

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.61 Physical Chemistry
Fall, 2017

Professor Robert W. Field

FIFTY MINUTE EXAMINATION III **Thursday,**

November 30

Question	Possible Score	My Score
I	40	
II	30	
III	30	
Total	100	

Name: _____

I. LCAO-MO**(40 POINTS)**

A. (20 points) This problem deals with homonuclear diatomic molecules from the Li-Ne row of the periodic table.

(i) (5 points) Draw an MO diagram for Be_2 and use it to answer the two questions:

(a) (3 points) Is Be_2 expected to be bound in its electronic ground state? Justify your answer.

(b) (2 points) Do you expect that the lowest energy excited state of Be_2 is bound? Justify your answer.

- (ii) (5 points) Electronic states of diatomic molecules are specified as $^{2S+1}\Lambda$ (Σ for $\Lambda = 0$, Δ for $\Lambda = 2$). A π^2 configuration gives rise to three electronic states: $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$. Which one of these three states is predicted by Hund's first rule to have the lowest energy?
- (iii) (5 points) Draw an MO diagram that explains why O_2 has a triplet ground state. Explain why this is a safe prediction.

- (iv) (5 points) A similar argument might predict that C_2 also has a triplet ground state. The three lowest lying electronic configurations for C_2 are:

$$\sigma_g(2s)^2\sigma_u^*(2s)^2\sigma_g(2p)^2\pi_u(2p)^2 : \quad {}^3\Sigma_g^-, {}^1\Delta_g, {}^1\Sigma_g^+$$

$$\sigma_g(2s)^2\sigma_u^*(2s)^2\sigma_g(2p)^1\pi_u(2p)^3 : \quad {}^3\Pi_u, {}^1\Pi_u$$

$$\sigma_g(2s)^2\sigma_u^*(2s)^2\sigma_g(2p)^0\pi_u(2p)^4 : \quad {}^1\Sigma_g^+$$

Show, using an MO diagram, why the O_2 -like argument is unsafe for C_2 . [HINT: the two σ_g orbitals derive from the 2s and 2p AOs, which are relatively close in energy for carbon.]

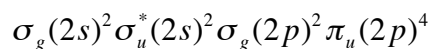
- B.** (10 points) *Isoelectronic* molecules with 8 valence electrons: C_2 , BN, BeO, LiF.

The vibrational frequencies in the electronic ground states of these four molecules are C_2 : $\omega_e = 1855 \text{ cm}^{-1}$, BN: 1515 cm^{-1} , BeO: 1489 cm^{-1} , LiF: 910 cm^{-1} . Use MO diagrams to explain this trend in bond order.

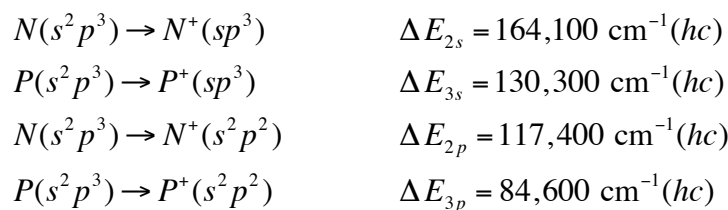
- C. (10 points) The $X^1\Sigma_g^+$ Electronic Ground States of *Homologous* Molecules: N_2 and P_2 .

	$\underline{\omega}_e$	\underline{R}_e	
N_2	2359 cm^{-1}	1.10 \AA	extremely stable and non-reactive
P_2	781 cm^{-1}	1.89 \AA	extremely unstable and reactive

These molecular constants suggest that N_2 has a *triple* bond while P_2 has a *single* bond. Given that the electronic ground state configuration in N_2 is

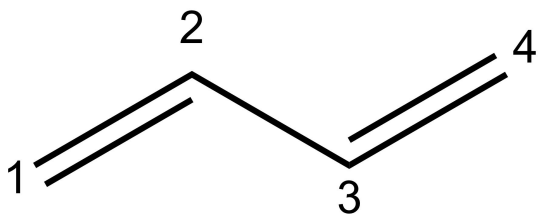


and



Speculate about the $\sigma(3s)$ vs. $\sigma(3p)$ vs. $\pi(3p)$ dominant character of the single bond in P_2 and the reason for the absence or weakness of the bonds associated with the other two normally bonding LCAO-MO orbitals. Recall that the orbital ionization energy roughly determines the orbital radius and that the probability density in an orbital is proportional to r^{-3} .

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II. Hückel Theory**(30 POINTS)**Consider the butadiene molecule, $\text{CH}_2\text{CHCHCH}_2$ 

The four Hückel Theory orbital eigen-energies are

$$\alpha + \beta[3 + 5^{1/2}/2]^{1/2}$$

$$\alpha + \beta[3 - 5^{1/2}/2]^{1/2}$$

$$\alpha - \beta[3 + 5^{1/2}/2]^{1/2}$$

$$\alpha - \beta[3 - 5^{1/2}/2]^{1/2}$$

and the four eigenvectors are

$$\begin{pmatrix} -0.37 \\ 0.60 \\ -0.60 \\ 0.37 \end{pmatrix}, \begin{pmatrix} 0.37 \\ 0.60 \\ 0.60 \\ 0.37 \end{pmatrix}, \begin{pmatrix} 0.60 \\ -0.37 \\ -0.37 \\ 0.60 \end{pmatrix}, \text{ and } \begin{pmatrix} -0.60 \\ -0.37 \\ 0.37 \\ 0.60 \end{pmatrix}$$

- A. (5 points) Match each of the four orbital eigen-energies to the corresponding eigenvector. HINT: count the nodes and remember that both α and β are < 0 .

B. (13 points)

- (i) (3 points) How many p_z electrons are there in the π -system of butadiene?
- (ii) (3 points) Specify the number of electrons in each of the four orbitals.
- (iii) (7 points) For only the **H**ighest energy **O**ccupied **M**olecular **O**rbital (HOMO), specify the non-integer number of π -electrons on each of the carbon atoms.

C. (7 points) Calculate the total bond-order *between atoms 1 and 2* and *between atoms 2 and 3*. For a doubly occupied orbital, the bond order between atoms a and b is

$$O_{ab} = 2c_a c_b$$

and the total bond-order between atoms a and b is given by the sum over all of the occupied molecular orbitals.

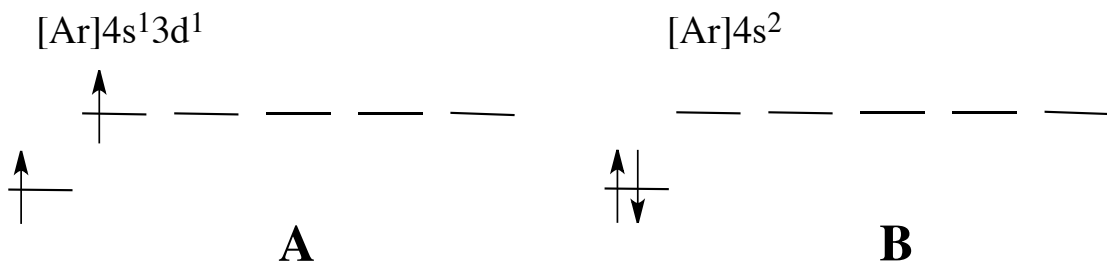
D. (5 points) Calculate the bond-order between atoms 1 and 4. Why is this calculated bond-order surprising?

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III. Many Electron Atoms and “Shielding” (30 POINTS)

The lowest energy electronic configuration for Sc is $[\text{Ar}]4s^23d^1$. This notation means the electronic configuration of Ar plus $4s^23d^1$.

- A. (6 points) If we remove one electron from the electronic ground state of Sc, we have Sc^+ in one of the two possible configurations:



Express the energy of the two configurations using the symbols

ϵ_{4s}	Energy of the 4s orbital
ϵ_{3d}	Energy of the 3d orbital
J_{4s4s}	Coulomb integral between 4s and 4s
J_{4s3d}	Coulomb integral between 4s and 3d
J_{3d3d}	Coulomb integral between 3d and 3d
K_{4s3d}	Exchange integral between 4s and 3d

- B (2 points) The values of several of these integrals are found to be (in atomic units)

$$J_{4s4s} = 0.303$$

$$J_{4s3d} = 0.150$$

$$K_{4s3d} = 0.002$$

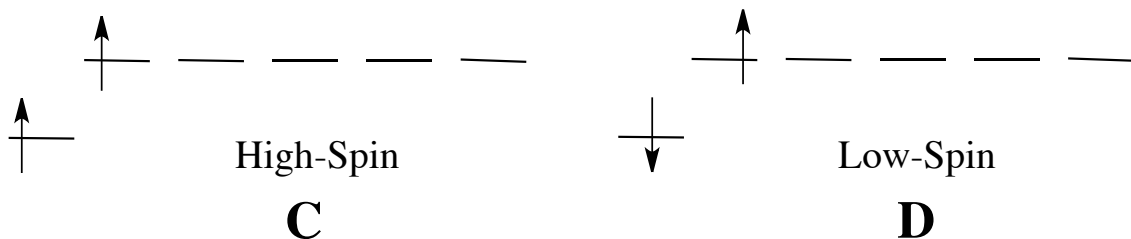
J_{4s4s} is larger than J_{4s3d} . Why is this consistent with our expectations?

- C.** (4 points) For Sc^{2+} the experimentally measured energy difference between the $[\text{Ar}]4s^1$ and $[\text{Ar}]3d^1$ configurations is

$$\epsilon_{4s} - \epsilon_{3d} = 0.1164.$$

Going from Sc^{2+} to Sc^+ , use the cited numerical values of ϵ , J , and K to determine which of the Sc^+ $[\text{Ar}]4s^13d^1$ or $[\text{Ar}]4s^2$ configurations has the lowest energy. *Which configuration is more stable?*

- D.** (6 points) Next we consider the high-spin and low-spin energy states of Sc^+ in the $[\text{Ar}]4s3d$ configuration



*Calculate the energies of configurations **C** and **D** and express your answer in terms of the relevant symbols.*

- E.** (4 points) *Which configuration, **C** (high-spin) or **D** (low-spin) is more stable? You do not need to do a numerical calculation to answer this question. Why?*

- F.** (3 points) Your answers to parts **A** and **B** are surprising because the lowest energy state for the iso-electronic atom, Ca, is $[\text{Ar}]4s^2$. *Suggest a possible explanation for why the lowest energy state for Ca comes from the $[\text{Ar}]4s^2$ configuration and the lowest energy state for Sc^+ comes from the $[\text{Ar}]4s^1 3d^1$ configuration.*
- G.** (5 points) In parts **A** and **B** you were given numerical values for some Coulomb and exchange integrals. Without a computer, you cannot derive values for J and K integrals. However, you should be able to predict which one of a pair of integrals is larger. [All of the integrals express electron-electron repulsion, thus are all positive.] For each of the following pairs of integrals, *specify which one is larger and, briefly, why it is larger:*

$$J_{1s,2s} \text{ vs. } J_{1s,4s}$$

$$J_{1s,1s} \text{ vs. } J_{1s,2s}$$

$$J_{1s,1s} \text{ vs. } J_{10s,10s}$$

$$K_{2s,2p_z} \text{ vs. } K_{2p_x,2p_z}$$

$$J_{2s,2s} \text{ vs. } K_{2s,2s}$$

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Some Possibly Useful Constants and Formulas

$$h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}$$

$$\hbar = 1.054 \times 10^{-34} \text{ J} \cdot \text{s}$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ kg}^{-1} \text{ m}^{-3}$$

$$c = 3.00 \times 10^8 \text{ m/s}$$

$$c = \lambda \nu$$

$$\lambda = h/p$$

$$m_e = 9.11 \times 10^{-31} \text{ kg}$$

$$m_H = 1.67 \times 10^{-27} \text{ kg}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$E = h\nu$$

$$a_0 = 5.29 \times 10^{-11} \text{ m}$$

$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta$$

$$\bar{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{where } R_H = \frac{me^4}{8\epsilon_0^2 h^3 c} = 109,678 \text{ cm}^{-1}$$

Free particle:

$$E = \frac{\hbar^2 k^2}{2m}$$

$$\psi(x) = A\cos(kx) + B\sin(kx)$$

Particle in a box:

$$E_n = \frac{\hbar^2}{8ma^2} n^2 = E_1 n^2$$

$$\psi(0 \leq x \leq a) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right) \quad n = 1, 2, \dots$$

Harmonic oscillator:

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega \quad [\text{units of } \omega \text{ are radians/s}]$$

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}, \quad \psi_1(x) = \frac{1}{\sqrt{2}} \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha^{1/2} x) e^{-\alpha x^2/2}, \quad \psi_2(x) = \frac{1}{\sqrt{8}} \left(\frac{\alpha}{\pi}\right)^{1/4} (4\alpha x^2 - 2) e^{-\alpha x^2/2}$$

$$\hat{x} \equiv \sqrt{\frac{m\omega}{\hbar}} \hat{x}$$

$$\hat{p} \equiv \sqrt{\frac{1}{\hbar m \omega}} \hat{p} \quad [\text{units of } \omega \text{ are radians/s}]$$

$$\mathbf{a} \equiv \frac{1}{\sqrt{2}} (\hat{x} + i\hat{p})$$

$$\frac{\hat{H}}{\hbar\omega} = \mathbf{a}\mathbf{a}^\dagger - \frac{1}{2} = \mathbf{a}^\dagger \mathbf{a} + \frac{1}{2} \quad \hat{N} = \mathbf{a}^\dagger \mathbf{a}$$

$$\mathbf{a}^\dagger \equiv \frac{1}{\sqrt{2}} (\hat{x} - i\hat{p})$$

$$2\pi c \tilde{\omega} = \omega \quad [\text{units of } \tilde{\omega} \text{ are cm}^{-1}]$$

Semi-Classical

$$\lambda = h/p$$

$$p_{\text{classical}}(x) = [2m(E - V(x))]^{1/2}$$

$$\text{period: } \tau = 1/\nu = 2\pi/\omega$$

For a *thin* barrier of width ε where ε is very small, located at x_0 , and height $V(x_0)$:

$$H_{nm}^{(1)} = \int_{x_0-\varepsilon/2}^{x_0+\varepsilon/2} \psi_n^{(0)*} V(x) \psi_n^{(0)} dx = \varepsilon V(x_0) |\psi_n^{(0)}(x_0)|^2$$

Perturbation Theory

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$$

$$\Psi_n = \psi_n^{(0)} + \psi_n^{(1)}$$

$$E_n^{(1)} = \int \psi_n^{(0)*} \hat{H}^{(1)} \psi_n^{(0)} dx = H_{nn}^{(1)}$$

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{H_{nm}^{(1)}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|H_{nm}^{(1)}|^2}{E_n^{(0)} - E_m^{(0)}}$$

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