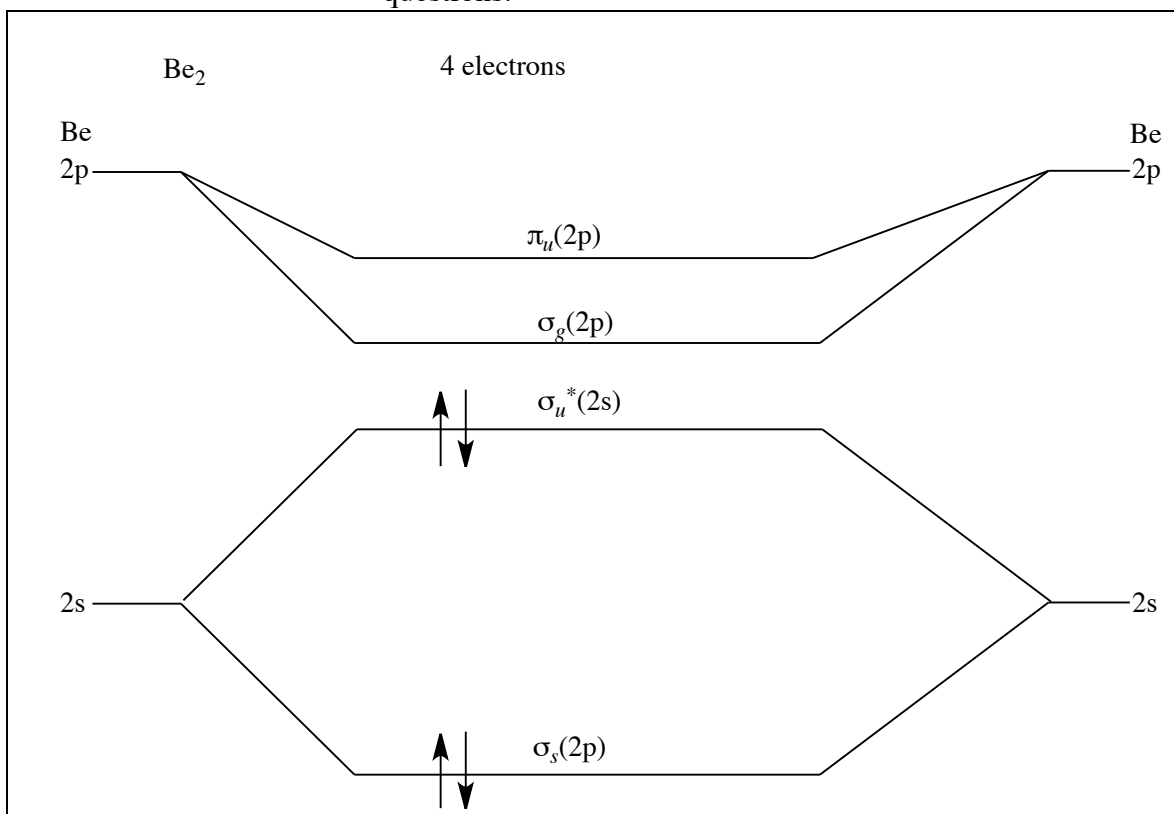


## MASSACHUSETTS INSTITUTE OF TECHNOLOGY

**5.61 Physical Chemistry  
Fall, 2017**Professor Robert W. FieldFIFTY MINUTE EXAMINATION III **ANSWERS****Thursday, November 30****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  $\text{Be}_2$  and use it to answer the two questions:



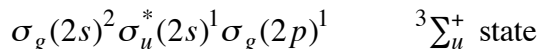
- (a) (3 points) Is  $\text{Be}_2$  expected to be bound in its electronic ground state? Justify your answer.

Key points:  $\sigma_u^*(2s)$  is more anti-bonding than  $\sigma_g(2s)$  is bonding. The interaction between  $\sigma_g(2p)$  and  $\sigma_g(2s)$  will make  $\sigma_g(2s)$  more bonding. The interaction between  $\sigma_u^*(2p)$  and  $\sigma_u^*(2s)$  will have a small effect on reduction of anti-bonding character because of a much larger energy denominator.

The expectation is that the single bond from  $\sigma_g(2s)^2$  will be almost perfectly cancelled by the single anti-bond from  $\sigma_u^*(2s)^2$ . The ground state of  $\text{Be}_2$  is likely to be unbound.

- (b) (2 points) Do you expect that the lowest energy excited state of  $\text{Be}_2$  is bound? Justify your answer.

The first excited state will involve promotion of an electron from the  $\sigma_u^*(2s)$  orbital to the  $\sigma_g(2p)$  orbital. This



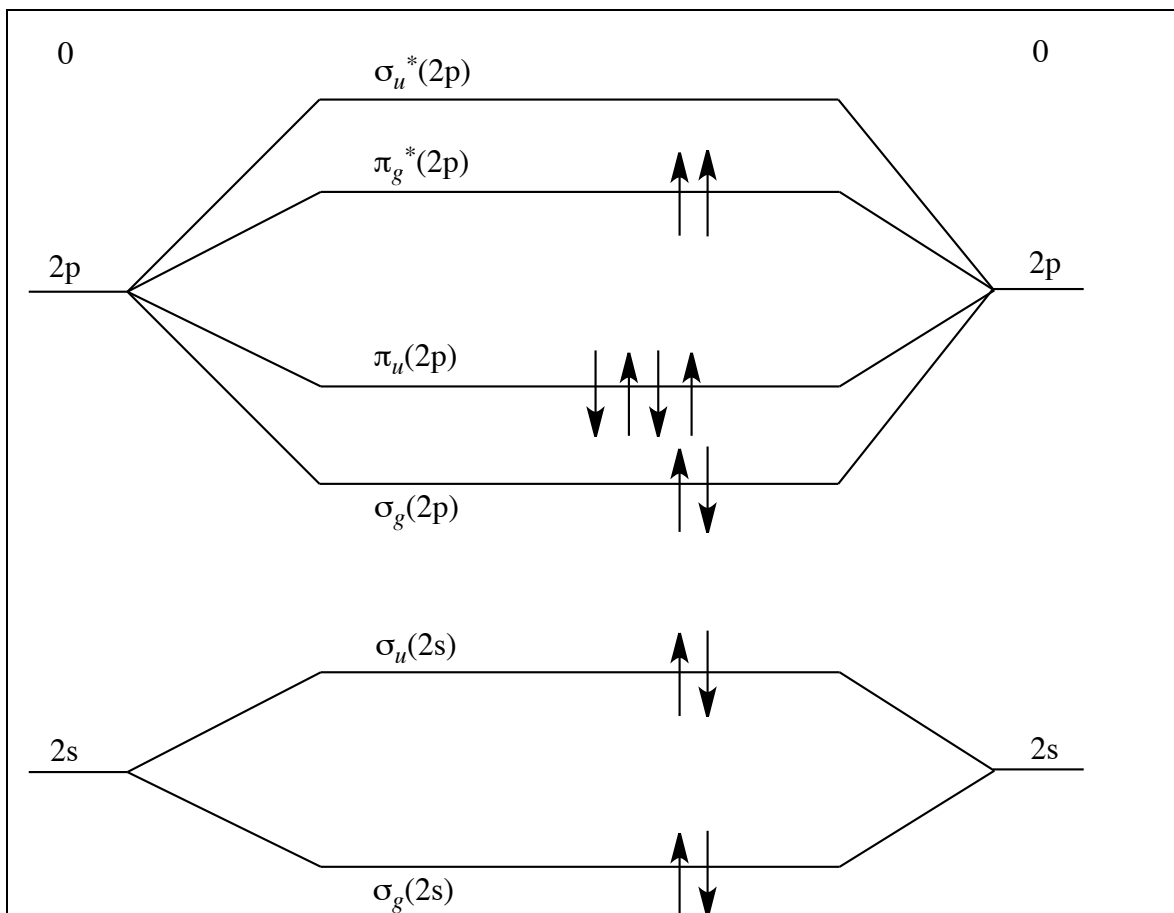
will certainly be bound. The isoconfigurational  ${}^1\Sigma_u^+$  state is also likely to be bound.

- (ii) (5 points) Electronic states of diatomic molecules are specified as  ${}^{2S+1}\Lambda$  ( $\Sigma$  for  $\Lambda = 0$ ,  $\Delta$  for  $\Lambda = 2$ ). A  $\pi^2$  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?

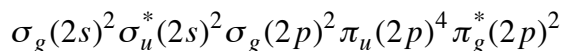
Hund's first rule specifies that the lowest energy electronic state from each electronic configuration has maximum multiplicity. For a  $\pi^2$  configuration the lowest energy state would be  ${}^3\Sigma^-$ .

- (iii) (5 points) Draw an MO diagram that explains why  $\text{O}_2$  has a triplet ground state. Explain why this is a safe prediction.

$\text{O}_2$  has 12 valence electrons. The MO diagram is



The 12 electrons are filled into the molecular orbitals from the lowest one in energy order:



The lowest energy state is  ${}^3\Sigma_g^-$ . There is no other choice.  $\sigma_u^*(2p)$  is slightly pushed up (more antibonding) by interaction with  $\sigma_u^*(2s)$ . There is no  $\pi_g^*$  valence orbital for  $\pi_g^*(2p)$  to interact with. So the energy gap between the predicted HOMO and predicted LUMO is very large. The prediction is iron-clad!

- (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:

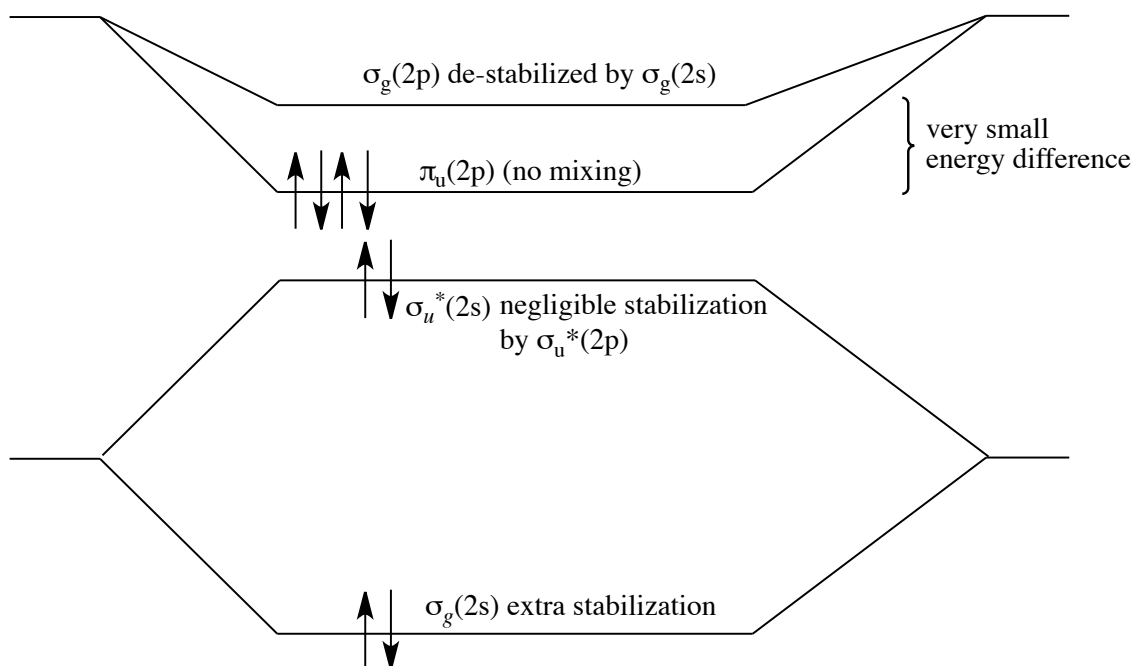
$$\sigma_g(2s)^2\sigma_u^*(2s)^2\sigma_g(2p)^2\pi_u(2p)^2 : \quad {}^3\Sigma_g^-, {}^1\Delta_g, {}^1\Sigma_g^+$$

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

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

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

MO diagram for  $C_2$ .  $C_2$  has 8 valence electrons.

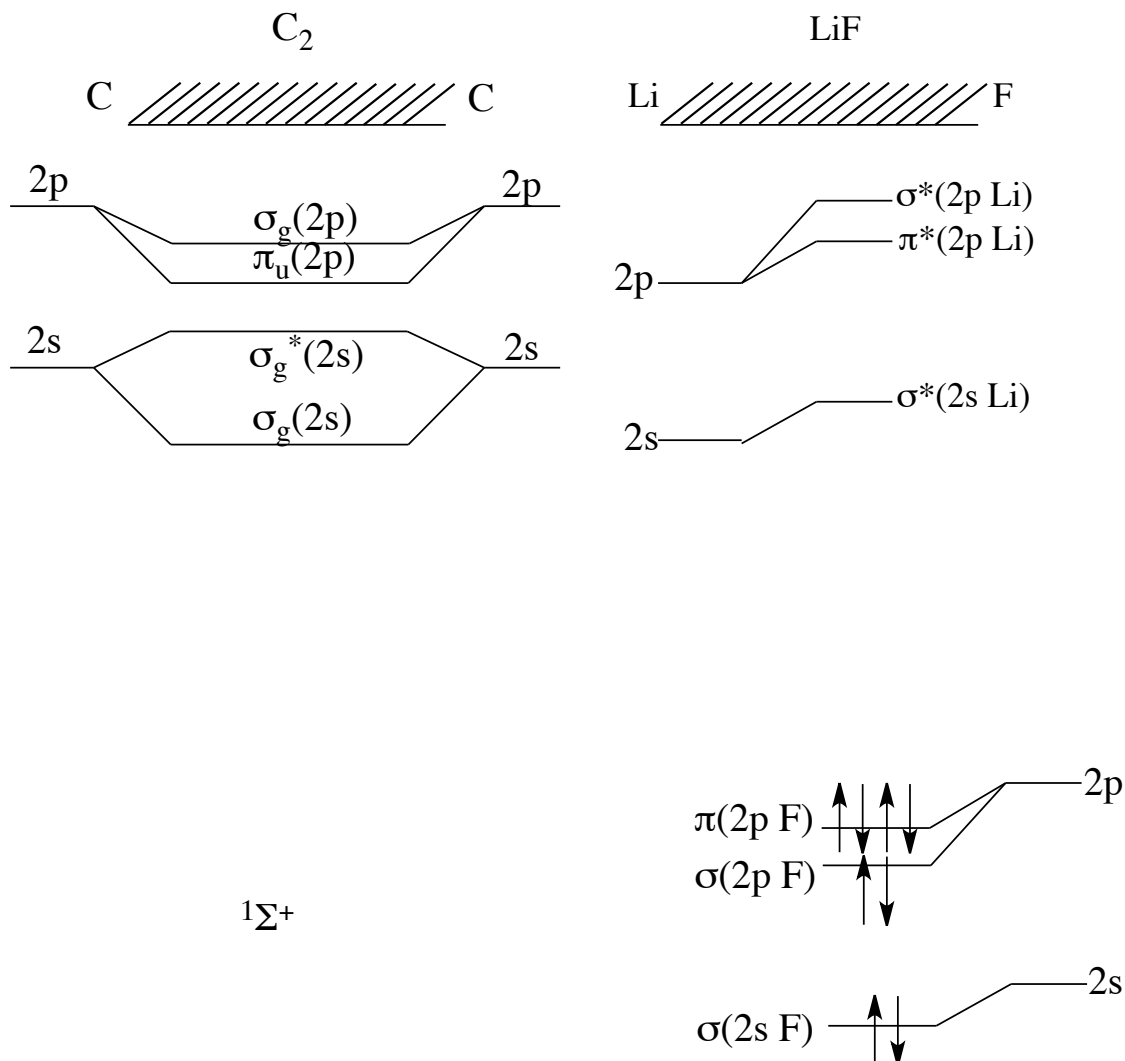


It is likely that the ground state of  $C_2$  is  $\sigma_g(2s)^2\sigma_u^*(2s)^2\pi_u(2p)^4 {}^1\Sigma_g^+$ . It is possible that the  $\pi_u(2p) \rightarrow \sigma_g(2p)$  promotion energy is small relative to the  $e^-e^-$  repulsion due to 4 electrons in the  $\pi_u(2p)$  orbital. So the  $\sigma_g(2s)^2\sigma_u^*(2s)^2\pi_u(2p)^3\sigma_g(2p) {}^3\Pi_u$  state is very low-lying. The analogous state to  $O_2$ ,  $\sigma_g(2s)^2\sigma_u^*(2s)^2\pi_u(2p)^2\sigma_g(2p)^2 {}^3\Sigma_g^-$  state is definitely out of contention for being the electronic ground state. Everything is far less conclusive than for  $O_2$ .

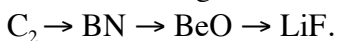
- B.** (10 points) *Isoelectronic* molecules with 8 valence electrons:  $C_2$ , BN, BeO, LiF.

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

We are looking at hetero-nuclear 8 electron molecules. The ionization energy from the highest energy AO increases as you go from Li to C and also from C to F.



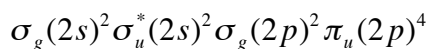
Ionic bonding. Negligible covalent character.  $C_2$  has a covalent bond order of 2. The covalent bonding character decreases as the ionization energy difference increases:



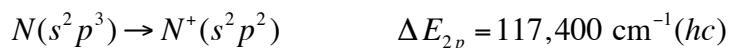
C. (10 points) The  $X^1\Sigma_g^+$  Electronic Ground States of *Homologous* Molecules:  $N_2$  and  $P_2$ .

	$\omega_e$	$R_e$	
$N_2$	$2359\text{ cm}^{-1}$	$1.10\text{ \AA}$	extremely stable and non-reactive
$P_2$	$781\text{ cm}^{-1}$	$1.89\text{ \AA}$	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



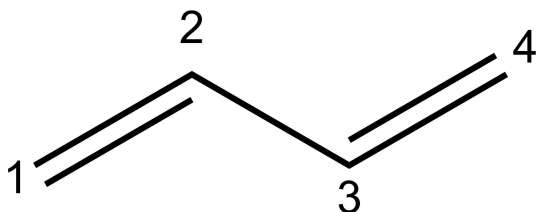
and



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  $r^{-3}$ .

Why is the bonding so different between  $N_2$  and  $P_2$ ? There is no simple correct answer to this question. Several factors are relevant:

- 1) The orbital size decreases as ionization energy increases. The orbitals on N are smaller than the corresponding orbitals on P. This suggests that  $R_e$  will be larger for  $P_2$ .
- 2) Orbital density decreases as orbital size increases. This means that bonding ( $\omega_e$ ) will be weaker for  $P_2$ .
- 3) The largest and most directed orbital is  $\sigma(2p)$ . If there is only one bond for  $P_2$ , it will be from  $\sigma_g(2p)^2$ .
- 4) The larger size of the valence MOs on  $P_2$  suggest that a smaller fraction of the electrons are in the region along the bond axis between the two atoms. The electrons outside the spatial region of overlap will be extremely susceptible to reaction.

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

The four Hückel Theory orbital eigen-energies are

$$\alpha + \beta[3 + 5^{1/2}/2]^{1/2} \quad \boxed{E_0}$$

$$\alpha + \beta[3 - 5^{1/2}/2]^{1/2} \quad \boxed{E_1}$$

$$\alpha - \beta[3 + 5^{1/2}/2]^{1/2} \quad \boxed{E_2}$$

$$\alpha - \beta[3 - 5^{1/2}/2]^{1/2} \quad \boxed{E_3}$$

and the four eigenvectors are

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

$\boxed{C_3}$        $\boxed{C_0}$        $\boxed{C_2}$        $\boxed{C_1}$

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

See above for  $C_0 \rightarrow C_3$  (counted by number of nodes), and the matching  $E_0 \rightarrow E_3$ . Note that  $3 > \sqrt{5}/2$ .

- B.** (13 points)

- (i) (3 points) How many  $p_z$  electrons are there in the  $\pi$ -system of butadiene?

Each carbon donates one electron, for a total of 4. Also,  $2 \times 2$  pi bonds is 4

(ii) (3 points) Specify the number of electrons in each of the four orbitals.

We have 4 electrons, so fill the two lowest orbitals.  $C_0$  and  $C_1$  then will have two electrons each.

(iii) (7 points) For only the **H**ighest energy **O**ccupied **M**olecular **O**rbital (HOMO), specify the non-integer number of  $\pi$ -electrons on each of the carbon atoms.

$C_1$  is filled and is  $(-0.6, -0.37, 0.37, 0.6)$  2 electrons  $\times C_1$  squared (element wise) gives  $2(0.6^2, 0.37^2, 0.37^2, 0.6^2) = (0.72, 0.27, 0.27, 0.72)$

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.

O12:  $2*(C1_1*C1_2) + 2*(C0_1*C0_2) = 2*(0.37*0.6+(-0.6)*(-0.37)) = 0.89$   
 (or 1.89 if you include the sigma bond).  
 O23:  $2*(0.6*0.6 + (0.37)(-0.37)) = 0.45$  (or 1.45)

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

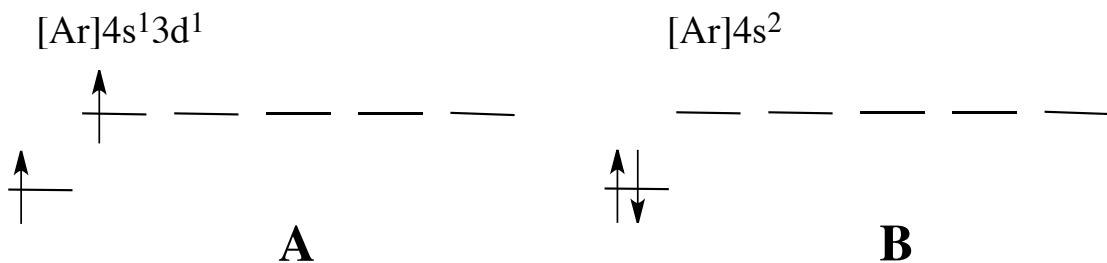
O<sub>14</sub>:  $2(0.37 \times 0.37 + (-0.6)(0.6)) = -0.45$ . No sigma bond. Lewis diagrams and chemical intuition tell us that there should be no bond order between non-adjacent atoms. This calculation indicates that there is actually bond order, and that atoms 1 and 4 are antibonding with respect to one another. This is due to the 4 atom orbitals (and thus multiple atom-long bonds) that are the molecular orbitals.



### 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  $\text{Sc}^+$  in one of the two possible configurations:



Express the energy of the two configurations using the symbols

$\epsilon_{4s}$	Energy of the 4s orbital
$\epsilon_{3d}$	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

$$E_A = \epsilon_{4s} + \epsilon_{3d} + J_{4s3d} - K_{4s3d} \quad (1)$$

$$E_B = 2\epsilon_{4s} + J_{4s4s} \quad (2)$$

- 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?

$J_{ij}$  is the average coulomb repulsion felt by an electron in orbital  $i$  with an electron in orbital  $j$ . An electron in the 4s orbital feels greater repulsion with another electron sharing the 4s orbital as opposed to an electron in a different orbital.

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

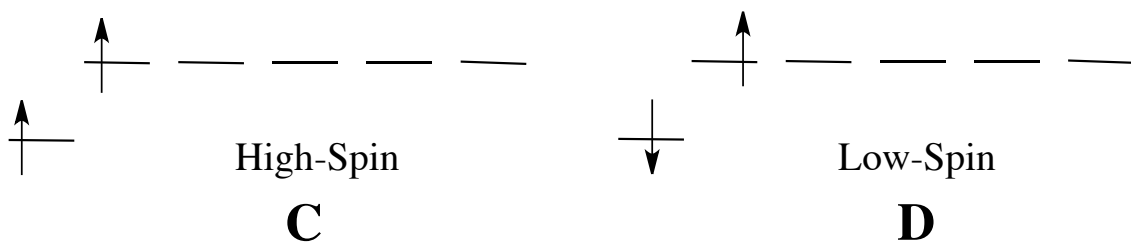
$$\epsilon_{4s} - \epsilon_{3d} = 0.1164.$$

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

$$E_B - E_A = \epsilon_{4s} - \epsilon_{3d} + J_{4s4s} - J_{4s3d} + K_{4s3d} = 0.2714 > 0$$

This means that Configuration A is more stable.

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



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

$$E_C = \epsilon_{4s} + \epsilon_{3d} + J_{4s3d} - K_{4s3d}$$

$$E_D = \epsilon_{4s} + \epsilon_{3d} + J_{4s3d}$$

- 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?*

$$E_D - E_C = K_{4s3d} > 0$$

So Configuration C (high-spin) is more favorable. Hund's First Rule favors high spin. It can also be explained using the fact that an exchange force keeps the electrons apart in C, so there is less coulomb repulsion.

- 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  $\text{Sc}^+$  comes from the  $[\text{Ar}]4s^1 3d^1$  configuration.

One acceptable answer is provided. A large positive contribution to  $E_B - E_A$  comes from  $J_{4s4s}$ .  $\text{Sc}^{2+}$  has the same electrons, but a higher nuclear and effective charge than Ca. The 4s orbital for Ca is farther from the nucleus and thus, larger, which means that  $J_{4s4s}$  is smaller for Ca. This may be enough to shift the inequality to

$$E_B - E_A < 0$$

Physically, this means that electron repulsion drives the second valence electron out of the 4s orbital and into the 3d orbital in the case of  $\text{Sc}^{2+}$ .

- 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:*

$$\begin{array}{ll} J_{1s,2s} & \text{vs.} \quad J_{1s,4s} \\ J_{1s,1s} & \text{vs.} \quad J_{1s,2s} \\ J_{1s,1s} & \text{vs.} \quad J_{10s,10s} \\ K_{2s,2p_z} & \text{vs.} \quad K_{2p_x,2p_z} \\ J_{2s,2s} & \text{vs.} \quad K_{2s,2s} \end{array}$$

$J_{1s2s} > J_{1s4s}$ : 4s is more diffuse than 2s, so electrons in the 1s orbitals feel less coulomb repulsion.

$J_{1s1s} > J_{1s2s}$ : Electrons in the 1s orbital are, on average, closer to other electrons sharing the 1s orbital than an electron in the 2s orbital, and thus feels more repulsion with other 1s electrons.

$J_{1s1s} > J_{10s10s}$ : The 1s orbital is smaller than the 10s orbital, so electrons in the 1s orbital spend more time near each other, resulting in a larger coulomb repulsion.

$K_{2s2p_z} > K_{2p_x2p_z}$ : Exchange is larger when there is more overlap between the orbitals. 2s and 2p<sub>z</sub> overlap but 2p<sub>x</sub> and 2p<sub>z</sub> do not.



$J_{2s2s} = K_{2s2s}$ : This is by definition of the integrals.

**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:**

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

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

**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  $\varepsilon$  where  $\varepsilon$  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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5.61 Physical Chemistry  
Fall 2017

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