
Diatomic molecules

Answers to worked examples

WE 3.1 The Lewis model

Use the Lewis model to describe the bonding in a P₂ molecule.

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 P₂ is a triple bond.

WE 3.3 Parity labels

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 3.5 O_2^+ , O_2^- and O_2^{2-}

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 less 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 3.7 Bond lengths in NO , NO^+ and NO^-

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 species 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^- .

Answers to boxes

Box 3.1 How can we measure bond lengths?

Diffraction of electromagnetic radiation is also used to determine structures, and for crystalline solids X-ray diffraction is commonly used (see Box 5.4, p.239) 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 3.3 Molecular wavefunctions for H₂

Why is the electron–electron repulsion greater for the ionic resonance forms of H₂ than for the covalent form?

Strategy

Write down the resonance structures and compare the arrangement of electrons with the covalent form.

Solution

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 3.7 Oxygen in the atmosphere

Suggest why H₂ is no longer an important component of the atmosphere.

Strategy

Consider why 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 3.9 The colours of the polar lights

What do the colours of the emissions from the excited N₂ molecules and N₂⁺ ions tell you about the relative energies of the photons involved?

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 2.1, $c = \lambda\nu$, and Equation 2.2, $E = h\nu$.

Solution

For the red lines and N₂:

$$\text{Using Equation 2.1, } \nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{661 \times 10^{-9} \text{ m}} = 4.54 \times 10^{14} \text{ (s}^{-1}\text{) Hz}$$

Using Equation 2.2, energy of the photon,

$$\begin{aligned} E &= h\nu && (h = 6.626 \times 10^{-34} \text{ J s}) \\ &= (6.626 \times 10^{-34} \text{ J s}^{-1}) \times (4.54 \times 10^{14} \text{ s}^{-1}) \\ &= 3.01 \times 10^{-19} \text{ J} \end{aligned}$$

For the blue lines and N_2^+ :

$$\text{Using equation 2.1, } \nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{391 \times 10^{-9} \text{ m}} = 7.67 \times 10^{14} \text{ (s}^{-1}\text{) Hz}$$

Using Equation 2.2, energy of the photon,

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

The red photons emitted from N_2 have a higher wavelength than the blue and purple photons from N_2^+ , so consequently their energy is lower.

Box 3.11 Using nitrogen monoxide to send biological signals

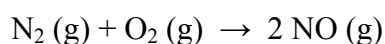
Nitrogen monoxide is produced in the internal combustion engine and is a common air pollutant. How is it formed?

Strategy

Most oxides are formed by combustion processes where elements combine with oxygen as bonds to oxide are strong and reactions are exothermic.

Solution

When fuels are burned at high temperature, NO is produced from reactions involving nitrogen and oxygen gases in the air. The overall equation for the process is



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 in the internal combustion engine.

Answers to end of chapter questions

1. 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



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

3. 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 lowest 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

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

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

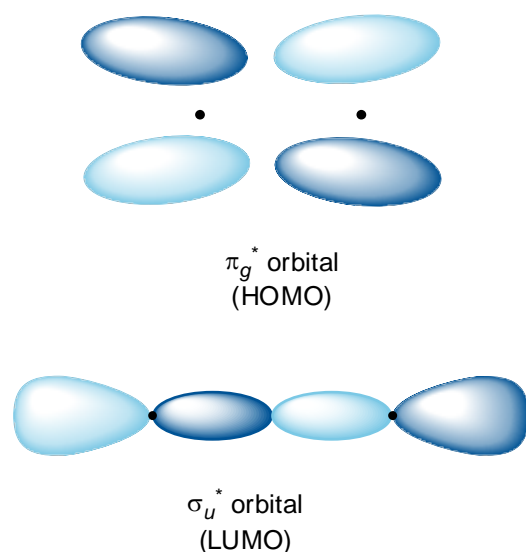
The in-phase combination corresponds to the $2\sigma_g$ bonding orbital, and the out-of-phase combination to the $2\sigma_u^*$ antibonding orbital.

5. Sketch boundary surface diagrams for the HOMO and LUMO in O₂

Strategy

The molecular orbital energy level diagram for O₂ is given in Figure 3.24 (p.157). The HOMO is the π_g^* orbital and the LUMO is the σ_u^* orbital.

Solution



7. Give examples of neutral homonuclear and heteronuclear diatomic molecules that are isoelectronic with C₂²⁻.

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 C₂²⁻. This gives a total of 10 valence electrons. This compares

with N₂ (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.

9. Predict the bond dissociation enthalpy of HI using the following information:

$$\begin{array}{ll} \chi^{\text{P}}(\text{H}) = 2.20 & D(\text{H-H}) = +435.8 \text{ kJ mol}^{-1} \\ \chi^{\text{P}}(\text{I}) = 2.66 & D(\text{I-I}) = +152.3 \text{ kJ mol}^{-1} \end{array}$$

Strategy

Using Pauling's theories relating electronegativity and the differences between the calculated and observed values of the bond dissociation enthalpy, the value of the HI heteronuclear bond can be calculated. The electronegativities (χ) of I (2.66) and H (2.20) are given in Figure 3.6 (p.138) and are related to the difference in bond dissociation enthalpy (ΔD) by Equation 3.3. The bond dissociation enthalpy for the homonuclear diatomics $D(\text{H-H})$ and $D(\text{I-I})$ are 435 kJ mol⁻¹ and 152.3 kJ mol⁻¹ respectively.

Solution

Using Equation 3.3 and remembering to take the positive difference between the electronegativities.

$$|\chi^{\text{P}}(\text{X}) - \chi^{\text{P}}(\text{Y})| = 0.102(\Delta D)^{1/2} = 2.66 - 2.20 = 0.46$$

$$\Delta D = \left(\frac{0.46}{0.102} \right)^2 = 20.3$$

Substituting this value into Equation 3.2 then gives

$$\begin{aligned}\Delta D &= D(\text{H-I}) - \frac{D(\text{H-H}) + D(\text{I-I})}{2} \\ &= D(\text{H-I}) - \frac{435.8 \text{ kJ mol}^{-1} + 152.3 \text{ kJ mol}^{-1}}{2} \\ &= D(\text{HI}) - 294.1 \text{ kJ mol}^{-1} \\ D(\text{HI}) &= (20.3 \text{ kJ mol}^{-1}) + (294.1 \text{ kJ mol}^{-1}) = 314 \text{ kJ mol}^{-1}\end{aligned}$$

11. 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^- ?

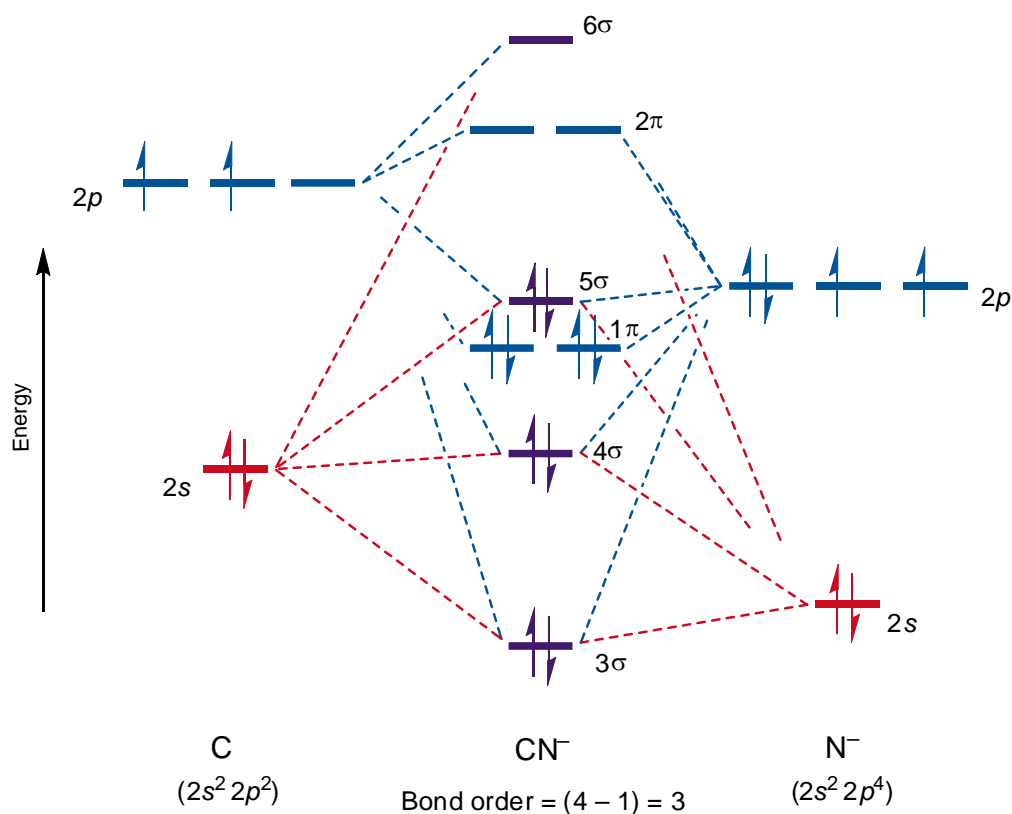
Strategy

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 $2\frac{1}{2}$ 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^- :



13. 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 2.1 and 2.2 to calculate the energy of the ultraviolet radiation and the molecular orbital diagram of dihydrogen given in Figure 3.14 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 $1s$ 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 2.1 to calculate the frequency of the transition gives

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

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

$$v = 2.75 \times 10^{15} \text{ s}^{-1}$$

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

$$E = hv \quad h = 6.626 \times 10^{-34} \text{ J s}$$

$$E = (6.626 \times 10^{-34} \text{ J s}) \times (2.75 \times 10^{15} \text{ s}^{-1})$$

$$E = 1.82 \times 10^{-18} \text{ J}$$

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 $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ gives

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

$$E = 1096 \text{ kJ mol}^{-1}$$

So, the energy gap between the $1\sigma_g$ and $1\sigma_u^*$ molecular orbitals in H_2 is 1096 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 $\frac{1}{2} - \frac{1}{2} = 0$, so this molecule is not stable and breaks apart into atoms.

