4

Diatomic molecules

Answers to worked examples

WE 4.1 **The Lewis model (on p. 174 in *Chemistry*[3])**

Use the Lewis model to describe the bonding in (a) a P_2 molecule and (b) an OH^- anion.

(a)

Strategy

Work out the electronic configuration of phosphorus, and draw a diagram with electrons shared so that the atoms both obey the octet rule.

Solution

Phosphorus has the electronic configuration $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^3$, so each phosphorus atom has five electrons in its outer shell. Three pairs of electrons are shared between the phosphorus atoms to give each a noble gas configuration, so the bond in P_2 is a triple bond.

(b)

Strategy

Work out the electronic configurations of O^- and hydrogen, and draw a diagram with electrons shared so that oxygen obeys the octet rule and hydrogen has two electrons in its outer shell.

Solution

O^- has the electronic configuration $1s^2\, 2s^2\, 2p^5$, so the O^- anion has seven electrons in its outer shell, whereas the hydrogen atom has one electron in its outer shell. One pair of electrons is shared between the atoms to give each a noble gas configuration, so the bond in OH^- is a single bond.

WE 4.2   **Valence bond treatment of LiH (on p. 183 in *Chemistry*[3])**

For the molecule, ICl, which of the ionic forms would you expect to contribute more to the molecular wavefunction?

Strategy

Consider the two possible ionic forms of the wavefunction and hence which form is likely to dominate based on the electronegativity of the two ions.

Solution

Chlorine is more electronegative than iodine, so the ionic form $Cl^- I^+$ would contribute more to the molecular wavefunction than $Cl^+ I^-$.

WE 4.3   **Parity labels (on p. 187 in *Chemistry*[3])**

What parity label does this hexagon have?

Strategy

Examine the hexagon and map each point on to its inverse. If the point is the same on inversion, then the object has *g* symmetry (like a spherical *s* orbital) whereas if the point change places on inversion (like a dumbbell shaped *p* orbital) then the object has *u* symmetry.

Solution

This hexagon is changed on inversion, so has the parity label *u*.

WE 4.4   **The Be$_2$ molecule (on p. 193 in *Chemistry*[3])**

Would you expect Be_2^+ to exist?

Strategy

Generate a molecular orbital diagram for Be$_2$ and remove an electron from the highest occupied molecular orbital to give the diatomic a positive charge. Now calculate the bond order of the cationic species. If the bond order is greater than zero, the molecule can exist.

Solution

To form Be_2^+ from Be_2, an electron is lost from the antibonding orbital $2\sigma_u^*$ level, so Be_2^+ has a bond order of $1 - \frac{1}{2} = \frac{1}{2}$. Therefore it can exist.

WE 4.5 **O_2^+, O_2^- and O_2^{2-} (on p. 198 in *Chemistry*³)**

Which of these ions would you expect to be paramagnetic?

Strategy

A species which is paramagnetic has unpaired electrons meaning it can be affected by an external magnetic field.

Solution

O_2 has two unpaired electrons in the doubly degenerate $1\pi_g^*$ orbital. The O_2^+ cation has one fewer electron and the O_2^- anion has one more electron in these orbitals meaning both have one unpaired electron and so would be paramagnetic. In O_2^{2-} there are two extra electrons in the $1\pi_g^*$ orbitals meaning the orbitals are full and hence all the electrons are paired, therefore it is not paramagnetic.

WE 4.6 **Equations for the molecular orbitals in HF (on p. 209 in *Chemistry*³)**

Write an expression for the wavefunction of the bonding orbital in a molecule of LiF.

Strategy

Follow the LCAO method described in Box 4.10, the wavefunction for the bonding orbital will be formed from orbitals of the right symmetry on the lithium and the fluorine that are relatively close in energy.

Solution

The bonding orbital will be formed from the in-phase combination of the Li($2s$) orbital with the F($2p_z$) orbital:

$\psi_{\text{in phase}} = N \left[\lambda\phi_{\text{Li}}(2s) + \phi_{\text{F}}(2p_z) \right]$, where $\lambda < 1$.

WE 4.7 **Bond lengths in NO, NO$^+$ and NO$^-$ (on p. 211 in *Chemistry*[3])**

What common anion is isoelectronic with NO$^+$?

Strategy

Species are described as isoelectronic when they have the same number of electrons. To solve this problem, write down the electronic configuration of both atoms involved in the heteronuclear diatomic. As the species is a monovalent cation, remove one electron from the total and compare with similar species in the same period of the Periodic Table.

Solution

Nitrogen has 5 valence electrons and oxygen has 6. Therefore the neutral species has 11 electrons. Removal of one electron to form the cation gives 10 electrons. NO$^+$ is isoelectronic with N$_2$, CO and CN$^-$, so CN$^-$ is the anion that is isoelectronic with NO$^+$.

Answers to boxes

Box 4.1 **How can we measure bond lengths? (on p. 172 in *Chemistry*[3])**

Diffraction of electromagnetic radiation is also used to determine structures, and for crystalline solids X-ray diffraction is commonly used (see Box 6.4, p.279) Suggest why these experiments use X-rays and not ultraviolet radiation or γ-rays.

Strategy

Interference effects are used to measure the distance between the atoms in diffraction studies. In order for the radiation to be scattered to produce the interference required, the wavelength must be similar to the atomic spacings. Atomic spacings typically lie between 100 pm and 300 pm.

Solution

X-rays have similar wavelengths to the distances between atoms in crystalline solids and hence are used for diffraction studies. The wavelength of ultraviolet radiation is too short and γ-rays too long for these effects to occur.

Box 4.2 **Magnetic behaviour (on p. 176 in *Chemistry*[3])**

Which of the atoms and ions, Na, Ne and O^{2-} are paramagnetic?

<u>Strategy</u>

For an atom/ion to be paramagnetic, it must have unpaired electrons. Therefore write down the electronic configurations of the atoms/ions and determine if they have any unpaired electrons.

<u>Solution</u>

Na has the electronic configuration [Ne] $3s^1$. It has an unpaired electron so it is paramagnetic. Both Ne and O^{2-} have the electronic configuration [He] $2s^2 2p^6$. All of the electrons are paired so Ne and O^{2-} are not paramagnetic.

Box 4.3 **Molecular wavefunctions for H_2 (on p. 180 in *Chemistry*[3])**

Why is the electron–electron repulsion greater for the ionic resonance forms of H_2 than for the covalent form?

<u>Strategy</u>

Write down the resonance structures and compare the arrangement of electrons with the covalent form.
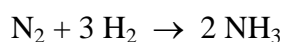
<u>Solution</u>

The ionic resonance structure is H^+H^-. The electrons are closer together when they are in the same $1s$ orbital as for H^-. This means the ionic resonance structure has greater electron–electron repulsion

Box 4.4 **How to make an unreactive molecule react (on p. 182 in *Chemistry*[3])**

Given that the high bond dissociation enthalpy of the N≡N bond, suggest why the reaction between N_2 and H_2 to give ammonia is exothermic.

<u>Strategy</u>

The reaction for forming ammonia from hydrogen and nitrogen is

$N_2 + 3 H_2 \rightarrow 2 NH_3$

To solve this problem, the enthalpy differences between reactants and products need to be compared.

Solution

Although strong N≡N bonds and strong H–H bonds are broken, strong N–H bonds are formed. The net enthalpy change of bond making and bond breaking is negative and the reaction is therefore exothermic.

Box 4.7   Oxygen in the atmosphere (on p. 198 in *Chemistry*[3])

Suggest why H_2 is no longer an important component of the atmosphere.

Strategy

Consider how hydrogen may be lost from the atmosphere in a way that heavier molecules are not.

Solution

Hydrogen molecules are light enough to escape the Earth's gravity, so have been lost to space in the 4 billion years since the formation of the Earth.

Box 4.8   Measuring the energies of molecular orbitals (on p. 200 in *Chemistry*[3])

In the PES experiment, a sample of nitrogen was irradiated with photons of frequency 5.13×10^{15} Hz. Ejected electrons with kinetic energy 8.97×10^{-19} J were observed. Calculate the orbital energy (in kJ mol^{-1}) of these electrons in N_2.

Strategy

Calculate the energy of the photon using Equation 3.2, $E = h\nu$.

Then use Equation 4.17, $h\nu = I + E_{KE}$, to calculate the ionization energy.

Solution

Using Equation 3.2, energy of the photon,

$$E = h\nu \qquad\qquad (h = 6.626 \times 10^{-34} \text{ J s})$$
$$= (6.626 \times 10^{-34} \text{ J s}^{-1}) \times (5.13 \times 10^{15} \text{ s}^{-1})$$
$$= 3.40 \times 10^{-18} \text{ J}$$

Using Equation 4.17, $hv = I + E_{KE}$

Rearranging this equation gives, $I = hv - E_{KE}$

$$= (3.40 \times 10^{-18} \text{ J}) - (8.97 \times 10^{-19} \text{ J})$$
$$= 2.50 \times 10^{-18} \text{ J}$$

This is the ionization energy for a single N_2 molecule. For a mole of molecules, this value must be multiplied by the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$).

$$I = (2.50 \times 10^{-18} \text{ J}) \times (6.022 \times 10^{23} \text{ mol}^{-1})$$
$$= 1510000 \text{ J mol}^{-1}$$
$$= 1510 \text{ kJ mol}^{-1}$$

Box 4.9 **The colours of the polar lights (on p. 203 in *Chemistry*³)**

Are the photons emitted by excited N_2^+ ions in aurorae of higher or lower energy than those emitted by excited N_2 molecules?

Strategy

The different colours of the emissions indicate different energies and lie at wavelengths between 661 nm and 686 nm for the neutral nitrogen species and 391 nm and 470 nm for the cation. The relative energies can be evaluated by converting the wavelengths to frequency using Equation 3.1, $c = \lambda v$, and Equation 3.2, $E = hv$.

Solution

For the red lines and N_2:

Using Equation 3.1, $n = \dfrac{c}{\lambda} = \dfrac{2.998 \times 10^8 \text{ m s}^{-1}}{661 \times 10^{-9} \text{ m}} = 4.54 \times 10^{14} \text{ (s}^{-1}) \text{ Hz}$

Using Equation 3.2, energy of the photon,

$$E = hv \qquad\qquad (h = 6.626 \times 10^{-34} \text{ J s})$$
$$= (6.626 \times 10^{-34} \text{ J s}^{-1}) \times (4.54 \times 10^{14} \text{ s}^{-1})$$
$$= 3.01 \times 10^{-19} \text{ J}$$

For the blue lines and N_2^+:

Using equation 3.1, $n = \dfrac{c}{\lambda} = \dfrac{2.998 \times 10^8 \text{ m s}^{-1}}{391 \times 10^{-9} \text{ m}} = 7.67 \times 10^{14} \text{ (s}^{-1}\text{) Hz}$

Using Equation 3.2, energy of the photon,

$$E = h\nu \qquad\qquad (h = 6.626 \times 10^{-34} \text{ J s})$$
$$= (6.626 \times 10^{-34} \text{ J s}^{-1}) \times (7.67 \times 10^{14} \text{ s}^{-1})$$
$$= 5.08 \times 10^{-18} \text{ J}$$

The photons emitted from the excited N_2^+ ions have higher energy than those emitted by the excited N_2 molecules.

Box 4.10 **Linear combinations of atomic orbitals in LiH (on p. 207 in *Chemistry*³)**
Write an expression for the bonding orbital in the molecule NaLi.

Strategy

As Group 1 is descended the elements become more electropositive, therefore sodium is more electropositive than lithium. The two orbitals of the right symmetry to form the bonding combination are the 2*s* and 3*s* orbitals on lithium and sodium respectively.

Solution

$\psi = N\,[\phi_{Li}(2s) + \lambda\phi_{Na}(3s)]$. $\lambda < 1$, as lithium is more electronegative than sodium.

Box 4.11 **Using nitrogen monoxide to send biological signals (on p. 212 in *Chemistry*³)**
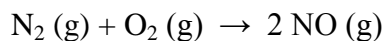Nitrogen monoxide is produced naturally in the atmosphere during thunderstorms. Suggest how it is formed.

Strategy

Consider the reaction involved, and th bonds that need to be broken and formed.

Solution

In a thunderstorm, NO is produced from reactions involving nitrogen and oxygen gases in the air. The overall equation for the process is

$$N_2 \text{ (g)} + O_2 \text{ (g)} \rightarrow 2 \text{ NO (g)}$$

This reaction is endothermic, and in practice, NO is not formed by direct collision of N_2 and O_2 molecules, but as a result of a series of radical reactions that take place at the high temperature generated by lightning.

Answers to end of chapter questions

1. Draw Lewis structures for the following molecules and ions, and in each case identify the bond order.

    $$Cl_2 \qquad Se_2 \qquad HBr \qquad ClO^-$$
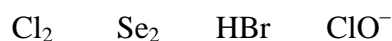
    Strategy

    Work out the electronic configuration of the atoms, and draw a diagram with electrons shared so that the atoms both obey obtain noble gas configurations.

    Solution

    Cl_2: Chlorine has 7 valence electrons ($3s^2\,3p^5$) so needs one electron to complete its octet. The two chlorine atoms form a single bond, sharing one pair of electrons. The bond order is 1.
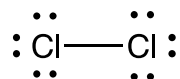
    Se_2: Selenium has 6 valence electrons ($4s^2\,4p^5$) so needs two electrons to complete its octet. The two selenium atoms form a double bond, sharing two pairs of electrons. The bond order is 2.
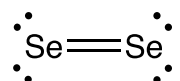
    HBr: Hydrogen has 1 valence electrons ($1s^1$) so needs one electron to complete its outer shell. Bromine has 7 valence electrons ($4s^2\,4p^5$) so needs one electron to complete its octet. The two atoms form a single bond, sharing one pair of electrons. The bond order is 1.
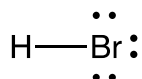
    ClO^-: Chlorine has 7 valence electrons ($3s^2\,3p^5$) so needs one electron to complete its octet. Oxygen has 6 valence electrons ($2s^2\,2p^5$) so needs two electrons to complete its

octet. One of these comes from the negative charge, so the two atoms form a single bond, sharing one pair of electrons. The bond order is 1.

$$\ddot{:}\ddot{O}\!-\!\ddot{C}\ddot{l}\!:$$

2. Use the following information to predict the electronegativity of iodine

$\chi^P_{(H)} = 2.20$ $D_{(H-H)} = +435.8$ kJ mol^{-1}

$D_{(I-I)} = +152.3$ kJ mol^{-1} $D_{(H-I)} = +298.3$ kJ mol^{-1}

Strategy

Using Pauling's theories relating electronegativity and the differences between the calculated and observed values of the bond dissociation enthalpy, the electronegativity for iodine can be calculated. Use Equation 4.2 (p.177) to calculate ΔD, then use Equation 4.3 to calculate the difference in electronegativity between hydrogen and iodine. Finally, use the electronegativity value for hydrogen together with the knowledge than iodine is more electronegative than hydrogen to calculate $\chi^P_{(I)}$.

Solution

Using Equation 4.2:

$$\Delta D = D_{(X-Y)} - \frac{D_{(X-X)} + D_{(Y-Y)}}{2}$$

$$= +298.3 \text{ kJ mol}^{-1} - \frac{+435.8 \text{ kJ mol}^{-1} + 152.3 \text{ kJ mol}^{-1}}{2}$$

$$= +298.3 \text{ kJ mol}^{-1} - 294.1 \text{ kJ mol}^{-1} = 4.2 \text{ kJ mol}^{-1}$$

Using Equation 4.3:

$$|\chi^P(X) - \chi^P(Y)| = 0.102(\Delta D)^{\frac{1}{2}}$$

So $|\chi^P(I) - \chi^P(H)| = 0.102(4.2)^{\frac{1}{2}}$

$|\chi^P(I) - 2.20| = 0.21$

$\chi^P(I) = 2.20 + 0.21 = 2.41.$

3. Use the data in Table 4.1 (p.171) and Figure 4.6 (p.178) to estimate a value for the bond dissociation enthalpy of ClBr.

Strategy

Use Equation 4.3 to calculate ΔD, then rearrange Equation 4.2 to obtain a value for $D_{(Cl-Br)}$.

Solution

From Table 4.1, $D_{(Cl-Cl)} = +242.4$ kJ mol^{-1} and $D_{(Br-Br)} = +193.9$ kJ mol^{-1}.

From Figure 4.6, $\chi^P_{(Cl)} = 3.16$ and $\chi^P_{(Br)} = 2.96$.

Using Equation 4.3:

$|\chi^P(Cl) - \chi^P(Br)| = 0.102(\Delta D)^{\frac{1}{2}}$

So $|3.16 - 2.96| = 0.102(\Delta D)^{\frac{1}{2}}$

$0.102(\Delta D)^{\frac{1}{2}} = 0.20$

$(\Delta D) = (0.20 / 0.102)^2 = 3.8$ kJ mol^{-1}

Rearranging Equation 4.2:

$$D_{(X-Y)} = \Delta D + \frac{D_{(X-X)} + D_{(Y-Y)}}{2}$$

So $D_{(Cl-Br)} = 3.8$ kJ mol^{-1} $+ \dfrac{+242.4 \text{ kJ mol}^{-1} + 193.9 \text{ kJ mol}^{-1}}{2}$

$= 222$ kJ mol^{-1} (3 SF)

4. An alternative scale of electronegativity to that of Pauling was proposed by Robert Mulliken, who argued that an electronegative atom was likely to have both a high ionization energy, as it would not readily lose electrons, and a high negative electron gain energy, as it would be energetically favourable for it to gain electrons. Mulliken defined electronegativity as an average of these terms, as shown below.

$$\chi^M = \tfrac{1}{2}(I_1 - E_{eg1})$$

Use the data in Figures 3.35 (p.156) and 3.38 (p.158) to calculate χ_M for the Group 17 elements, and comment on the trend observed.

Strategy

Use the equation given to calculate χ^M for fluorine, chlorine, bromine and iodine.

Solution

For fluorine, I_1 is 1681 kJ mol^{-1}, and E_{eg1} is –328 kJ mol^{-1}.

$\chi^M = 0.5(1681 - (-328))$ kJ mol^{-1} = 1004.5 kJ mol^{-1}.

For chlorine, I_1 is 1251 kJ mol^{-1}, and E_{eg1} is –349 kJ mol^{-1}.

$\chi^M = 0.5(1251 - (-349))$ kJ mol^{-1} = 800 kJ mol^{-1}.

For bromine, I_1 is 1140 kJ mol^{-1}, and E_{eg1} is –325 kJ mol^{-1}.

$\chi^M = 0.5(1140 - (-325))$ kJ mol^{-1} = 732.5 kJ mol^{-1}.

For iodine, I_1 is 1008 kJ mol^{-1}, and E_{eg1} is –295 kJ mol^{-1}.

$\chi^M = 0.5(1008 - (-295))$ kJ mol^{-1} = 651.5 kJ mol^{-1}

χ^M decreases going down Group 17, following a similar trend to χ^P.

5. Draw one covalent and two ionic resonance forms that contribute to the bonding in ClF in the valence bond approach. Which of the ionic forms are more important? Why?

Strategy

Write down the resonance forms and evaluate which ionic species are most stable on the basis of electronegativity.

Solution

Cl—F $\leftrightarrow$ Cl$^+$ F$^-$ $\leftrightarrow$ Cl$^-$ F$^+$
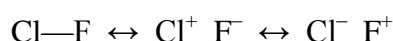
The ionic form Cl$^+$F$^-$ is more important than Cl$^-$F$^+$ as fluorine is more electronegative than chlorine.

6. Use valence bond theory to describe the bonding in the cyanide anion, CN$^-$. What orbitals interact to form the bonds between the atoms?

Strategy

Draw a Lewis structure for CN$^-$, and work out the bond order. Describe each of the bonds in terms of the orbitals that contribute to it. For the σ bond, you will need to consider the hybridization of the carbon and nitrogen atoms.

Solution

The bond order in CN^- is 3, which is consistent with *sp* hybridization of the carbon and nitrogen atoms. One of these hybrid orbitals from each of the atoms interact to form a σ bond. The other points at 180° from the other atom and carries a lone pair. The unhybridized p_x and p_y orbitals on the two atoms interact to form π bonds, so overall the triple bond consists of a σ bond and two π bonds.

7. H_2 absorbs ultraviolet radiation of the wavelength 109 nm. What is the origin of this absorption and what energy (in $kJ\ mol^{-1}$) does it correspond to? Why does absorbing ultraviolet radiation of this wavelength cause the H_2 molecule to split into atoms?

Strategy

Use Equations 3.1 and 3.2 to calculate the energy of the ultraviolet radiation and the molecular orbital diagram of dihydrogen given in Figure 4.14 to determine the origin of the absorption. This value for a single photon can then be converted to a molar quantity by multiplying by the Avogadro constant.

Solution

Hydrogen has only two molecular orbitals generated from the 1*s* orbitals. The absorption must be due to the molecule absorbing energy corresponding to the energy difference between $1\sigma_g \rightarrow 1\sigma_u^*$.

Using Equation 3.1 to calculate the frequency of the transition gives

$$v = c\ /\ \lambda \qquad\qquad c = 2.998 \times 10^8\ m\ s^{-1}$$

$$v = \frac{2.998 \times 10^8\ m\ s^{-1}}{109 \times 10^{-9}\ m}$$
$$v = 2.75 \times 10^{15}\ s^{-1}$$

This frequency can then by converted into energy using Equation 2.2, $E = hv$

$$E = hv \qquad\qquad h = 6.626 \times 10^{-34}\ J\ s$$
$$E = (6.626 \times 10^{-34}\ J\ s)\ \times\ (2.75 \times 10^{15}\ s^{-1})$$
$$E = 1.82 \times 10^{-18}\ J$$

This gives the energy of a single photon corresponding to one bond. To change this to the value for a whole mole, it must be multiplied by the Avogadro constant to

produce an answer in J mol^{-1} and then divided by 1000 to convert the answer to kJ mol^{-1}.

Multiplying by N_A and divide by 1000 to get the answer in kJ mol^{-1}, where N_A = 6.022×10^{23} mol^{-1} gives

$E = (1.82 \times 10^{-18}$ J$) \times (6.022 \times 10^{23}$ mol$^{-1}) / 1000$
$E = 1100$ kJ mol^{-1} (3 SF)

So, the energy gap between the $1\sigma_g$ and $1\sigma_u{}^*$ molecular orbitals in H$_2$ is 1100 kJ mol^{-1}.

In the excited state, there is one electron in the $1\sigma_g$ molecular orbital and one electron in the $1\sigma_u{}^*$ molecular orbital. The bond order is $^1/_2 - {}^1/_2 = 0$, so this molecule is not stable and breaks apart into atoms.

8. Use the molecular orbital energy level diagram for Li$_2$ (Figure 4.17, p.192) to work out the bond orders of Li$_2$, Li$_2{}^+$ and Li$_2{}^-$. Which of these species is paramagnetic?

Strategy
The ground state configuration for Li is $1s^2 2s^1$. Using the diagram for Li$_2$, there are two electrons in the bonding $2\sigma_g$ level. Forming the cation and anion and determining the bond order is just a matter of removing/adding the appropriate number of electrons.

Solution
The bond orders for neutral Li$_2$, cationic Li$_2{}^+$ with one less electron in $2\sigma_g$ and Li$_2{}^-$ where there is an extra electron in the $2\sigma_u{}^*$ are 1 [*i.e.* $1 - 0$], $\frac{1}{2}$ [*i.e.* $\frac{1}{2} - 0$] and $\frac{1}{2}$ [*i.e.* $1 - \frac{1}{2}$] respectively. Li$_2{}^+$ and Li$_2{}^-$ are paramagnetic, but Li$_2$ is diamagnetic.

9. Use the linear combination of atomic orbitals approach to write expressions for the wavefunctions for the in-phase and out-of-phase combinations of lithium $2s$ orbitals. Which molecular orbitals in Li$_2$ do these combinations correspond to?

Strategy

As there are two *s* orbitals, one from each lithium atom, these atomic orbitals combine to give two molecular orbitals on the molecule. The lower in energy is in the in-phase combination with bonding character and the higher in energy is the out-of-phase combination which has antibonding character.

Solution

$\psi_{\text{in phase}} = 0.5^{1/2} \times [\phi_{2s}(Li_A) + \phi_{2s}(Li_B)]$.

$\psi_{\text{out of phase}} = 0.5^{1/2} \times [\phi_{2s}(Li_A) - \phi_{2s}(Li_B)]$.

The in-phase combination corresponds to the $2\sigma_g$ bonding orbital, and the out-of-phase combination to the $2\sigma_u^*$ antibonding orbital.

10. The mass spectrum of a sample of beryllium contains an intense peak at *m/z* 9 and a less intense peak at *m/z* 18. Identify the species involved and use molecular orbital theory to support the existence of the species giving rise to the peak of lower intensity.

Strategy

The mass spectrum is a cation spectrum and hence species can form that may not be expected as neutral species. The MO energy level diagram for Be_2 is shown in Worked Example 4.4 (p.193). This molecule has a bond order of zero, so does not exist. However, removal of an electron to form a cationic species gives a non-zero bond order and hence a species that can exist.

Solution

The peak at *m/z* 9 is from Be^+ and the peak at *m/z* 18 is from Be_2^+. Since the HOMO is an antibonding orbital, removal of an electron gives a positive ion, Be_2^+, with a bond order of $^1/_2$ [*i.e.* $1 - ^1/_2$].

11. Sketch boundary surface diagrams for the HOMO and LUMO in F_2

Strategy

The molecular orbital energy level diagram for F_2 is given in Figure 4.23 (p.197). From this, you can see that the highest occupied molecular orbital is the $1\pi_g$ antibonding orbital and the lowest unoccupied molecular orbital is the $3\sigma_u$ antibonding orbital.

Solution

The boundary surfaces for these orbitals are shown in Figure 4.21 (p.195) and Figure 4.20 (p.194) respectively.

π_g^* orbital
(HOMO)
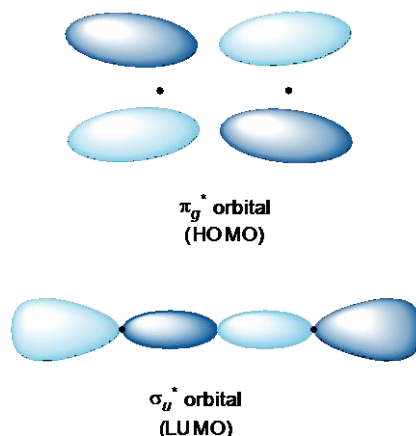
σ_u^* orbital
(LUMO)

12. Draw a molecular orbital diagram for Ne_2. Would you expect this molecule to exist?

Strategy

Draw the MO diagram and investigate the bond order. If the bond order is greater than zero, the molecule can exist.

Solution

Molecular orbital energy level diagram for Ne_2:

Ne
($2s^2\,2p^6$)

Ne$_2$
Bond order = $(4 - 4) = 0$

Ne
($2s^2\,2p^6$)
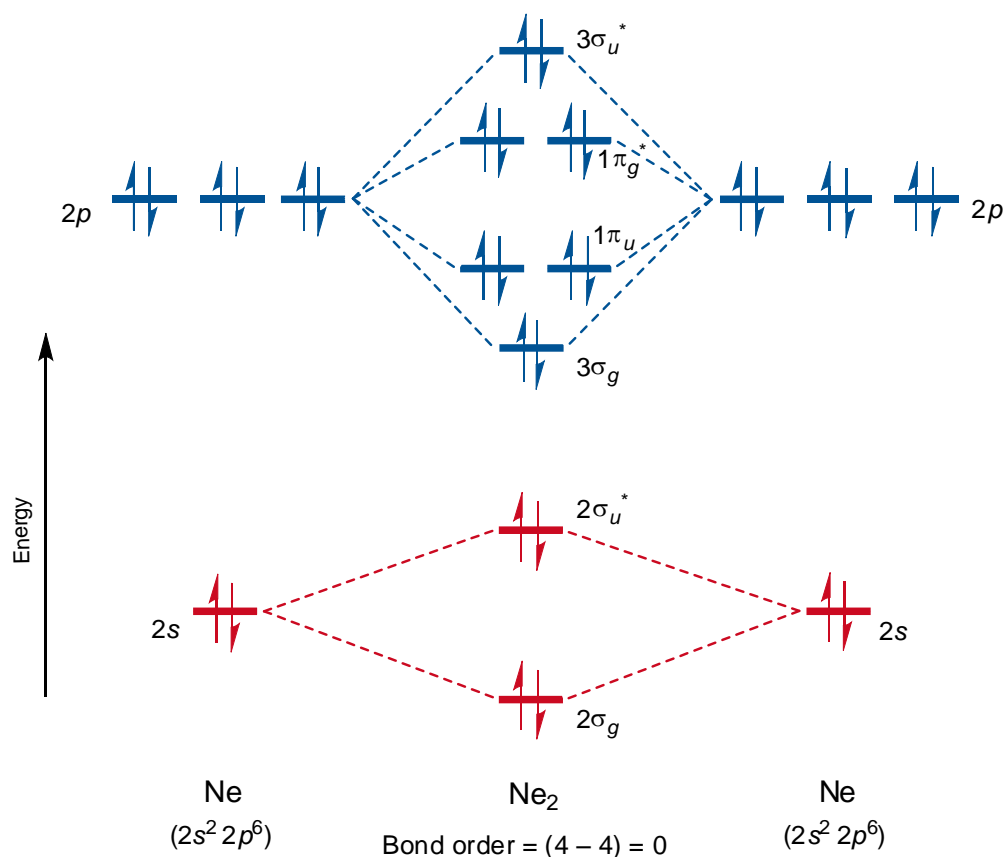
Ne$_2$ has a bond order of zero, so would not be expected to exist.

13. Which of the following pairs of molecules or ions are isoelectronic with each other?

(a) CO and NO$^-$

(b) CN$^-$ and NO$^+$

(c) N$_2^-$ and O$_2^+$

Strategy

Species are described as isoelectronic when they have the same number of electrons. Write down the electronic configuration of both atoms involved in each diatomic molecule, then add or subtract electrons as necessary to account for the charge.

Solution

(a) CO has 10 valence electrons (4 from carbon, 6 from oxygen). NO$^-$ has 12 valence electrons (5 from nitrogen, 6 from oxygen and one from the charge). They are not isoelectronic.

(b) CN^- has 10 valence electrons (4 from carbon, 5 from nitrogen and one from the charge). NO^+ has 10 valence electrons (5 from nitrogen, 6 from oxygen and minus one from the charge). They are isoelectronic.

(c) N_2^- has 11 valence electrons (5 from each nitrogen and one from the charge). O_2^+ has 11 valence electrons (6 from each oxygen and minus one from the charge). They are isoelectronic.

14. Draw a labelled molecular orbital energy level diagram for the acetylide dianion C_2^{2-} and use it to explain why the bond length in C_2^{2-} (119 pm) is less than that in C_2 (124 pm).

Strategy

Bond length and bond strength for the same pair of species can be directly correlated to bond order. As the bond order increases, the bond becomes shorter and stronger. Therefore determination of the bond order should explain the differences in the bond length.

Solution

Molecular orbital energy level diagram for C_2^{2-}:

C⁻ — C^- $(2s^2\, 2p^3)$

C_2^{2-} Bond order = (4 − 1) = 3

C⁻ — C^- $(2s^2\, 2p^3)$
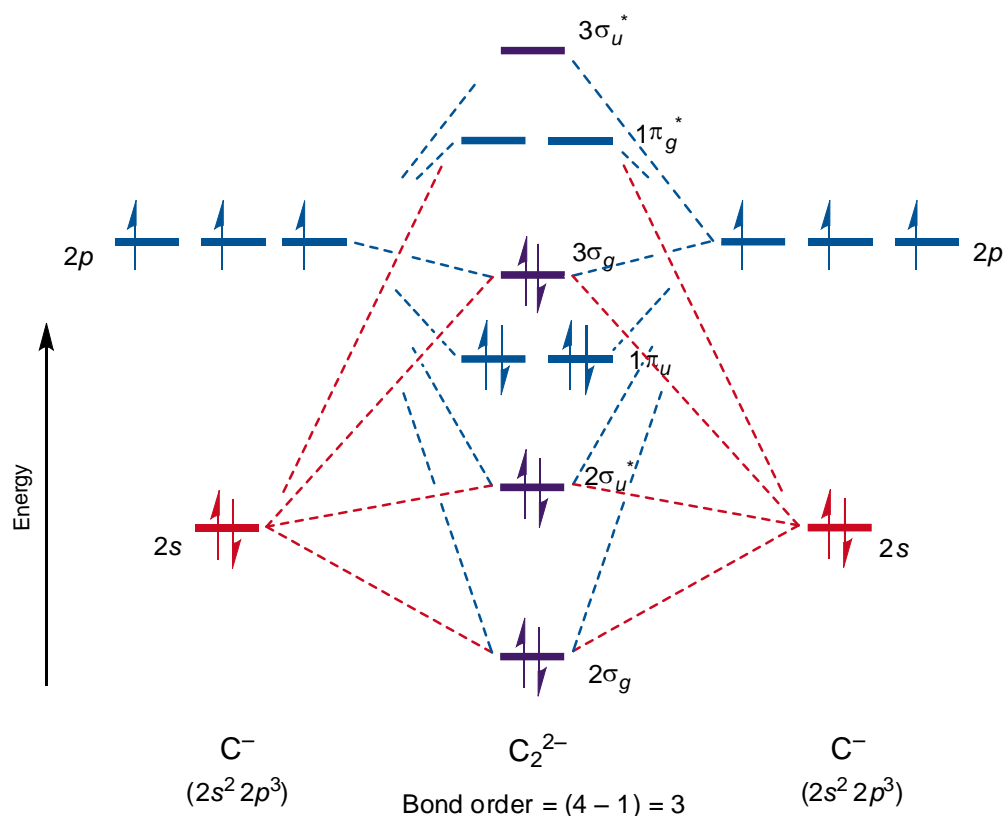
The bond order in C_2^{2-} is 3 whereas that in C_2 is 2 (Figure 4.27, p.204). A higher bond order between the same two atoms leads to a shorter, stronger bond length.

15. Give examples of neutral homonuclear and heteronuclear diatomic molecules that are isoelectronic with C_2^{2-}.

Strategy

Determine the total number of valence electrons by counting the electrons on both species and adding them together. Add two for the negative charge on the anion compare with near neighbours in the same period of the Periodic Table.

Solution

Each carbon has 4 valence electrons and the anion has an extra two electrons from the negative charge for C_2^{2-}. This gives a total of 10 valence electrons. This compares with N_2 (2 × 5 valence electrons) and CO (4 + 6 valence electrons) or CN^- (4 + 5 + 1 (for the negative charge), as all have 10 valence electrons.

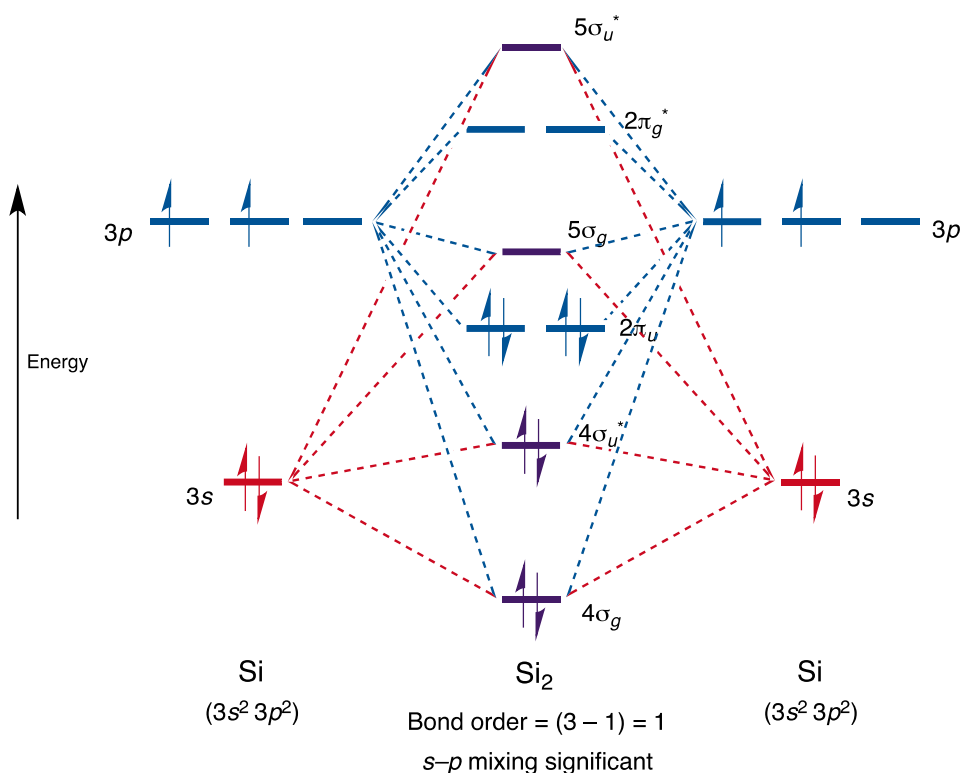**16.** Construct a labelled molecular orbital energy level diagram for Si_2, stating any assumptions you have made.

Measurements suggest that Si_2 is diamagnetic in the gas phase. Is this consistent with your diagram? If not, what changes could be made to the order of the molecular orbitals? How could these be justified?
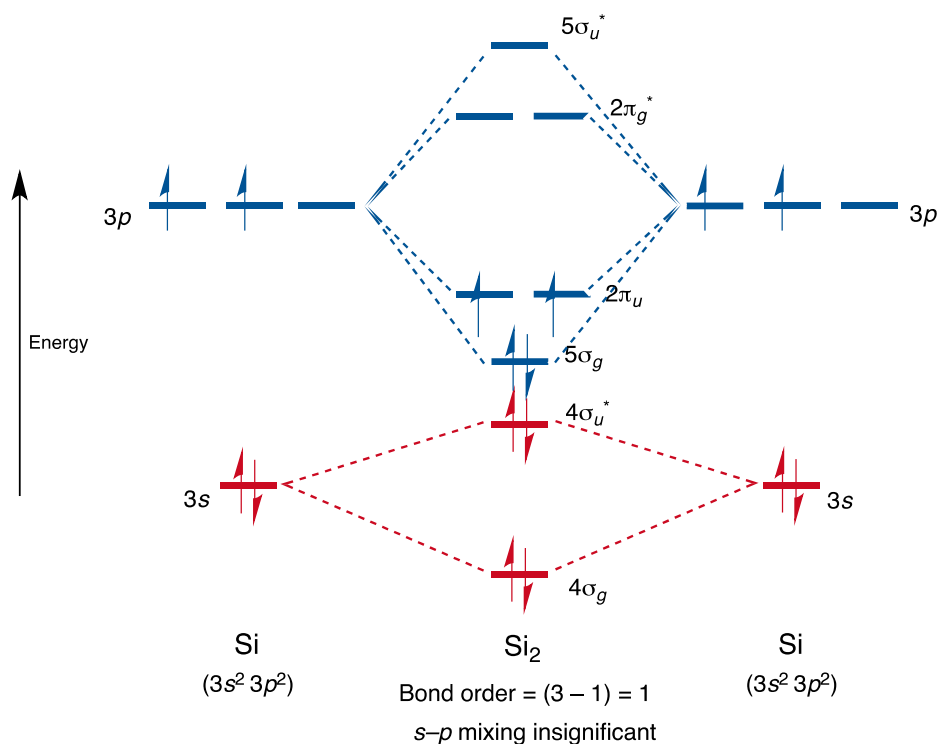
Strategy

Draw a molecular orbital energy level diagram for Si_2. You will need to make an assumption about the significance of *s*–*p* mixing, but the experimental magnetic data will help you decide how the *s*–*p* mixing affects the relative energies of the σ_g and π_u orbitals.

Solution

Two possible diagrams can be drawn depending on whether *s*–*p* mixing is significant or not.

$5\sigma_u^*$

$2\pi_g^*$

$3p$ $3p$

$2\pi_u$

Energy

$5\sigma_g$

$4\sigma_u^*$

$3s$ $3s$

$4\sigma_g$

Si   Si$_2$ Si

$(3s^2\,3p^2)$ Bond order = (3 − 1) = 1 $(3s^2\,3p^2)$

s–p mixing insignificant

If the $5\sigma_g$ orbital is lower in energy than the $2\pi_u$ orbital (*i.e. s–p* mixing insignificant) then the molecule is predicted to be paramagnetic, with two unpaired electrons. If the $5\sigma_g$ orbital is higher in energy than the $2\pi_u$ orbital (*i.e. s–p* mixing significant) then the molecule is predicted to be diamagnetic, not paramagnetic. The measurements reveal that Si$_2$ is diamagnetic, not paramagnetic, confirming that the $5\sigma_g$ orbital is higher in energy than the $2\pi_u$ orbital. Justification for *s–p* mixing comes from the relative small energy gap between the $3s$ and $3p$ orbitals for silicon.

17. Draw a labelled MO diagram for the ˙OH radical. The bonding orbital is described by the wavefunction

$$\psi = N[\lambda\phi(H_{1s}) + \phi O_{2p_z}]$$

Comment on the magnitude of λ, and any assumptions that have been made in obtaining this expression. What is the bond order in ˙OH and OH⁻.

Strategy

In order to solve this problem, the contribution of the individual orbitals must be considered. Only the H($1s$) and O($2p_z$) are considered as they have the similar energy and right symmetry with respect to the internuclear axis to combine.

Solution

Since the contribution from the $O(2p_z)$ orbital will be greater than that of the $H(1s)$ orbital to the bonding MO, λ must be less than 1. The expression assumes there is no contribution from the $O(2s)$ orbital as it is too far away in energy from the $H(1s)$ orbital. The bond order in both ˙OH and OH¯ is 1, since the electron is added to a non-bonding orbital.

Molecular orbital energy level diagram for ˙OH:
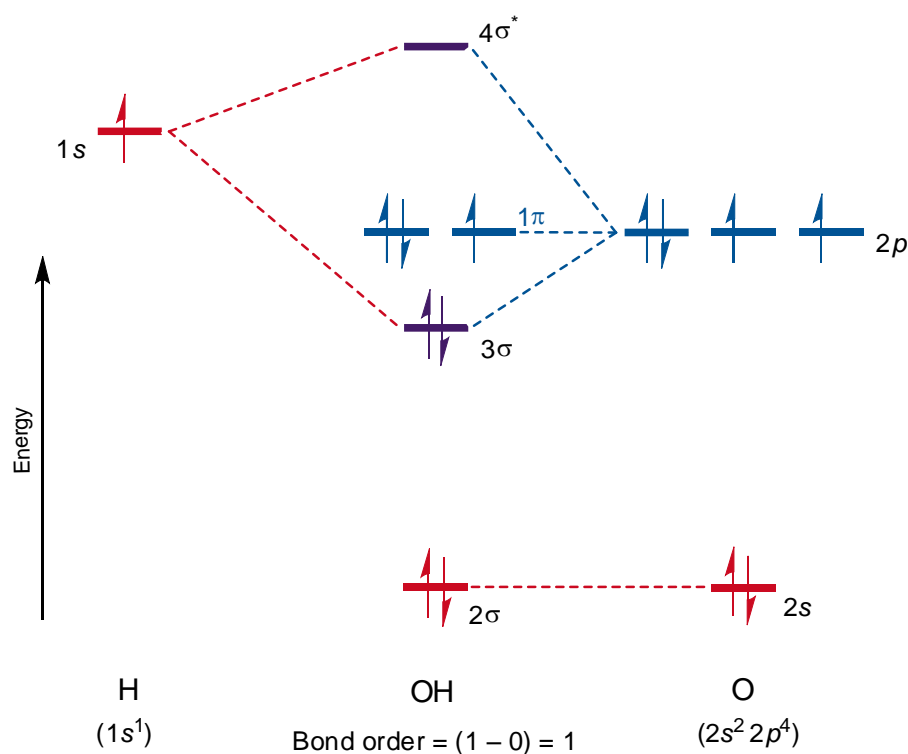
18.   Draw a labelled molecular orbital energy level diagram for the cyanide anion CN¯. What is the bond order in CN¯? How would the bond length and magnetic behaviour of neutral CN differ from those observed for CN¯?
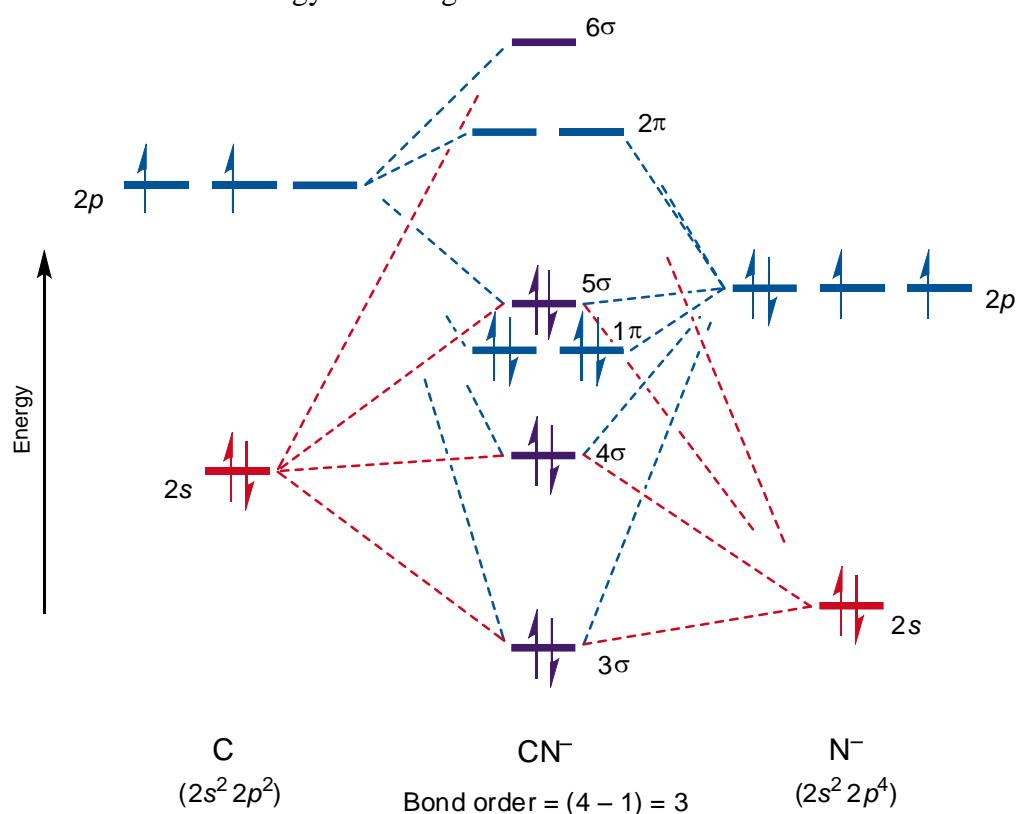
Strategy

Draw the molecular orbital diagram for CN¯, remembering that a common pitfall in drawing heteronuclear molecular orbital diagrams is to forget that the atomic orbitals of C and N will be at different energies due to the difference in electronegativity between the atoms. Consider the distribution of electrons in the molecular orbitals of

bonding and antibonding character and then calculate the bond order. As the bond order increases between the same pair of atoms, the bond becomes stronger and shorter. Finally, in order for a molecule to show magnetic behaviour (*i.e.* be affected by an external magnetic field) it must have some unpaired electrons (paramagnetic) rather than have all paired electrons (diamagnetic).

Solution

The bond order for CN⁻ is 3. On going from CN⁻ to CN an electron is removed from a bonding orbital. The bond order in CN is therefore $2^{1}/_{2}$ and the bond length would be greater than in CN⁻. CN has an unpaired electron so is paramagnetic, in contrast to CN⁻ which is diamagnetic.

Molecular orbital energy level diagram for CN⁻:

18.   What are the symmetry labels for the following molecular orbitals in the molecules A_2 and AB? Is A or B more electronegative?

Strategy

The type of orbital depends on the symmetry with respect to the internuclear axis. If an orbital is symmetric when rotated around this axis it will be a σ type orbital, if it is antisymmetric it will be a π type orbital. A subscript is then given to describe the parity labels which refer to the symmetry operation of inversion. If a point at *x*, *y*, *z* has the same sign as the point at −*x*, −*y*, −*z*, then the orbital is symmetric with the label *g*, if it has the opposite sign then the orbital will be antisymmetric and have the label, *u*. If inversion is not possible, the orbital is said to not have an inversion centre, and no parity label is used.

<u>Solution</u>

(a) π_u

(b) σ_g

(c) σ

(d) π^*

As described on p.206, the more electronegative element holds its electrons more tightly and is normally on the right in MO diagrams. B is more electronegative than A.