_2^2 + c_3^2 = 1 \Rightarrow c_1^2 + (\pm\sqrt{2}c_1)^2 + c_1^2 = 4c_1^2 \Rightarrow c_1 = \frac{1}{2}$  and by considering  $c_3$  the same way, we also get  $c_3 = \frac{1}{2}$ .

Thus we have:

$$E = \alpha + \sqrt{2}\beta \text{ with } c_1 = \frac{1}{2}, c_2 = \frac{1}{\sqrt{2}}, c_3 = \frac{1}{2}$$

$$E = \alpha - \sqrt{2}\beta \text{ with } c_1 = \frac{1}{2}, c_2 = -\frac{1}{\sqrt{2}}, c_3 = \frac{1}{2}$$

For  $E = \alpha$ , we have:  $c_1 = \frac{1}{\sqrt{2}}, c_2 = 0, c_3 = -\frac{1}{\sqrt{2}}$ .

The electron density on atom 1 can be obtained by squaring the atomic basis function coefficients and weighing this by the number of electrons on that orbital:

$$\text{Atom 1 (} i = 1 \text{): } \sum_{j=1}^3 |c_i^j|^2 n_j = \left(\frac{1}{2}\right)^2 \times 2 + \left(\frac{1}{\sqrt{2}}\right)^2 \times 1 + \left(\frac{1}{2}\right)^2 \times 0 = 1.$$

$$\text{Atom 2 (} i = 2 \text{): } \sum_{j=1}^3 |c_i^j|^2 n_j = \left(\frac{1}{\sqrt{2}}\right)^2 \times 2 + 0^2 \times 1 + \left(-\frac{1}{\sqrt{2}}\right)^2 \times 0 = 1.$$

$$\text{Atom 3 (} i = 3 \text{): } \sum_{j=1}^3 |c_i^j|^2 n_j = \left(\frac{1}{2}\right)^2 \times 2 + \left(-\frac{1}{\sqrt{2}}\right)^2 \times 1 + \left(\frac{1}{2}\right)^2 \times 0 = 1.$$

The total charge (three  $\pi$  electrons) is distributed evenly to all three atoms and therefore the partial charges on carbon atoms are equal.

The bond orders can be valuated as follows:

Bond between atoms 1 and 2 ( $i = 1$  and  $j = 2$ ):

$$\sum_{k=1}^{N_{MO}} c_i^k c_j^k n_k = \left(\frac{1}{2}\right) \left(\frac{1}{\sqrt{2}}\right) \times 2 + \left(\frac{1}{\sqrt{2}}\right) \times 0 \times 1 + \left(\frac{1}{2}\right) \left(-\frac{1}{\sqrt{2}}\right) \times 0 = \frac{1}{\sqrt{2}}$$

Bond between atoms 2 and 3 ( $i = 2$  and  $j = 3$ ):

$$\sum_{k=1}^{N_{MO}} c_i^k c_j^k n_k = \left(\frac{1}{\sqrt{2}}\right) \left(\frac{1}{2}\right) \times 2 + 0 \times \left(-\frac{1}{\sqrt{2}}\right) \times 1 + \left(-\frac{1}{\sqrt{2}}\right) \left(\frac{1}{2}\right) \times 0 = \frac{1}{\sqrt{2}}$$

The bond order is less than one ( $\approx 0.707$ ), which indicates that the bond is not very strong.

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