

Chapter 8 Basic Concepts of Chemical Bonding

Chapter 9 Molecular Geometry and Bonding Theories

Valence Bond Theory

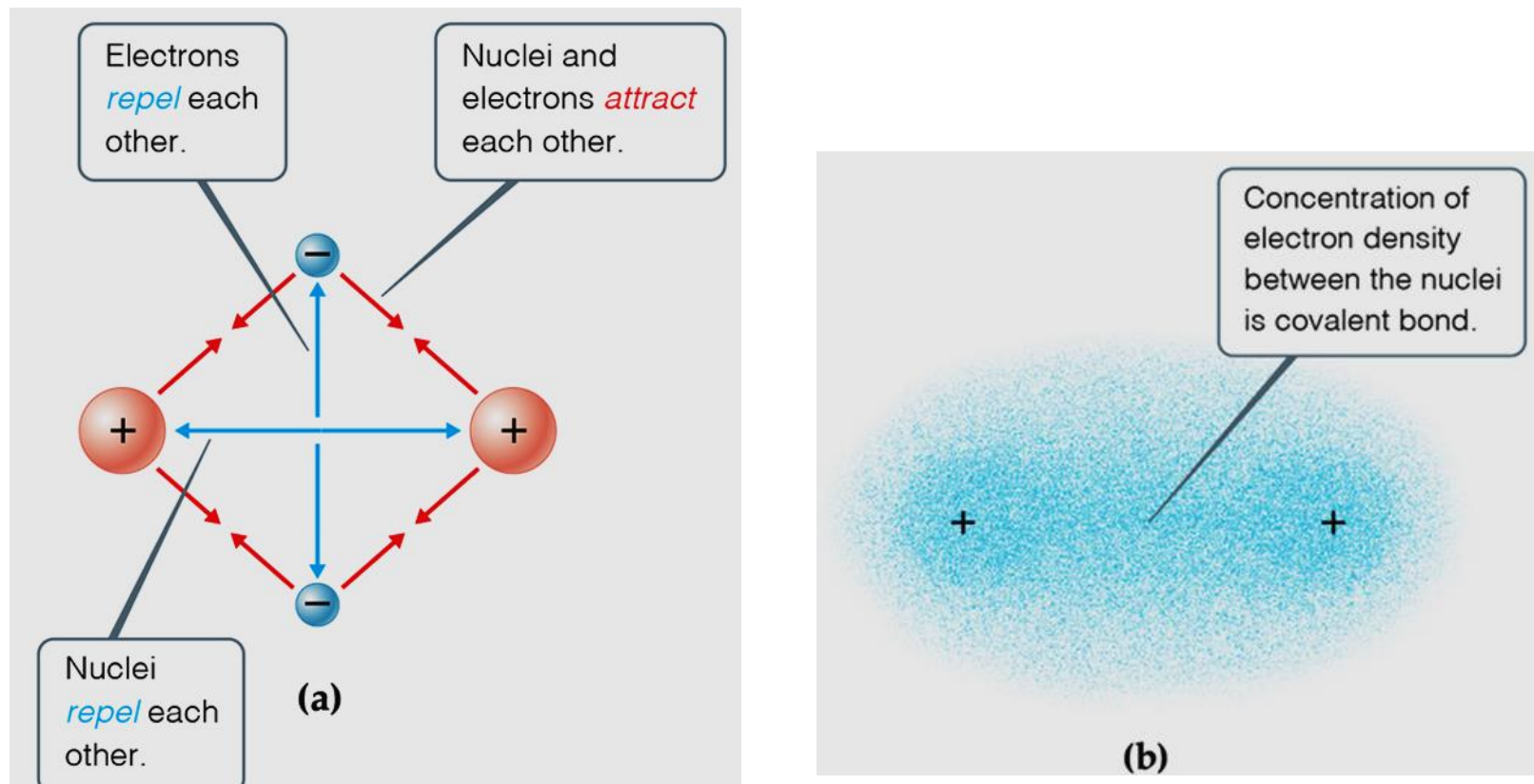


Figure 8.7 The covalent bond in H_2 . (a) The attractions and repulsions among electrons and nuclei in the hydrogen molecule. (b) Electron distribution in the H_2 molecule.

What would happen to the concentration of electron density between the nuclei in (b) if you pulled the nuclei further apart?

From this graph, what are the bond length and bond strength in the H_2 molecule?

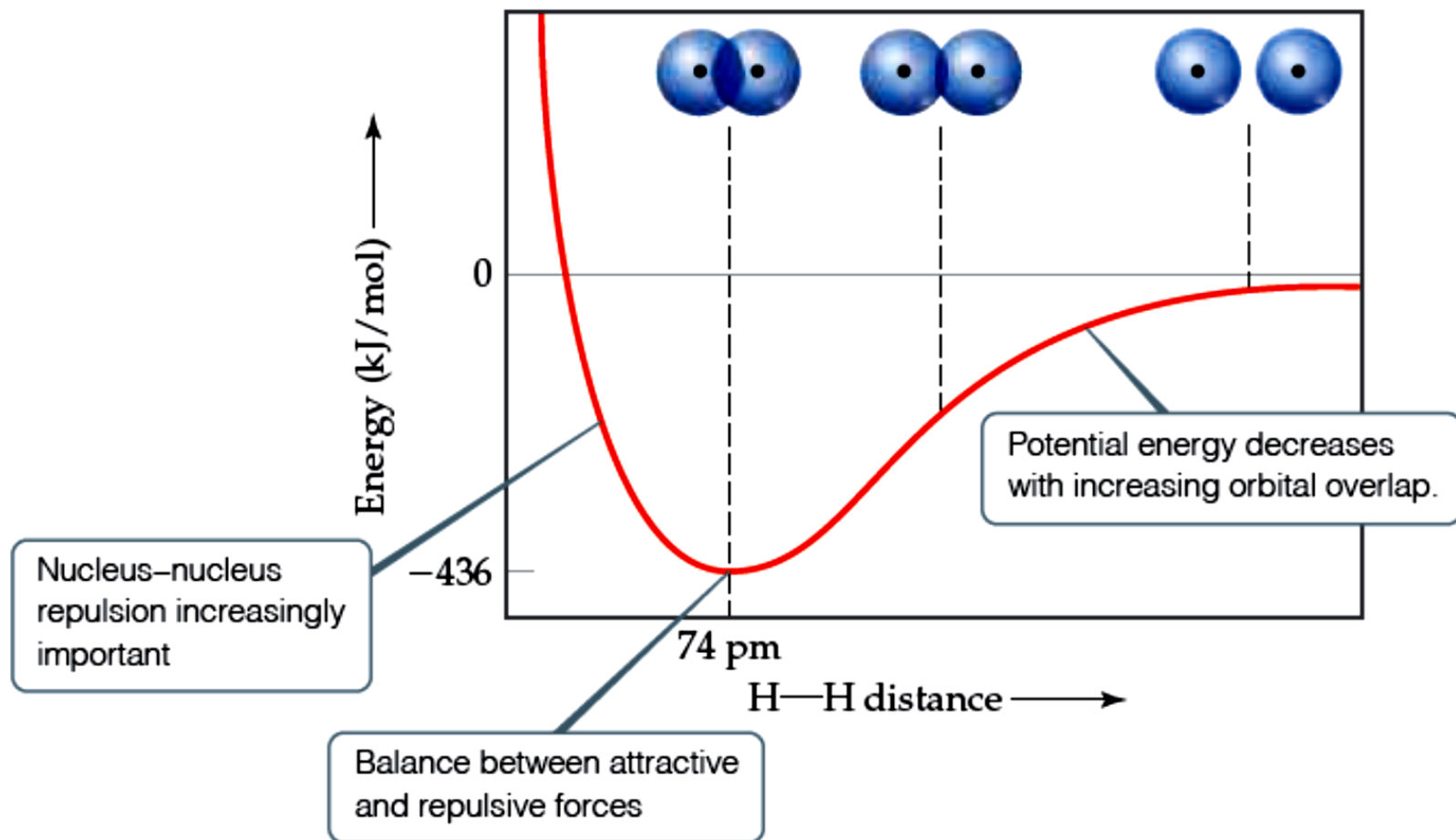
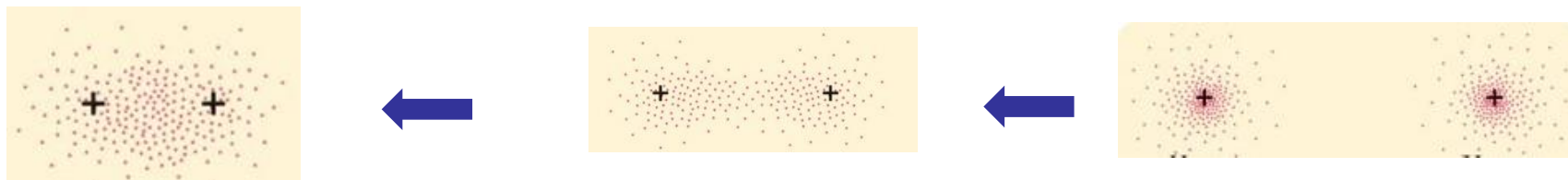


Figure 9.13 Formation of the H_2 molecule as atomic orbitals overlap.

What are so-called chemical bonds?



A chemical bond is to describe the **interatomic distance** when the system reaches its lowest energy for two atoms approaching each other.

9.7 | Molecular Orbitals

While valence-bond theory helps explain some of the relationships among Lewis structures, atomic orbitals, and molecular geometries, it does not explain all aspects of bonding. It is not successful, for example, in describing the excited states of molecules, which we must understand to explain how molecules absorb light, giving them color.



H

Ne

Figure 6.10 Atomic emission of hydrogen and neon. Different gases emit light of different characteristic colors **when an electric current is passed through them.**

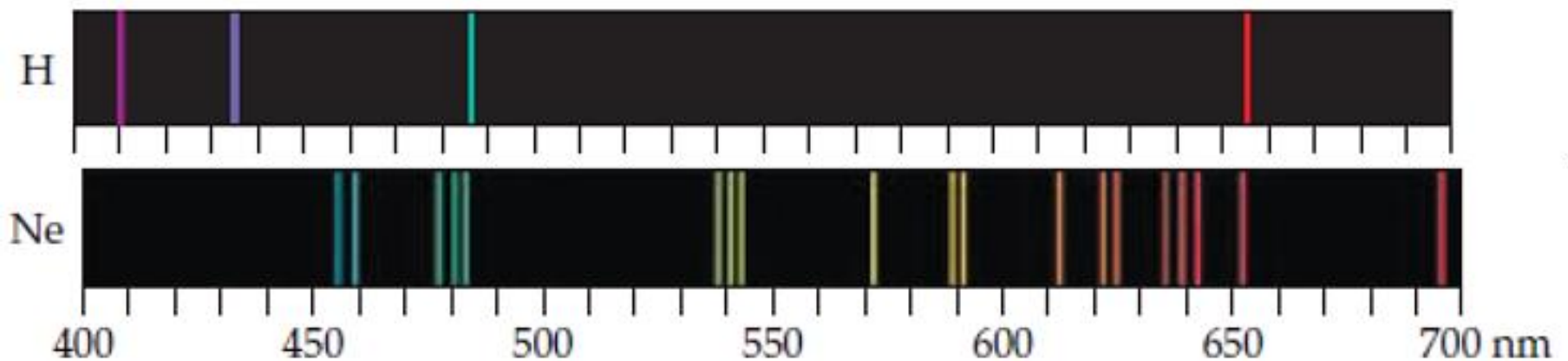


Figure 6.11 Line spectra of hydrogen and neon. The colored lines occur at wavelengths present in the **emission**. The black regions are wavelengths for which no light is produced in the emission.

In the **Bohr model of the Hydrogen atom**, electrons are confined to orbits with fixed radii. The radii of the first four orbits are 0.53, 2.12, 4.76, and 8.46 Å, respectively, as depicted below. (p. 267)

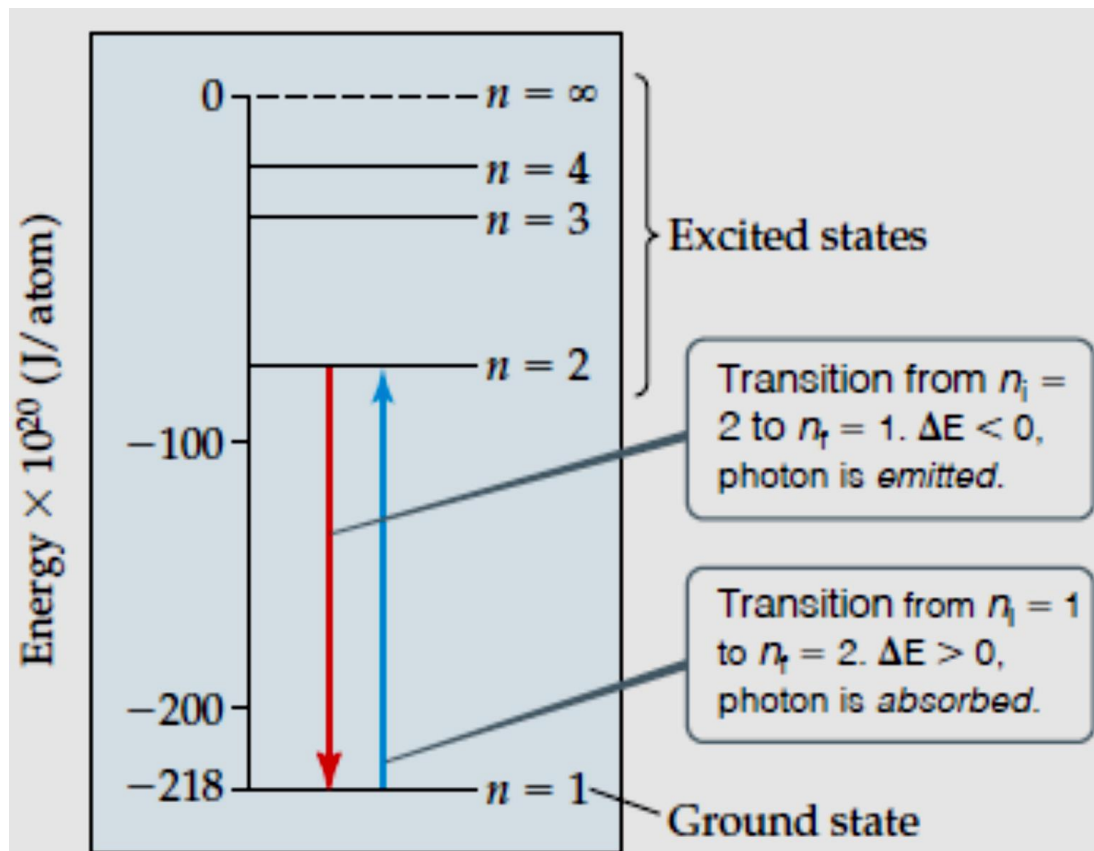
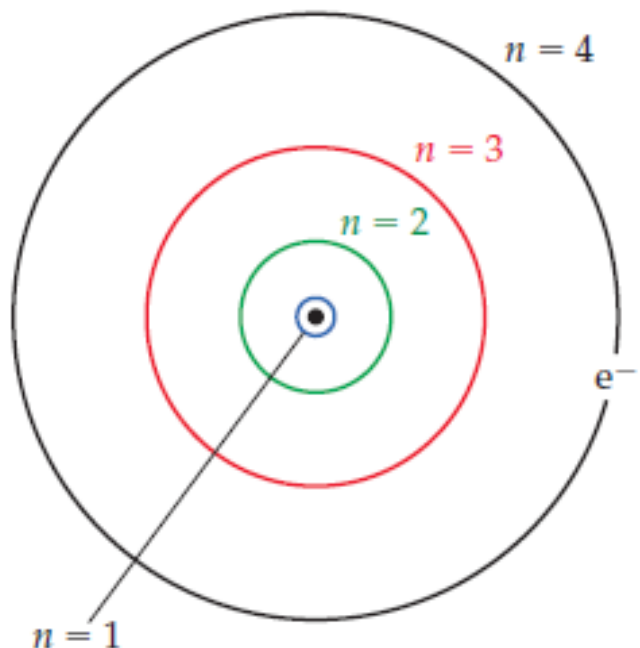
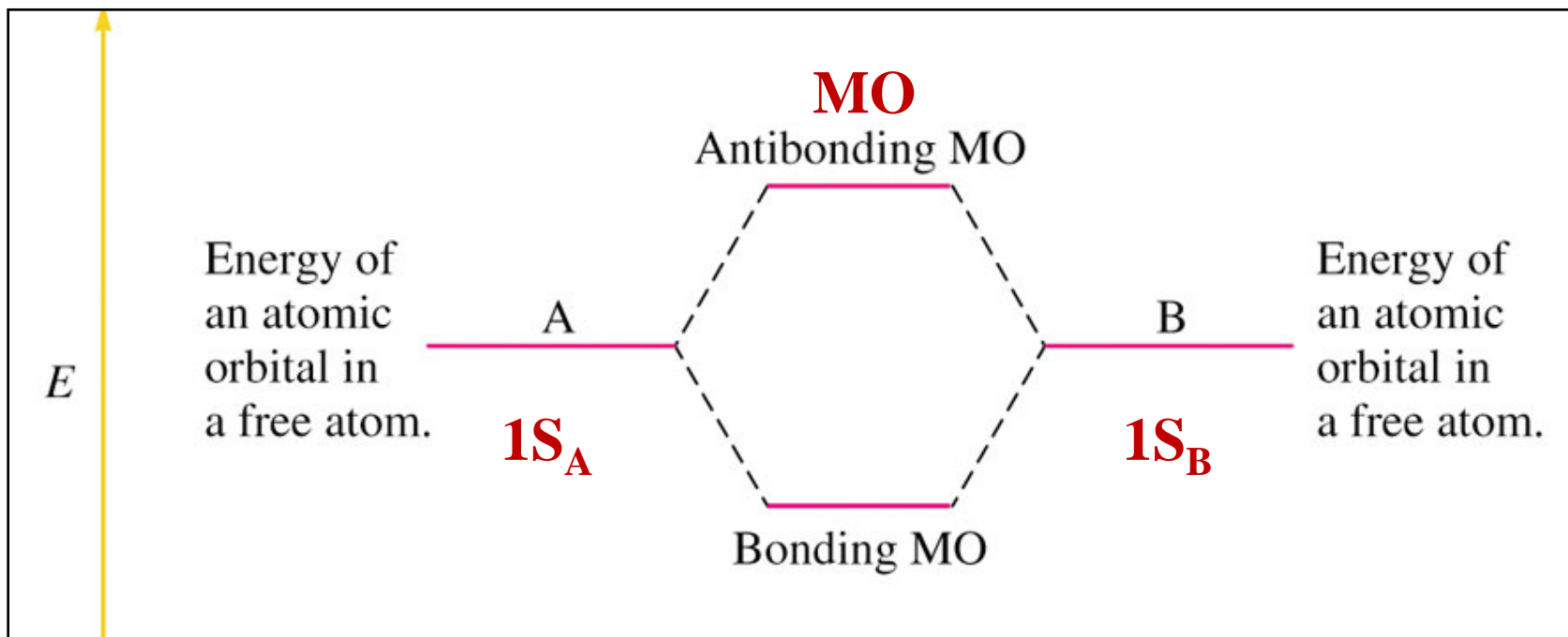


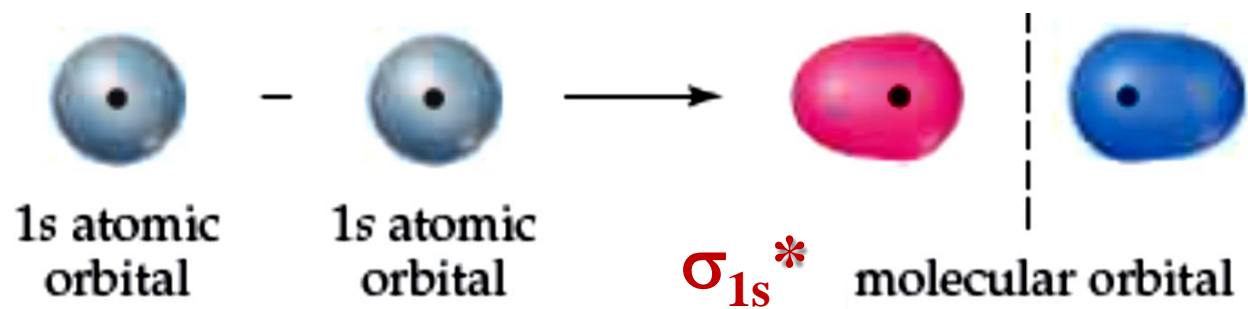
Figure 6.13 Change in energy states for absorption and emission of a photon in a hydrogen atom.

The Molecular Orbital Model



In atoms, electrons occupy **atomic orbitals (AOs)**, but in molecules they occupy **molecular orbitals (MOs)** which surround the molecule.

The simplest molecule is hydrogen, H_2 . There are **two MOs for hydrogen molecule** which are constructed from the two $1s$ AOs of hydrogen atoms. One is the **bonding** molecular orbital and is of lower energy than that of two separated $1s$ AOs of hydrogen atoms. The other is **anti-bonding** molecular orbital and is of higher energy than that of the $1s$ AO.



Constructive addition

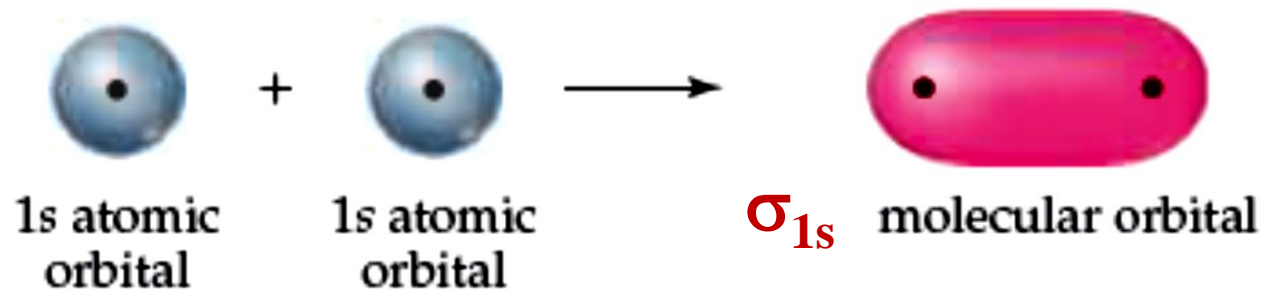
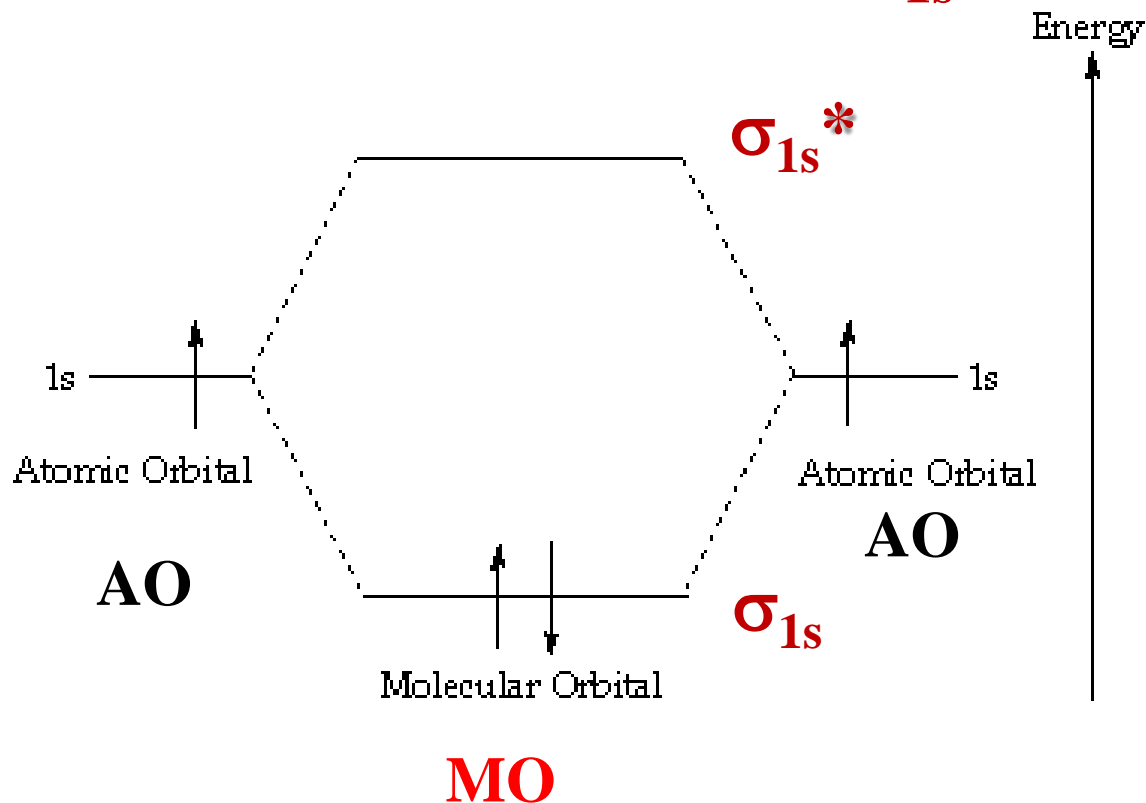


Figure 9.40 Molecular orbitals from atomic orbital wave functions.

The electron configuration for H_2 : σ_{1s}^2



The energy levels in a hydrogen molecule can be represented in a diagram - showing how the two $1s$ atomic orbitals combine to form two MOs, one **bonding (σ)** and one **anti-bonding (σ^*)**. Normally, **the two electrons in hydrogen occupy the bonding molecular orbital, with anti-parallel spins.**

There is only one σ bond in H_2 with bond order = 1.

Bond Order

In molecular orbital theory, the stability of a covalent bond is related to its **bond order**

bond order: the difference between the number of bonding electrons and the number of antibonding electrons, divided by 2.

$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

used to indicate *bond strength*

Bonds are perceived in terms of pairs of electrons

Larger bond order means greater *bond strength*

If molecular hydrogen is irradiated by ultra-violet (UV) light, the molecule may absorb the energy, and promote one electron into its anti-bonding orbital (σ^*), and the atoms will separate. Why?

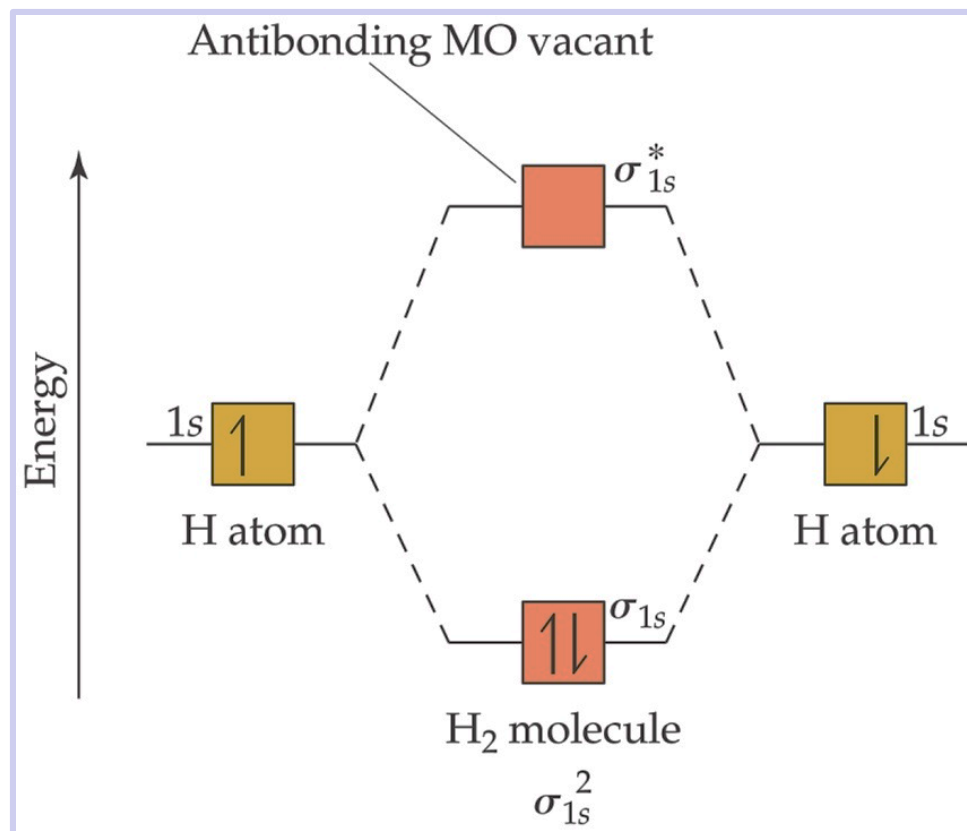
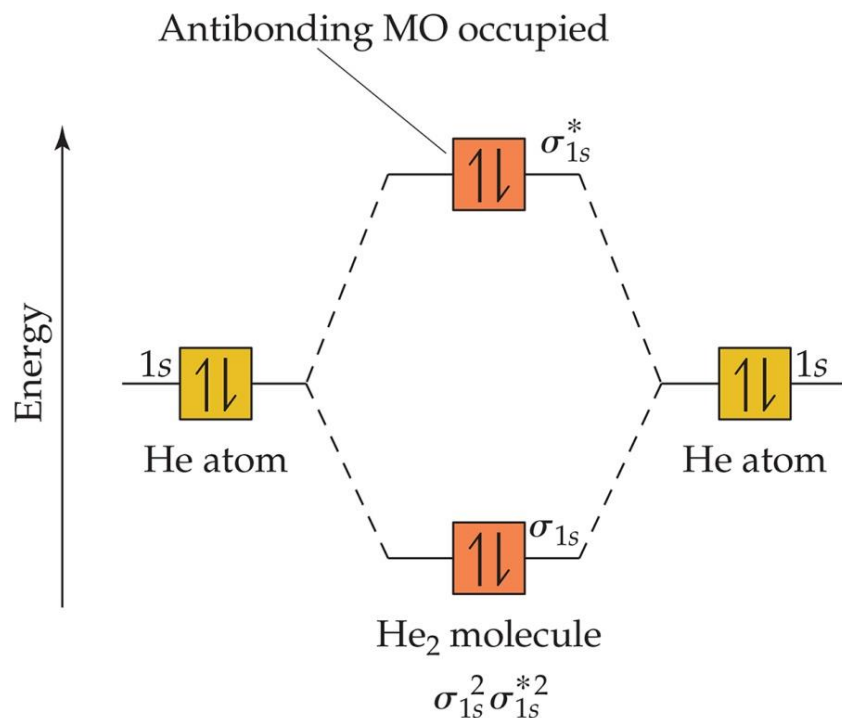


Figure 9.32 Energy-level diagram and electron configuration for H_2 .

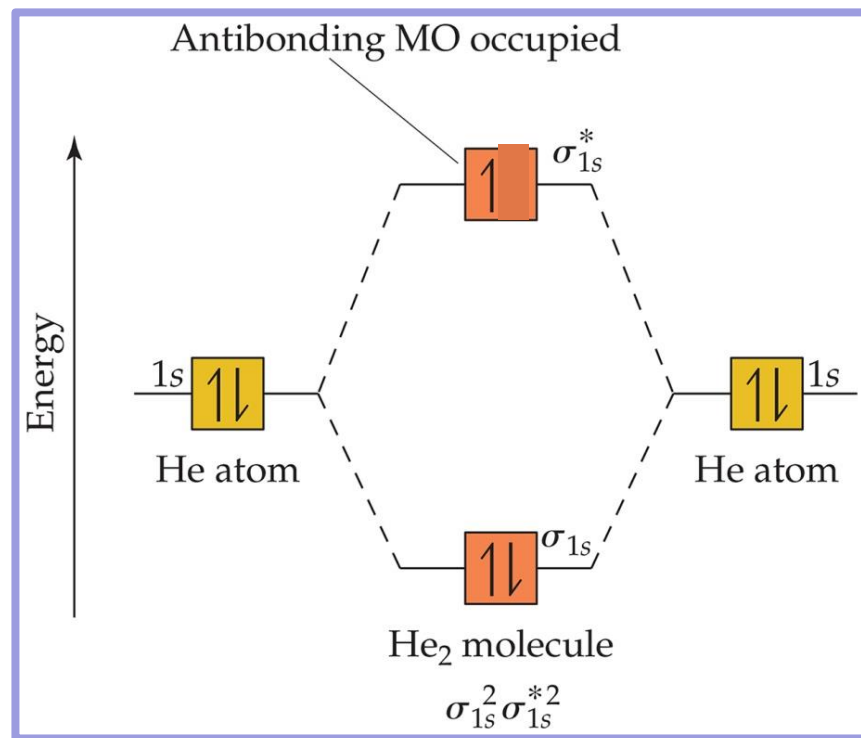
9.71 Consider the H_2^+ ion. **(a)** Sketch the molecular orbitals of the ion and draw its energy-level diagram. **(b)** How many electrons are there in the H_2^+ ion? **(c)** Write the electron configuration of the ion in terms of its MOs. **(d)** What is the bond order in H_2^+ ? **(e)** Suppose that the ion is excited by light so that an electron moves from a lower-energy to a higher-energy MO. Would you expect the excited-state H_2^+ ion to be stable or to fall apart? **(f)** Which of the following statements about part (e) is correct: (i) The light excites an electron from a bonding orbital to an antibonding orbital, (ii) The light excites an electron from an antibonding orbital to a bonding orbital, or (iii) In the excited state there are more bonding electrons than antibonding electrons?

9.72 **(a)** Sketch the molecular orbitals of the H_2^- ion and draw its energy-level diagram. **(b)** Write the electron configuration of the ion in terms of its MOs. **(c)** Calculate the bond order in H_2^- . **(d)** Suppose that the ion is excited by light, so that an electron moves from a lower-energy to a higher-energy molecular orbital. Would you expect the excited-state H_2^- ion to be stable? **(e)** Which of the following statements about part (d) is correct: (i) The light excites an electron from a bonding orbital to an antibonding orbital, (ii) The light excites an electron from an antibonding orbital to a bonding orbital, or (iii) In the excited state there are more bonding electrons than antibonding electrons?

Can He₂ Form?



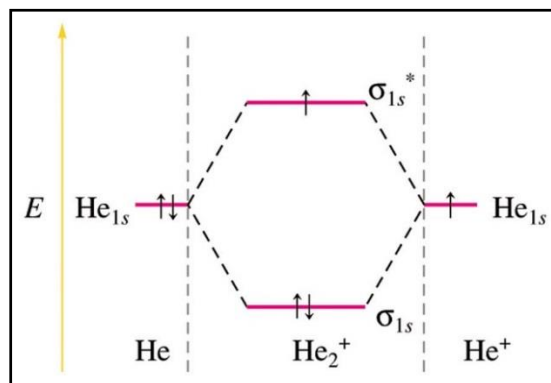
Can He₂⁺ ion Form?



Bond order = $\frac{1}{2} (2 - 2) = 0$ bonds

He₂ does *not* exist.

Electron Configuration of H₂-type Molecules



The MOs with electrons for the H₂-type molecule:

Molecular species	e-config.	Bond order	bond length (pm)
H ₂ ⁺	1s (1s ¹)	1/2	106
H ₂ , He ₂ ²⁺	1s ²	1	~75
H ₂ ⁻ , He ₂ ⁺	1s ² 1s*	1/2	~106, 108
H ₂ ²⁻ , He ₂	1s ² 1s* ²	0	not formed

Describe the relationship of bond length & bond order and e-configurations. Explain the reasoning behind it.

Sample Exercise 9.8

What is the bond order of the He_2^+ ion?

Would you expect this ion to be stable relative to the separated He atom and He^+ ion?

Practice Exercise 1

How many of the following molecules and ions have a bond order of $\frac{1}{2}$: H_2 , H_2^+ , H_2^- , and He_2^{2+} ?

(a) 0 (b) 1 (c) 2 (d) 3 (e) 4

Practice Exercise 2

What are the electron configuration and the bond order of the H_2^- ion?

9.8 | Bonding in Period 2 Diatomic Molecules

Period 2 atoms have valence $2s$ and $2p$ orbitals, and we need to consider how they interact to form MOs.

The following rules summarize some of the guiding principles for the formation of MOs and for how they are populated by electrons:

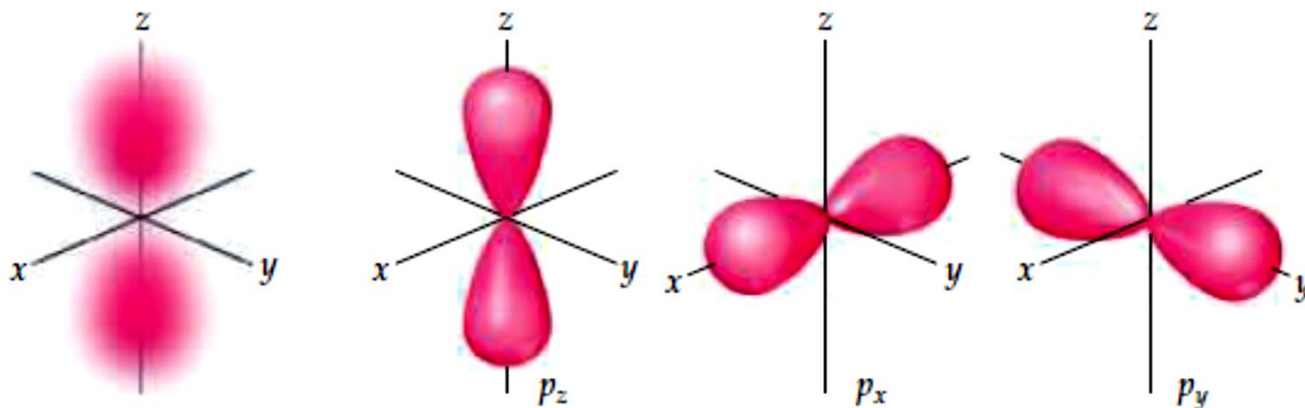


Figure 6.23 The p orbitals. The dumbbell-shaped orbital has two *lobes*.

Guiding Principles for the Formation of Molecular Orbitals

- 1) The **number of MOs** formed **equals** the **number of AOs** combined.
- 2) AOs combine with AOs of **similar energy**.

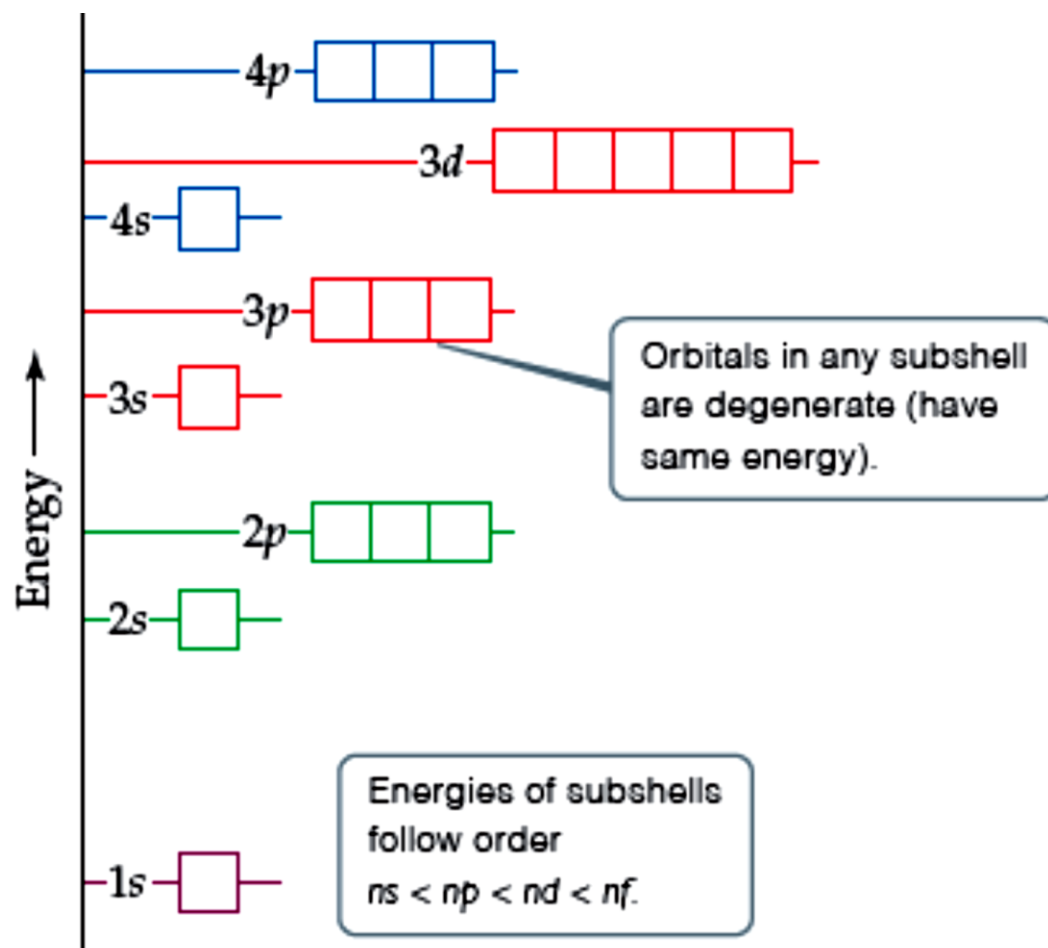


Figure 6.25 General energy ordering of orbitals

Guiding Principles for the Formation of Molecular Orbitals

- 3) The effectiveness with which two AOs combine is proportional to their overlap.
- 4) **Each MO** can accommodate at most **two electrons** with opposite spin. (They follow the **Pauli exclusion principle**: it states **that no two electrons in an atom can have the same set of four quantum numbers n , l , m_l , and m_s**) When

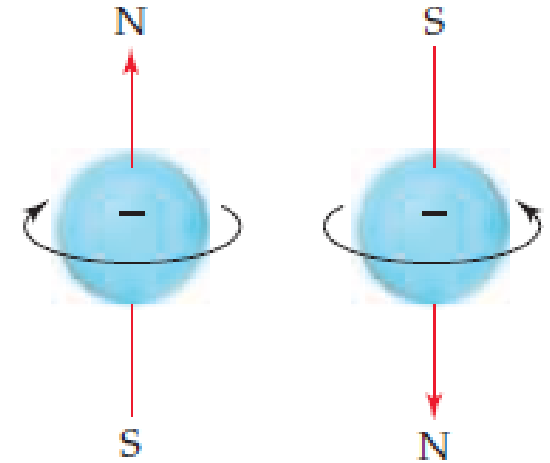






























Figure 6.26 Electron spin

- 5) When MOs of the same energy are populated, one electron enters each orbital (same spin) before pairing. (They follow **Hund's rules**.)

Hund's rule states that that when filling degenerate orbitals the lowest energy is attained when the number of electrons having the same spin is maximized.

TABLE 6.3 Electron Configurations of Several Lighter Elements

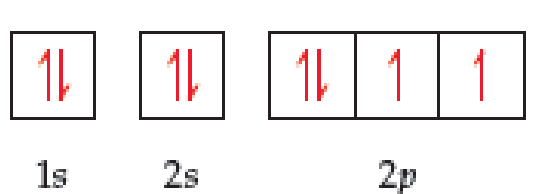
Element	Total Electrons	Orbital Diagram				Electron Configuration
		1s	2s	2p	3s	
Li	3					$1s^2 2s^1$
Be	4					$1s^2 2s^2$
B	5					$1s^2 2s^2 2p^1$
C	6					$1s^2 2s^2 2p^2$
N	7					$1s^2 2s^2 2p^3$
Ne	10					$1s^2 2s^2 2p^6$
Na	11					$1s^2 2s^2 2p^6 3s^1$

Sample Exercise 6.7

Write the electron configuration for oxygen, atomic number 8.



Draw the orbital diagram for the electron configuration of oxygen.



How many unpaired electrons does an oxygen atom possess?

Practice Exercise 1

How many of the elements in the second row of the periodic table (Li through Ne) will have at least one unpaired electron in their electron configurations?

(a) 3 (b) 4 (c) 5 (d) 6 (e) 7

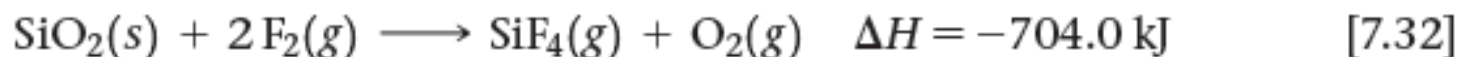
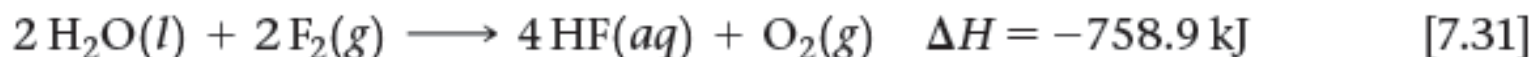
Practice Exercise 2

(a) Write the electron configuration for silicon, element 14, in its ground state. (b) How many unpaired electrons does a ground-state silicon atom possess?

TABLE 7.7 Some Properties of the Halogens

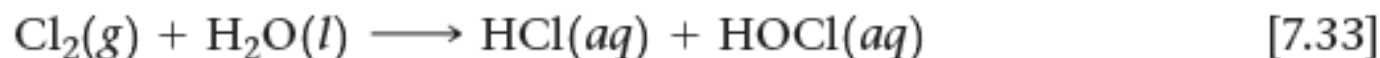
Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (pm)
Fluorine	[He]2s ² 2p ⁵	−220	1.69 g/L	57
Chlorine	[Ne]3s ² 3p ⁵	−102	3.12 g/L	102
Bromine	[Ar]4s ² 3d ¹⁰ 4p ⁵	−7.3	3.12 g/cm ³	120
Iodine	[Kr]5s ² 4d ¹⁰ 5p ⁵	114	4.94 g/cm ³	139

indicate any one of the halogen elements.) Fluorine and chlorine are more reactive than bromine and iodine. In fact, fluorine removes electrons from almost any substance with which it comes into contact, including water, and usually does so very exothermically, as in the following examples:



As a result, fluorine gas is difficult and dangerous to use in the laboratory, requiring specialized equipment.

Chlorine is the most industrially useful of the halogens. It is produced by a process called electrolysis, where an electrical current is used to oxidize chloride anions to molecular chlorine, Cl_2 . Unlike fluorine, chlorine reacts slowly with water to form relatively stable aqueous solutions of HCl and HOCl (hypochlorous acid):



Chlorine is often added to drinking water and swimming pools because the $\text{HOCl}(aq)$ that is generated serves as a disinfectant.

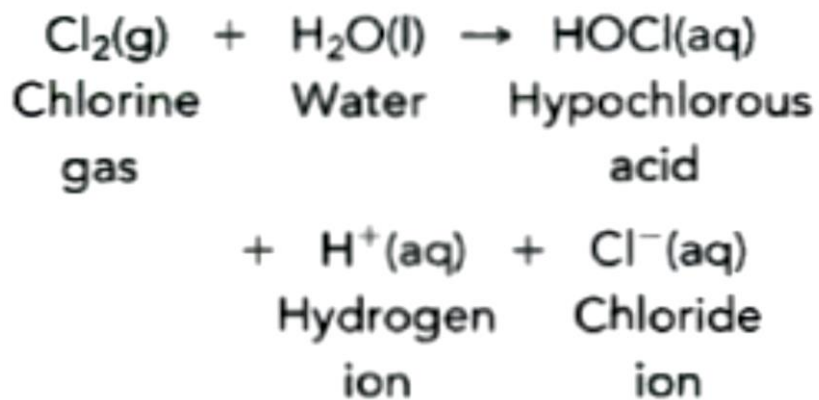
What chemical holds the record for saving the most lives? Penicillin? Aspirin? Guess again. When it comes to saving lives, perhaps the most successful chemical is chlorine, which has saved many millions of us by disinfecting our drinking water. For this reason alone, chlorine ranks as a "wonder chemical," but wait, there's more!

The Wonder Chemical

About 85 percent of all pharmaceuticals and about 95 percent of all crop protection chemicals are synthesized using chlorine. Chlorine is also an important component of many plastics, and it is used in the manufacture of a countless number of products. In

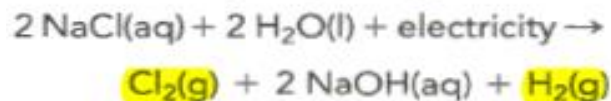
The Wonder Chemical, but...

Municipalities chlorinate both drinking water and wastewater by bubbling chlorine gas, Cl_2 , through the water. The chlorine reacts with the water to produce hypochlorous acid, HOCl , and hydrogen and chloride ions. The hypochlorous acid is a weak acid, so it stays in a molecular form, as shown next. The hypochlorous acid molecule is able to penetrate the nonpolar microbial cell walls, which makes it an effective disinfectant.



Chlorine and hypochlorous acid, as well as water-disinfecting bleach solutions, can react with organic components of drinking and waste waters, creating chlorinated hydrocarbons, many of which are **cancer causing**. Some municipalities have therefore switched to chlorine dioxide, ClO_2 , which doesn't form chlorinated hydrocarbons so readily.

Most chlorine is manufactured from the **electrolysis of salt water**, as shown next. Notably, this reaction also produces two other valuable chemicals, sodium hydroxide, NaOH, and hydrogen, H₂.

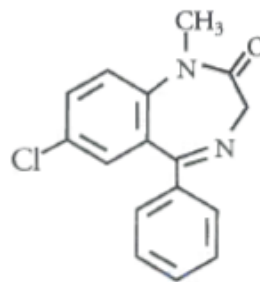


Chlorine is useful for the manufacture of many chemical products, even though these products themselves **contain no chlorine**. To create titanium metal, for example, the mineral titanium dioxide is reacted with chlorine to form titanium tetrachloride, **TiCl₄** (sometimes humorously called "tickle"), which is then reduced by magnesium metal, Mg, as shown in the following equations:



Interestingly, **titanium tetrachloride is the "ink" used by skywriters**. When the pilot is ready to maneuver the airplane to spell out words, she releases a spray of **TiCl₄**, which **reacts with atmospheric moisture to form visibly white titanium dioxide particles**.

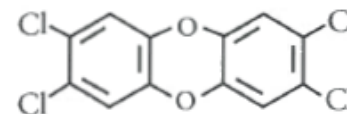
Chemists designing pharmaceuticals and crop protection chemicals often add chlorine atoms to the structure in order to modify their potency. The anti-anxiety agent Valium® is an example.



About one-third of the 40 million tons of chlorine produced annually goes to the manufacture of polyvinyl chloride, **PVC**, which is one of the most versatile of all plastics. PVC is ubiquitous, being used for pipes, flooring, electrical insulation, wallpaper, school supplies, swimming pools, and many other common products.

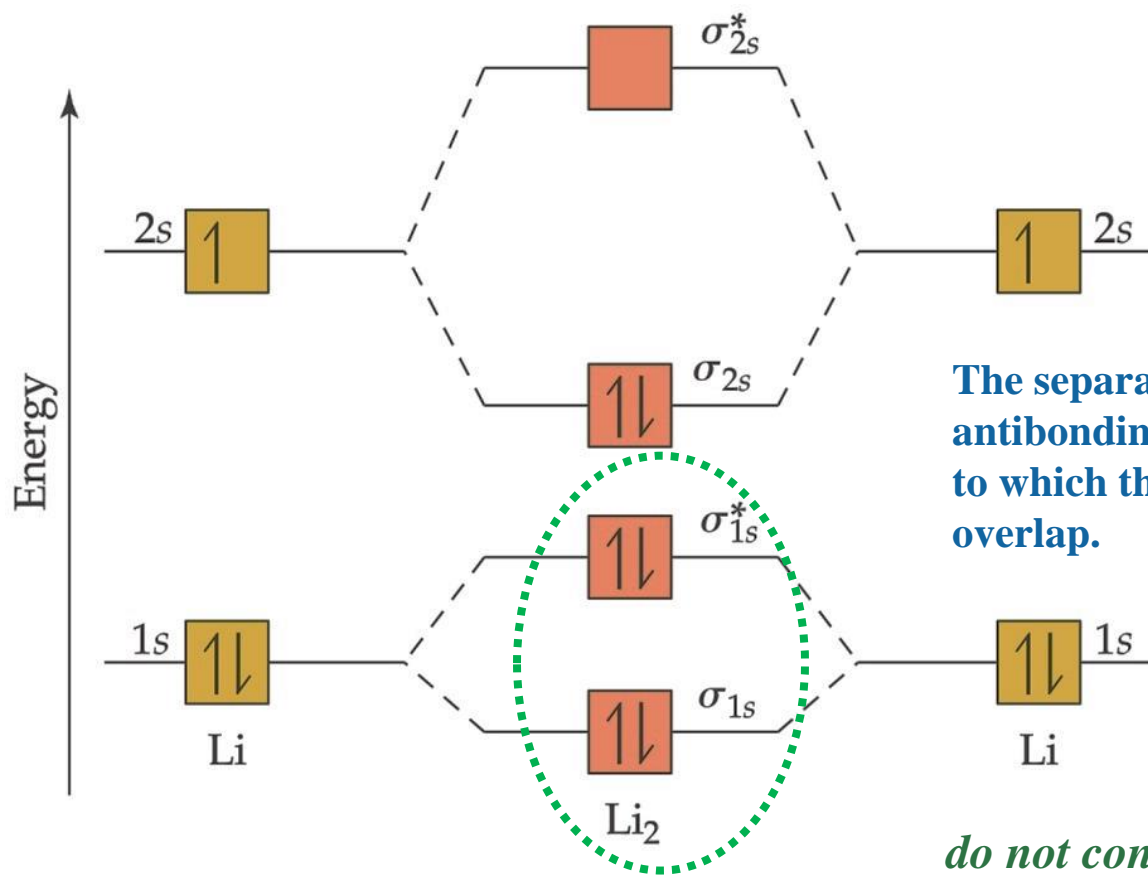
Chlorine is indeed a wonder chemical, but as with any technology, we need to make sure that the benefits are well worth the risks. Becoming a well-informed citizen is a good place to start.

So **chlorine has become an integral part of modern life**. There is an important aspect of chlorine chemistry, however, that everyone should be aware of. Specifically, **chlorine reacts with organic molecules to form a class of toxic molecules known as persistent organic pollutants, also known as POPs**. A well-known group of POPs are the **dioxins**, which are represented by the compound 2, 3, 7, 8-tetrachloro-benzo-p-dioxin, also known as TCDD. These agents cause cancer and disrupt many bodily systems, especially those related to **reproduction, immune responses, and hormones**. Children are particularly susceptible because their bodies are still developing.



Some POPs, such as the insecticide DDT, are created on purpose. Many persistent organic pollutants, however, are created inadvertently, such as POPs that form upon the chlorine bleaching of paper. When possible, these POPs are sequestered as wastes. **In the past, these wastes were not known to be harmful and they were often improperly buried, only to create later environmental hazards, as occurred at Love Canal, New York, in the late 1970s.**

MOs, Bonding, and Core Electrons



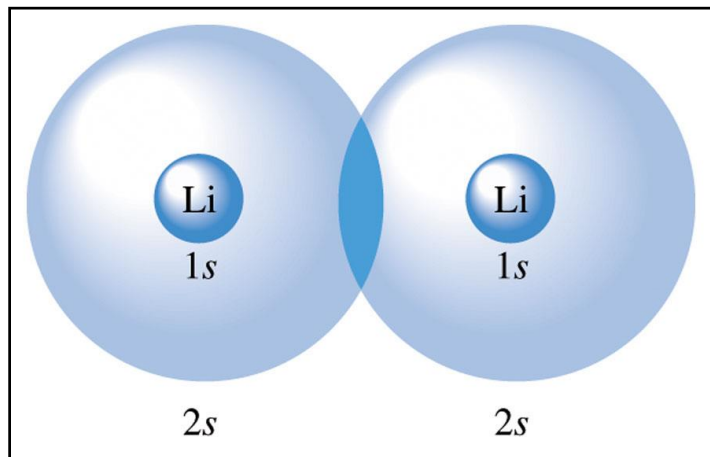
The separation bw. bonding and antibonding MOs depends on the extent to which the constituent atomic orbitals overlap.

do not contribute significantly to bonding in molecules

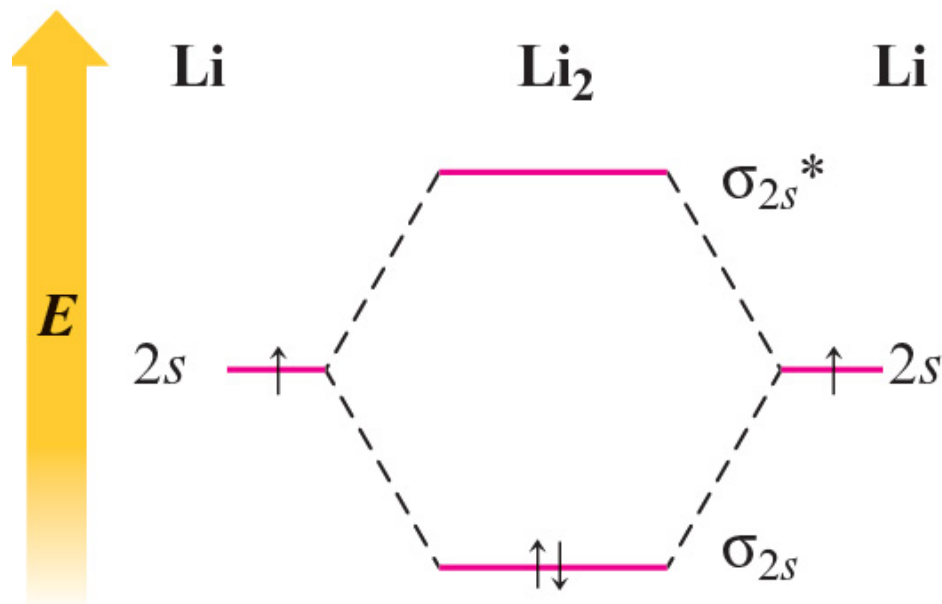
Notice that core electrons don't play a major part in bonding, so we usually don't include them in the MO diagram.

Bonding in **Homonuclear** Diatomic Molecules

The MO for Li_2



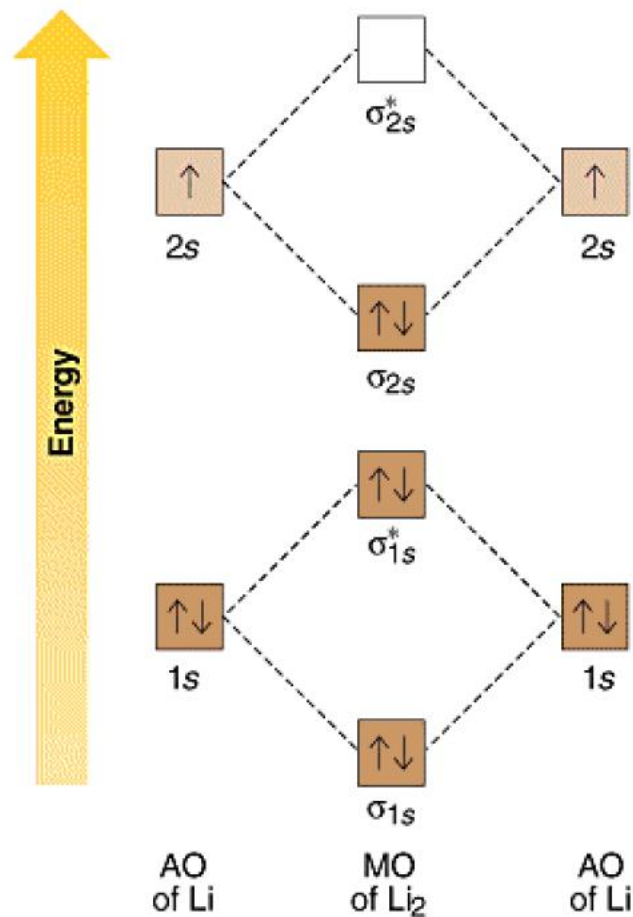
The relative sizes of the lithium 1s and 2s atomic orbitals and their overlap in Li_2 .



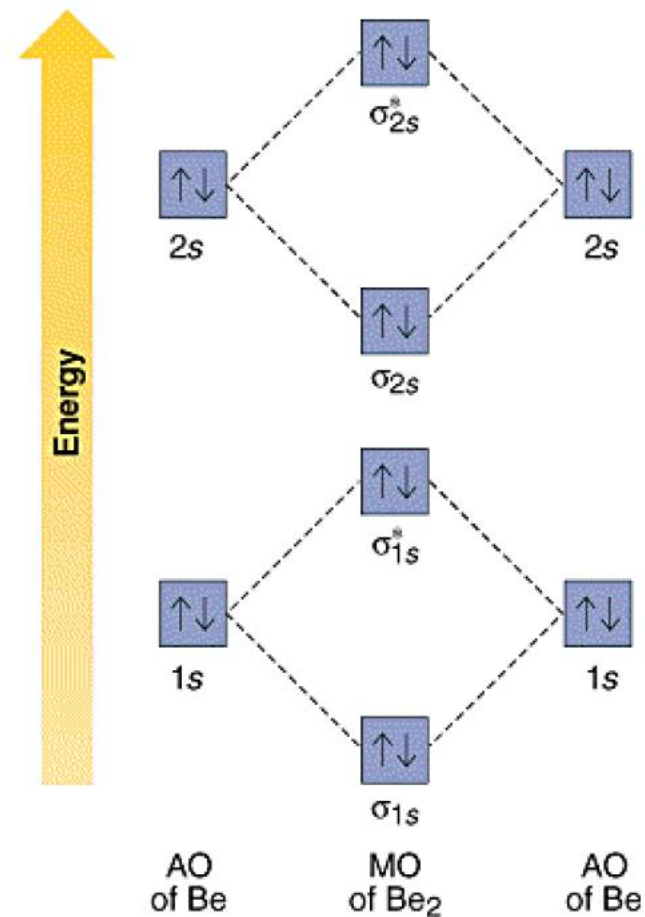
bond order = 1

What's the bond order for Be_2 ?

Molecular Orbitals for Period 2 Diatomic Molecules

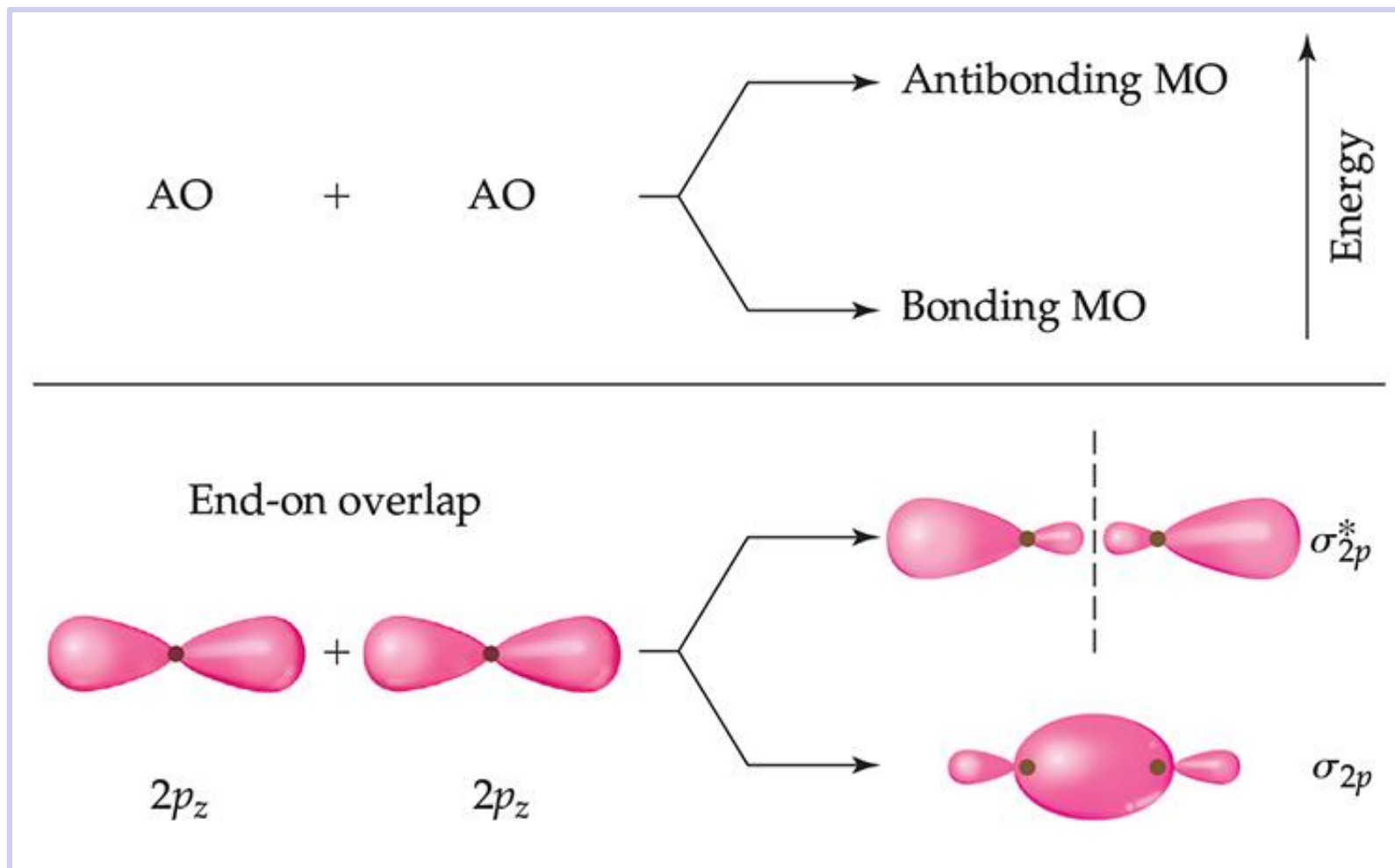


A Li_2 bond order = 1



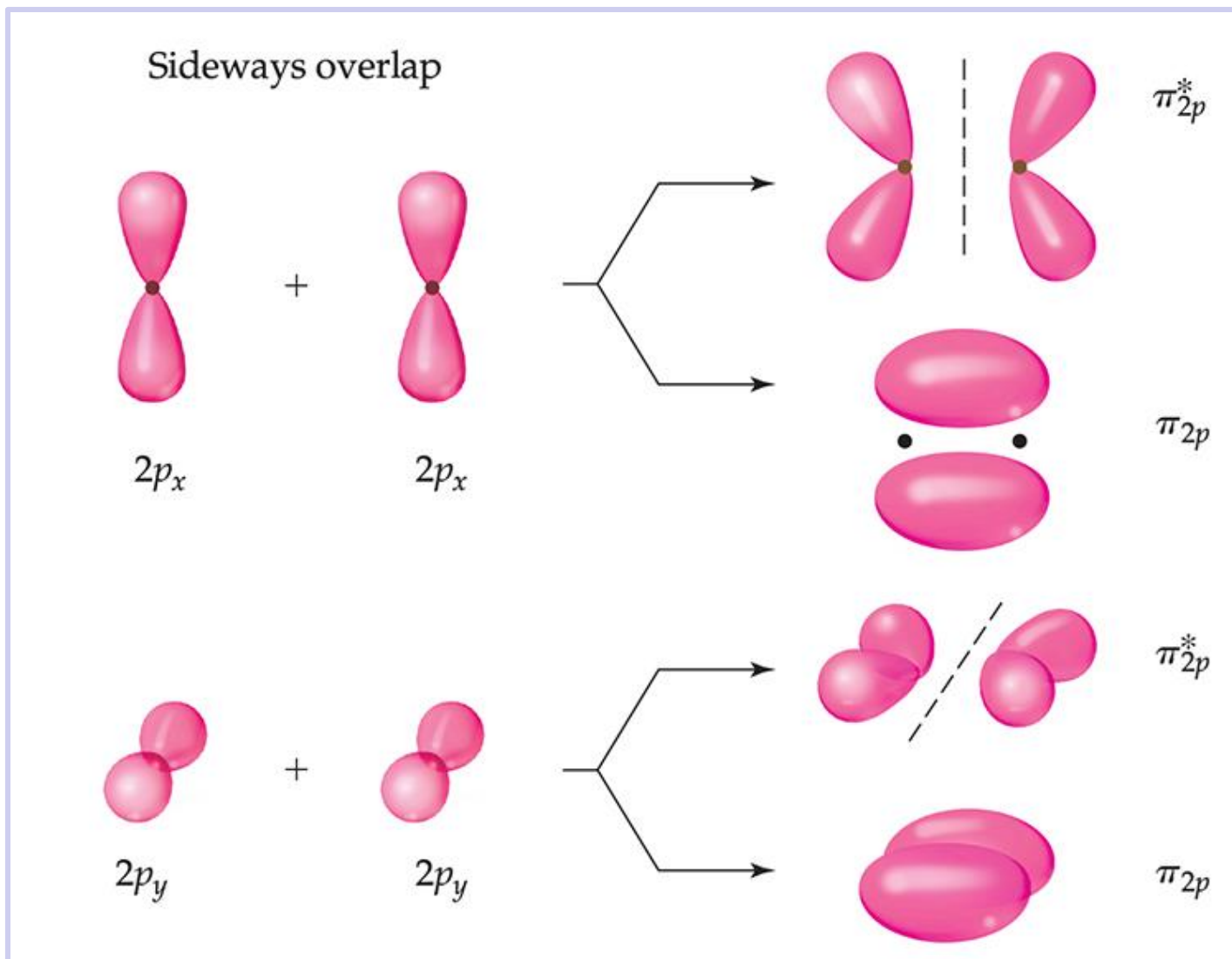
B Be_2 bond order = 0

MOs from p -Orbitals



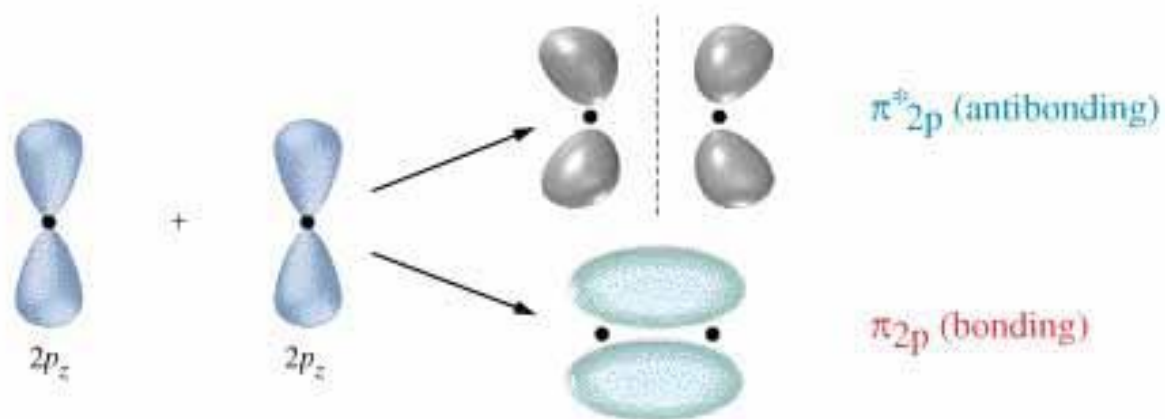
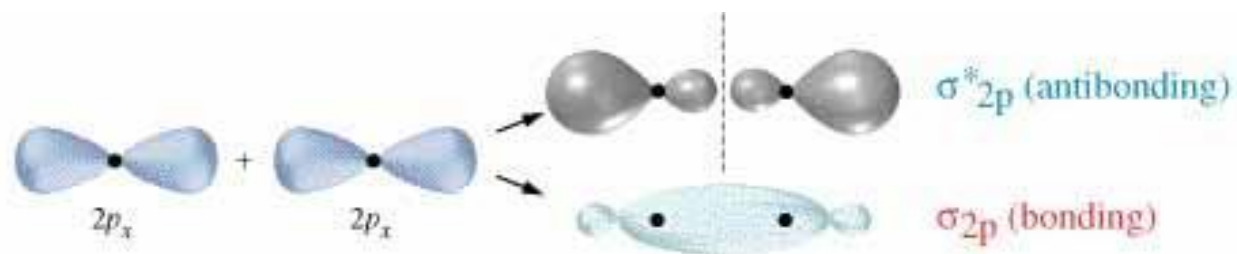
p -orbitals undergo overlap direct ways.

MOs from p -Orbitals

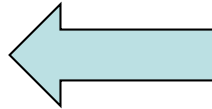


p -orbitals also undergo overlap sideways.

Molecular Orbitals of the Second Energy Level (2s and 2p together)



Oct. 15, 2018



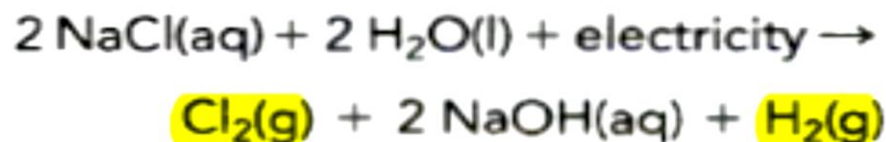
Oct. 17, 2018



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The Wonder Chemical, but...

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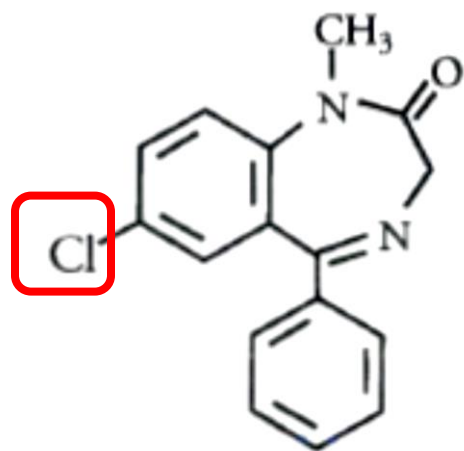


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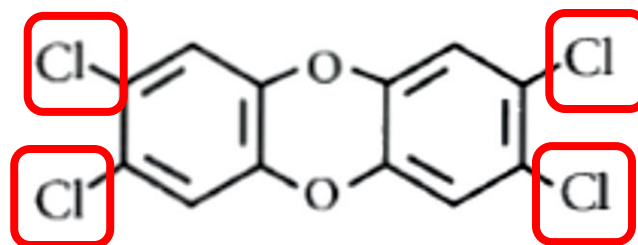
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MO Diagrams for the Second Period *p*-Block Elements

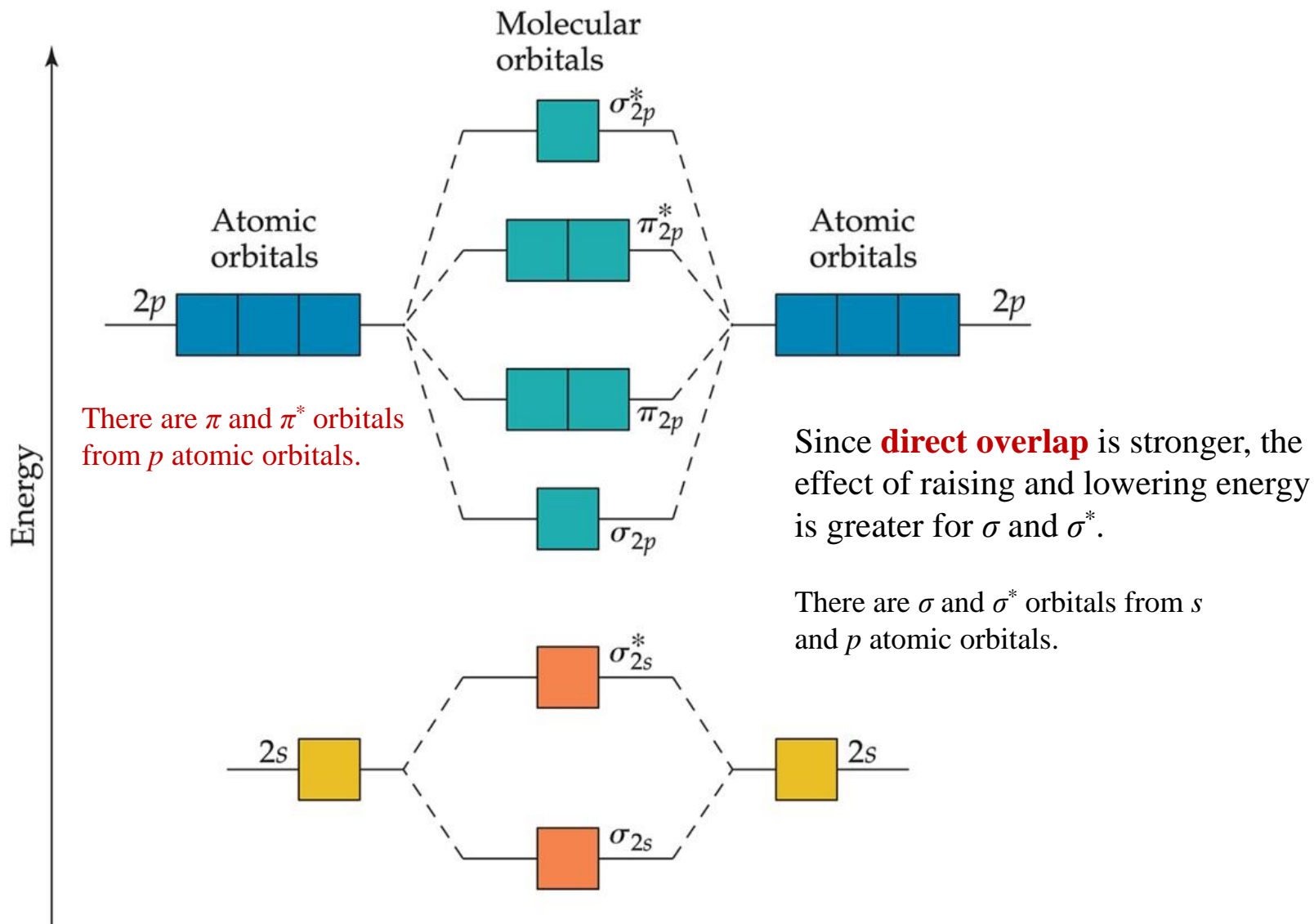
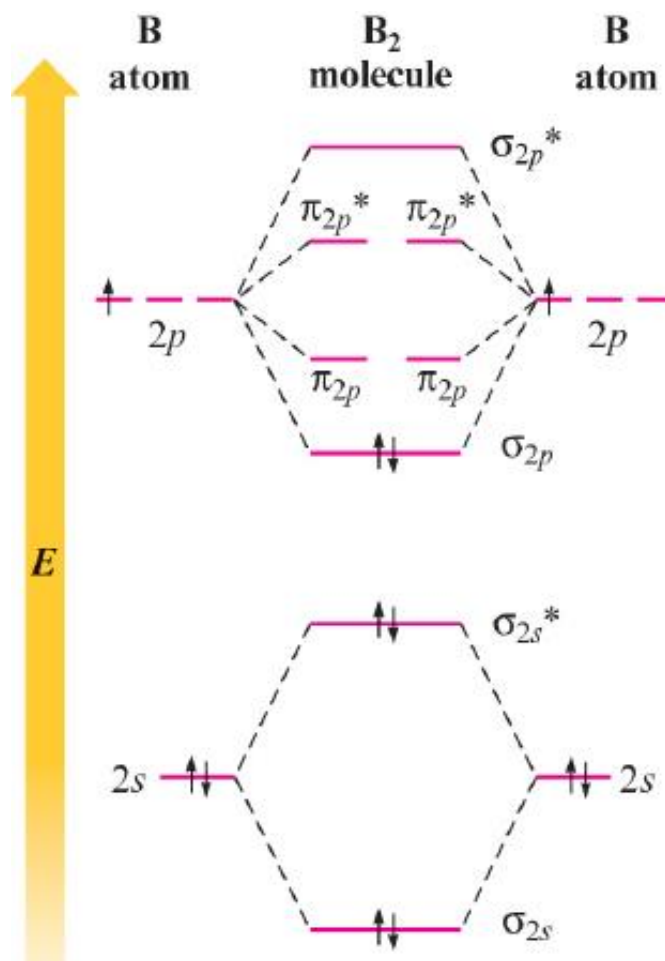
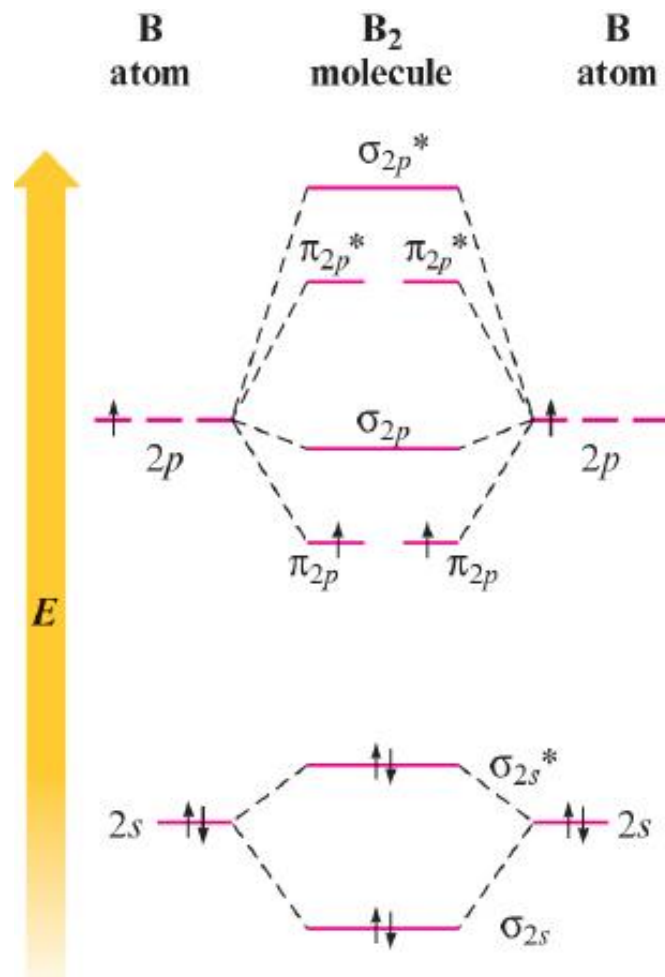


Figure 9.41 Energy-level diagram for MOs of period 2 homonuclear diatomic molecules. The diagram assumes no interaction between the 2s atomic orbital on one atom and the 2p atomic orbitals on the other atom.

Bonding in **Homonu**uclear Diatomic Molecules

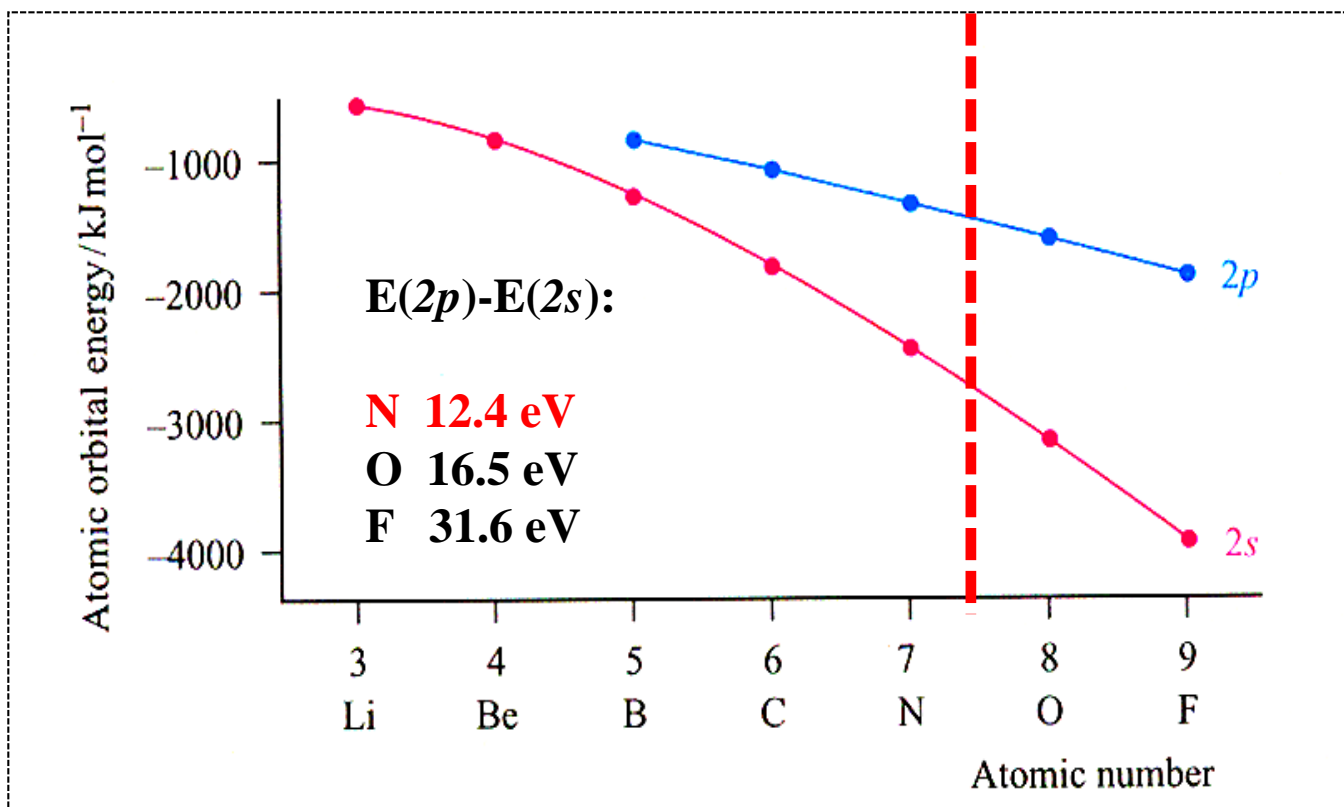


The **expected** MO for B_2 .



The **correct** MO for B_2 .

s-p Energy Separation

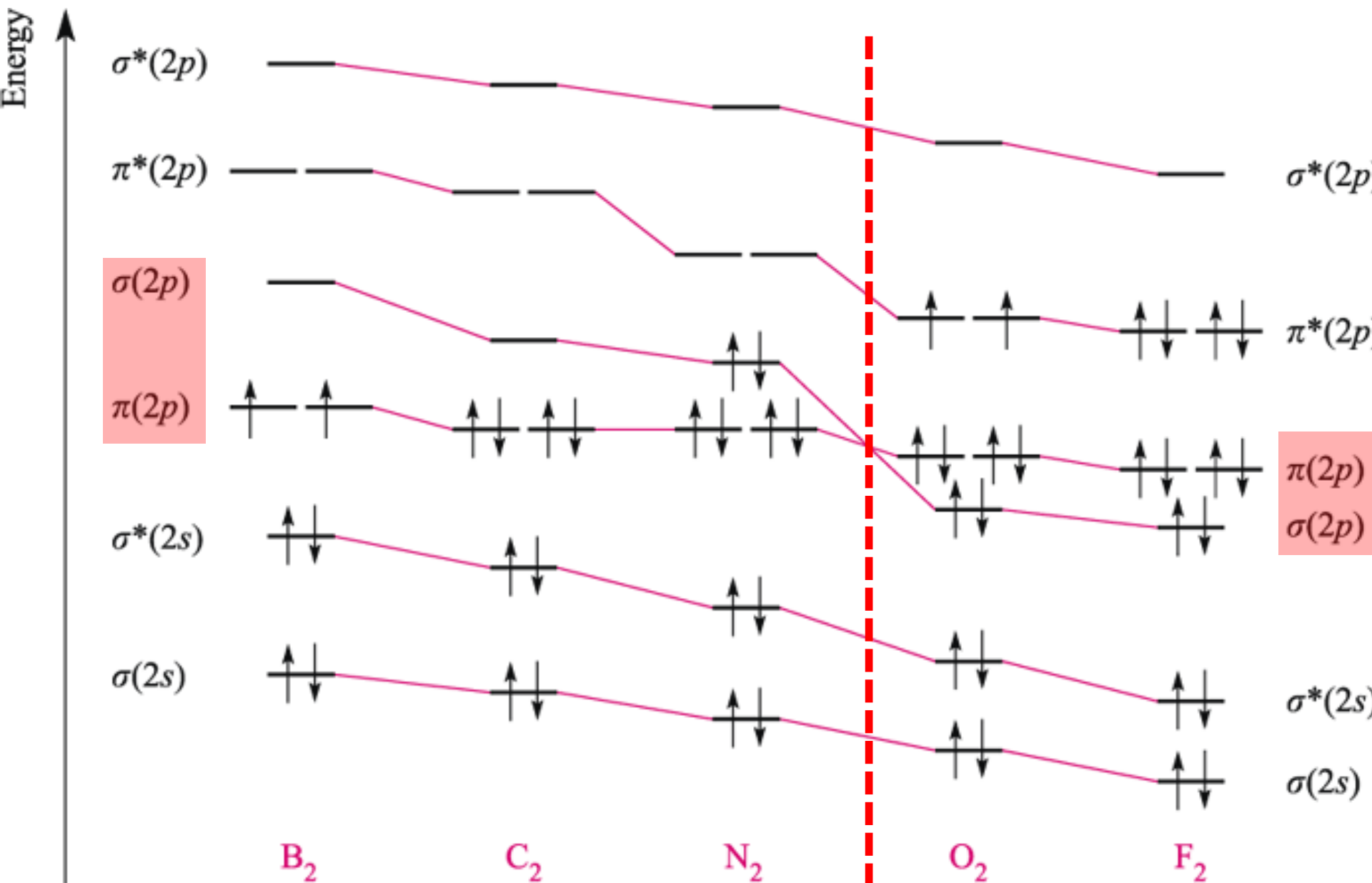


> half filled *p* orbitals (O, F, Ne) energy $\sigma_{2p} < 2\pi_{2p} < 2\pi^*_{2p} < \sigma^*_{2p}$

≤ half filled *p* orbitals (B, C, N) energy $2\pi_{2p} < \sigma_{2p} < 2\pi^*_{2p} < \sigma^*_{2p}$

When *s-p* energy separation is smaller, s orbital can interact with *p* orbital more (interact with the *p_z* orbitals more than the *p_x* and *p_y* orbitals).

s-p orbital Mixing



s and *p* Orbital Interactions

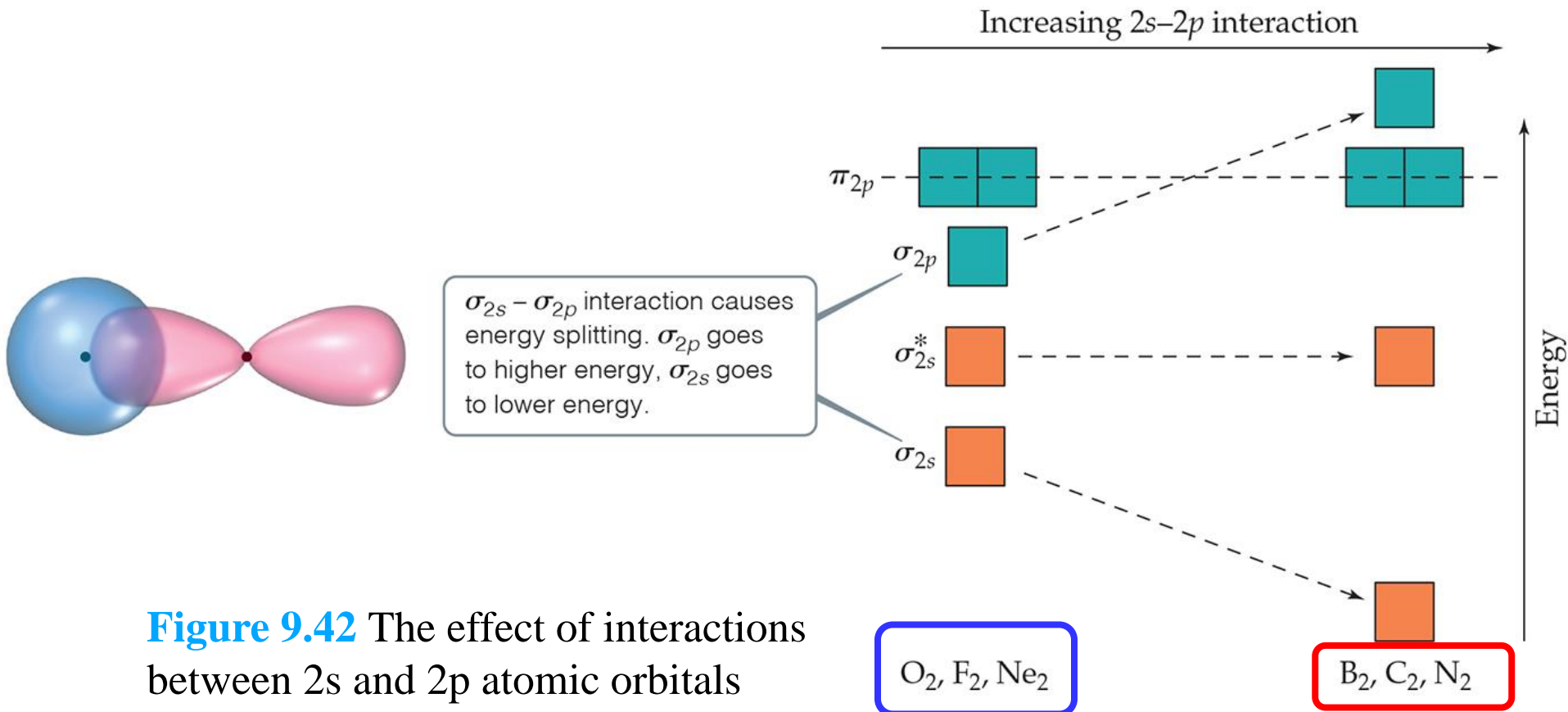
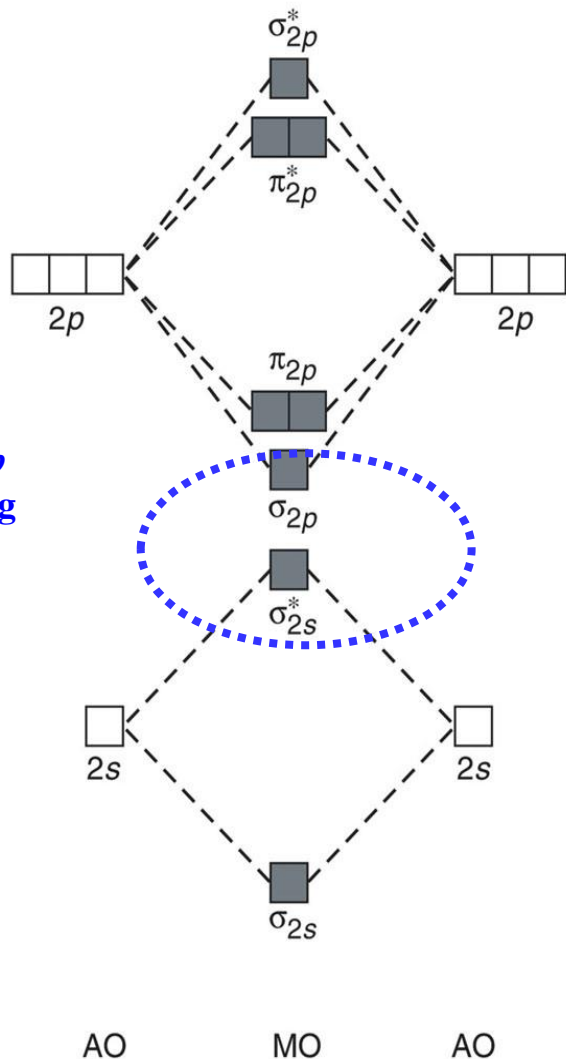


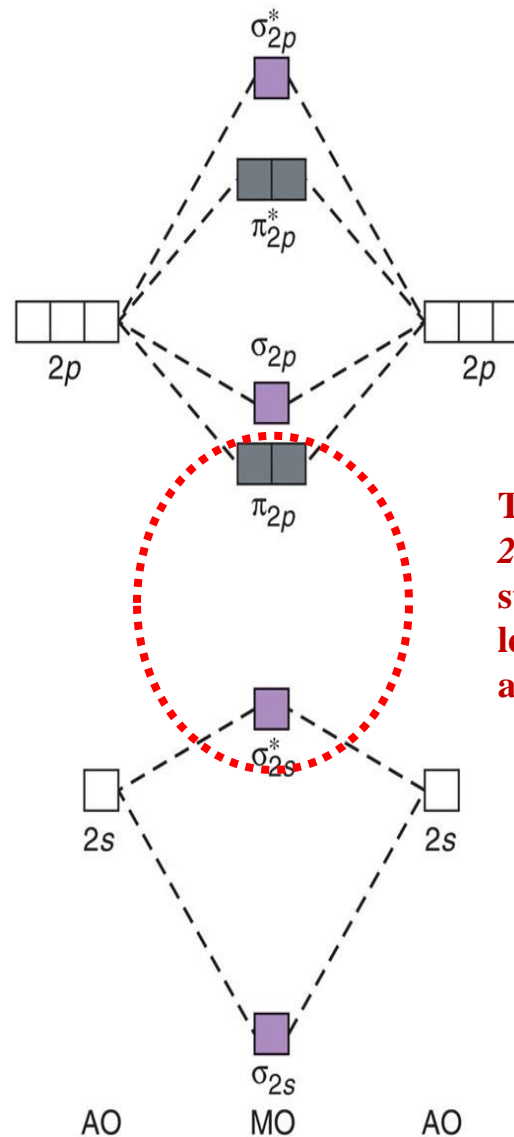
Figure 9.42 The effect of interactions between 2s and 2p atomic orbitals

In the cases of B_2 , C_2 and N_2 , s orbitals interact with the p_z orbitals more than the p_x and p_y orbitals. **It raises the energy of the p_z orbital and lowers the energy of the s orbital and alter the energy ordering of MOs.**

Relative Energy Levels for 2s & 2p



The case of big 2s-2p separation: no strong interactions in the formation of MOs



The case of small 2s-2p separation: strong interactions leading to further apart MOs

MO energy levels for O_2 , F_2 , and Ne_2

MO energy levels for B_2 , C_2 , and N_2

Figure 9.43 MO Diagrams for Diatomic Molecules of Second Period Elements

Small 2s-2p separation

Large 2s-2p separation

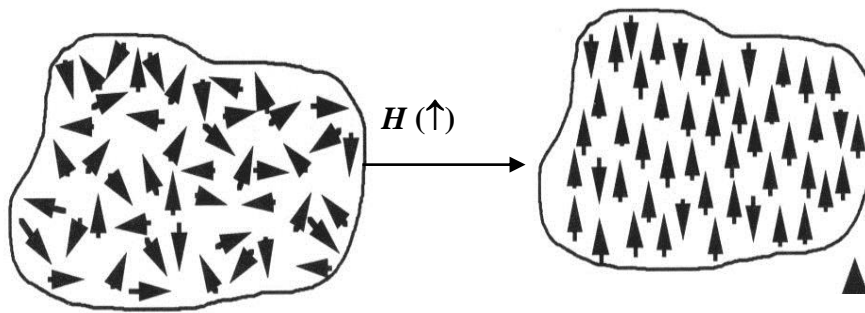
Energy ↑	<u>Large 2s–2p interaction</u>			<u>Small 2s–2p interaction</u>		
	B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂
σ_{2p}^*						
π_{2p}^*						
σ_{2p}						
π_{2p}						
σ_{2s}^*						
σ_{2s}						
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (pm)	159	131	110	121	143	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

Why is O₂ paramagnetic while N₂ diamagnetic?

Magnetic Properties

Substances with **no unpaired electrons** are weakly repelled by a magnetic field. This property is called **diamagnetism**.

Molecules **with one or more unpaired electrons** are attracted to a magnetic field. The more unpaired electrons in a species, the stronger the attractive force. This type of magnetic behavior is called **paramagnetism**.



paramagnetism is associated with unpaired electrons; causes the substance to be attracted toward the inducing magnetic field.

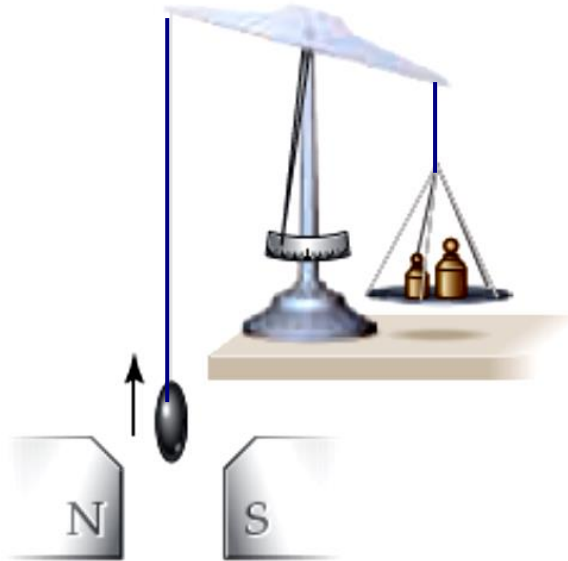
The **distinction between paramagnetism and diamagnetism** is nicely illustrated in an older method for **measuring magnetic properties**.

Magnetic Property Measurements

Weigh sample in absence of a magnetic field



A diamagnetic sample appears to weigh less in magnetic field (weak effect)



A paramagnetic sample appears to weigh more in magnetic field

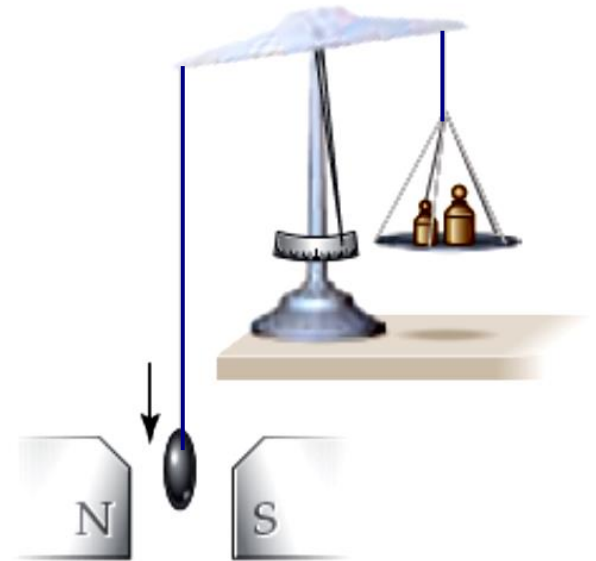


Figure 9.44 Determining the magnetic properties of a sample