

Homon Exercises 11.3b, 11.5b

- method: ① Write electron configuration
 ② If an added electron would go into a bonding orbital, it would be stabilizing; into an antibonding orbital, destabilizing
 ③ If a removed electron would come from a bonding orbital, it is destabilizing; from an antibonding orbital, stabilizing.

molecule	config.	add electron	remove electron
N_2	$1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$	destabilize	dest.
NO	$1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2 2\pi^{*1}$	dest.	stabilize
O_2	$1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}$	dest.	stab.
C_2	$1\sigma^2 2\sigma^{*2} 1\pi^4$	stab.	dest.
F_2	$1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}$	dest.	stab.
CN	$1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^1$	stab.	dest.

↑
 [alternative nomenclature: $1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^1$]

E 11.5b The same principle applies here. It is also instructive to determine the bond order, b . The larger b , the smaller the bond length.

	config.	$b = \frac{1}{2}(n - n^*)$
O_2	$1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*2}$	$\frac{1}{2}(8 - 4) = 2.0$
O_2^+	$1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*1}$	$\frac{1}{2}(8 - 3) = 2.5$
O_2^-	$1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*3}$	$\frac{1}{2}(8 - 5) = 1.5$
O_2^{2-}	$1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*4}$	$\frac{1}{2}(8 - 6) = 1.0$

Order of increasing bond length: O_2^+ O_2 O_2^- O_2^{2-}

2.

Atkins 11.8b

$\psi = x^2(L-x)$ can be used as a trial function if it satisfies the necessary boundary conditions (in a particle in a box):

$$\psi = 0 \text{ at } x=0, L$$

$$\psi(0) = 0 \quad \checkmark$$

$$\psi(L) = -L^3 \quad \times$$

This trial function cannot be used.

Notes: By comparison, the trial function in 11.8a can be used:

$$\psi = x(L-x) \quad \psi(0) = 0 \quad \psi(L) = 0$$

$$E_{\text{trial}} = \frac{\int \psi^* \hat{H} \psi dx}{\int \psi^* \psi dx}$$

$$\begin{aligned} \int_0^L \psi^* \psi dx &= \int_0^L (x(L-x))^2 dx = \int_0^L x^2 L^2 dx - \int_0^L 2Lx^3 dx + \int_0^L x^4 dx \\ &= \frac{1}{3} L^5 - \frac{2}{4} L^5 + \frac{1}{5} L^5 = \frac{1}{15} L^5 \end{aligned}$$

$$\int_0^L \psi^* \hat{H} \psi dx = -\frac{\hbar^2}{2m} \int_0^L \psi \frac{d^2}{dx^2} \psi dx$$

$$\frac{d}{dx} \psi = \frac{d}{dx} x(L-x) = -2$$

$$\int_0^L \psi^* \hat{H} \psi dx = \frac{\hbar^2}{m} \int_0^L x(L-x) dx = \frac{\hbar^2 L^3}{6m}$$

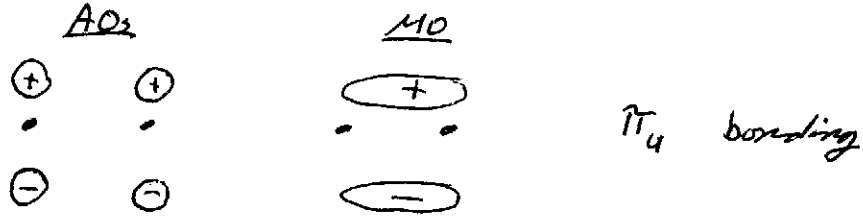
$$\begin{aligned} E_{\text{trial}} &= \frac{\frac{\hbar^2 L^3}{6m}}{\frac{1}{15} L^5} \\ &= \frac{5 \hbar^2}{47 m L^2} \end{aligned}$$

True ground state energy:

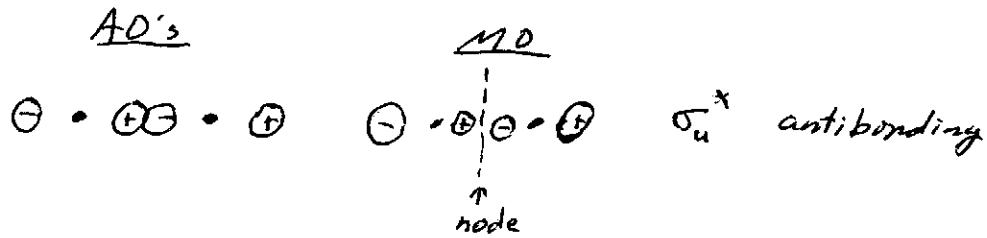
$$E = \frac{\hbar^2}{8mL^2}$$

$$\frac{E_{\text{trial}}}{E} = 1.013 \quad \text{slightly larger } \checkmark$$

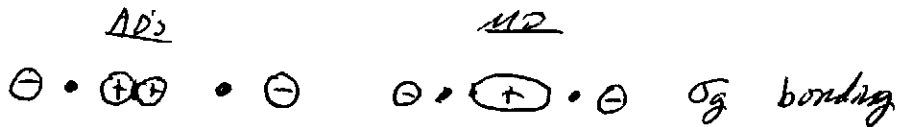
3. a) $2p_y(A) + 2p_y(B)$



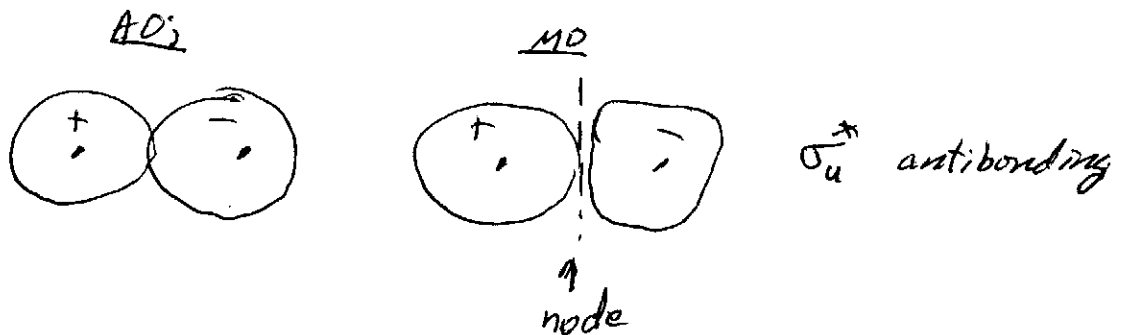
b) $2p_z(A) + 2p_z(B)$



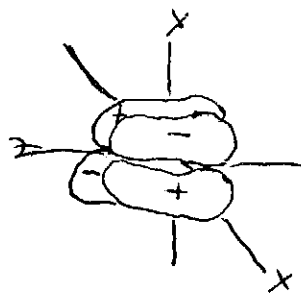
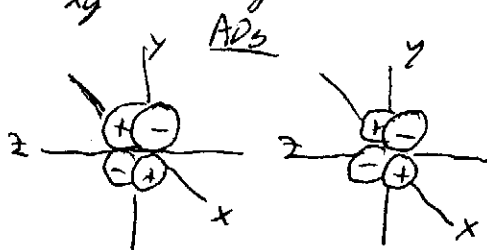
c) $2p_z(A) - 2p_z(B)$



d) $2s(A) - 2s(B)$

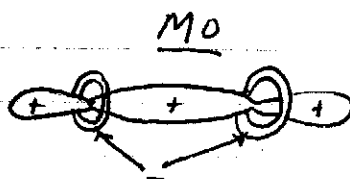
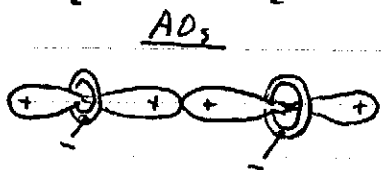


e) $d_{xy}(A) + d_{xy}(B)$



σ_g bonding

f) $3d_{z^2}(A) + 3d_{z^2}(B)$



σ_g bonding

Note that sign of both lobes of a d orbital is positive, while sign of torus (doughnut-shaped) is negative

4. From notes or from Atkins, we know that for a homonuclear diatomic molecule, and for a given set of basis functions ϕ_a, ϕ_b , where we express the ground state (lowest-energy) wavefunction as

$$\psi_{gs} = \sum c_i \phi_i = c_a \phi_a + c_b \phi_b$$

the ground-state energy is given by

$$E_{gs} = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$

$$\text{where } H_{aa} = \int \phi_a^* \hat{H} \phi_a d\tau = -2 \text{ a.u. (called } \alpha \text{ in Atkins)}$$

$$H_{ab} = \int \phi_a^* \hat{H} \phi_b d\tau = -1 \quad (\dots \beta \dots)$$

$$S_{ab} = \int \phi_a^* \phi_b d\tau = \frac{1}{7} \quad (\dots S \dots)$$

$$E_{gs} = \frac{-2 - 1}{1 - \frac{1}{4}} = -4 \text{ a.u.}$$

$$\psi_{gs} = \left\{ \frac{1}{2(1+S)} \right\}^{1/2} (\phi_a + \phi_b) \quad (\text{p. 491})$$

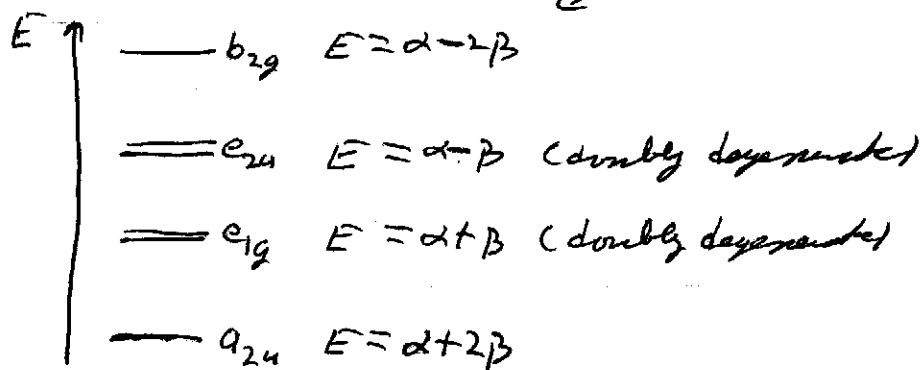
$$= 0.82 (\phi_a + \phi_b)$$

Note: Neither E_{gs} nor ψ_{gs} is exact. Both are the best we can do with a trial function of the form $\psi_{gs} = c_a \phi_a + c_b \phi_b$. We have left the form of \hat{H} , ϕ_a , & ϕ_b unspecified to make the problem simple. Since we know the values of the integrals, though, it is implied that \hat{H} , ϕ_a , & ϕ_b are known.

5.

Affine Exercise 11.12b

From text, p. 396



Note: Both α and β are negative

Neutral benzene has 6 electrons, so using the Aufbau principle, the electron configuration is:



Species	E_{π}
neutral	$6\alpha + 8\beta$
cation	$5\alpha + 7\beta$
anion	$7\alpha + 7\beta$

$$7. a) \begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix}$$

$$b) \begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix}$$

$$c) \begin{vmatrix} x & 1 & 0 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 1 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 1 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 0 & 1 & x \end{vmatrix}$$

(Column 2 is connected to column 5, so 1 appears in each of the corresponding places in the secular determinant)

$$d) \begin{vmatrix} x & 1 & 1 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 & 0 \\ 1 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 0 & x & 1 & 1 \\ 0 & 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 1 & 1 & x \end{vmatrix}$$

$$e) \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix}$$

(The conjugated system includes only the last two carbons)